A Round In Alcohols World

Between :
Production , Properties , Uses , Applications , Fuel , & Compounds

By

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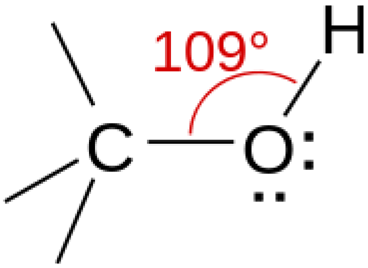
Part One

Alcohols

Mono Hydroxide

Alcohol



The hydroxyl (OH) functional group with bond angle, in a generic alcohol molecule

Contents

1 - Introduction

In chemistry, an **alcohol** is an organic compound in which the hydroxyl functional group (- OH) is bound to a carbon atom. In particular, this carbon center should be saturated, having single bonds

An important class of alcohols are the simple acyclic alcohols, the general formula for which is $C_nH_{2n+1}OH$. Of those, ethanol (C_2H_5OH) is the type of alcohol found in alcoholic beverages, and in common speech the word **alcohol** refers specifically to ethanol.

Other alcohols are usually described with a clarifying adjective, as in *isopropyl alcohol* (*propan-2-ol*) or *wood alcohol* (*methyl alcohol*, or methanol). The suffix *-ol* appears in the IUPAC chemical name of all substances where the hydroxyl group is the functional group with the highest priority; in substances where a higher priority group is present the prefix *hydroxy-* will appear in the IUPAC name. The suffix - *ol* in non-systematic names (such as para cetamol or cholesterol) also typically indicates that the substance includes a hydroxyl functional group and, so, can be termed an alcohol. But many substances, particularly sugars (examples glucose and sucrose) contain hydroxyl functional groups without using the suffix.

2 - Toxicity

Most significant of the possible long-term effects of ethanol. In addition, in pregnant women, it causes fetal alcohol syndrome.

Alcoholic beverages has been consumed by humans since prehistoric times for a variety of hygienic, dietary, medicinal, religious, and recreational reasons.

Primary alcohols (R- CH_2- OH) can be oxidized either to aldehydes (R-CHO) (e.g. acetaldehyde) or to carboxylic acids (R-CO_2H), while the oxidation of secondary alcohols (R^1R^2CH-OH) normally terminates at the ketone (R^1 R^2 C = O) stage. Tertiary alcohols (R^1 R^2 R^3 C- OH) are resistant to oxidation.

Ethanol's toxicity is largely caused by its primary metabolite; acetaldehyde (systematically ethanal) and secondary metabolite; acetic acid. All primary alcohols are broken down into aldehydes then to carboxylic acids whose toxicities are similar to acetaldehyde and acetic acid. Metabolite toxicity is reduced in rats fed N-acetyl cysteine and thiamine.

Tertiary alcohols cannot be metabolized into aldehydes and as a result they cause no hangover or toxicity through this mechanism.

Some secondary and tertiary alcohols are less poisonous than ethanol because the liver is unable to metabolize them into these toxic by- products. This makes them more suitable for recreational and medicinal use as the chronic harms are lower. *tert*-Amyl alcohol found in alcoholic beverages are a good example of a tertiary alcohol which saw both medicinal and recreational use.

Other alcohols are substantially more poisonous than ethanol, partly because they take much longer to be metabolized and partly because their metabolism produces substances that are even more toxic. Methanol (wood alcohol), for instance, is oxidized to formaldehyde and then to the poisonous formic acid in the liver by alcohol dehydrogenase and formaldehyde dehydrogenase enzymes, respectively; accumulation of formic acid can lead to blindness or death . Likewise, poisoning due to other alcohols such as ethylene glycol or di ethylene glycol are due to their metabolites, which are also produced by alcohol dehydrogenase.

Methanol itself, while poisonous (LD50 5628 mg / kg, oral, rat), has a much weaker sedative effect than ethanol.

Isopropyl alcohol is oxidized to form acetone by alcohol dehydrogenase in the liver but have occasionally been abused by alcoholics, leading to a range of adverse health effects.[17][18]

3 - Treatment

An effective treatment to prevent toxicity after methanol or ethylene glycol ingestion is to administer ethanol. Alcohol dehydrogenase has a higher affinity for ethanol, thus preventing methanol from binding and acting as a substrate. Any remaining methanol will then have time to be excreted through the kidneys.

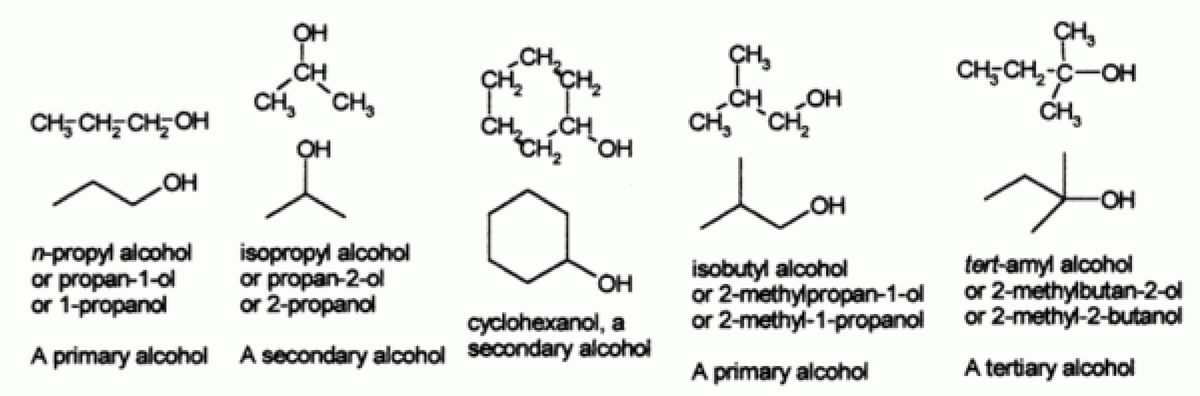
4 - Nomenclature

4 – 1 - Systematic names

In the IUPAC system, the name of the alkane chain loses the terminal "e" and adds "ol", e.g., "methanol" and "ethanol".[21] When necessary, the position of the hydroxyl group is indicated by a number between the alkane name and the "ol": propan-1-ol for $CH_3CH_2CH_2OH$, propan-2-ol for $CH_3CH(OH)CH_3$. Sometimes, the position number is written before the IUPAC name: 1-propanol and 2-propanol. If a higher priority group is present (such as an aldehyde, ketone, or carboxylic acid), then it is necessary to use the prefix "hydroxy", for example: 1-hydroxy-2-propanone (CH_3COCH_2OH).

The IUPAC nomenclature is used in scientific publications and where precise identification of the substance is important. In other less formal contexts, an alcohol is often called with the name of the corresponding alkyl group followed by the word "alcohol", e.g., methyl alcohol, ethyl alcohol. Propyl alcohol may be *n*-propyl alcohol or isopropyl alcohol, depending on whether the hydroxyl group is bonded to the 1st or 2nd carbon on the propane chain.

Alcohols are classified into 0°, primary (1°), secondary (2°; also italic abbreviated *sec*- or just *s*-), and tertiary (3°; also italic abbreviated *tert*- or just *t*-), based upon the number of carbon atoms connected to the carbon atom that bears the hydroxyl (OH) functional group. The primary alcohols have general formulas RCH_2OH; secondary ones are RR'CHOH; and tertiary ones are RR'R"COH, where R, R', and R" stand for alkyl groups. Methanol (CH_3OH or CH_4O) is a 0° alcohol. Some sources include methanol as a primary alcohol , including the 1911 edition of the Encyclopædia Britannica, but this interpretation is less common in modern texts.



Some examples of simple alcohols and how to name them

4 – 2 - Common names

Chemical Formula	IUPAC Name	Common Name
Mono hydric alcohols		
CH_3OH	Methanol	Wood alcohol
C_2H_5OH	Ethanol	Grain alcohol
C_3H_7OH	Isopropyl alcohol	Rubbing alcohol
C_4H_9OH	Butyl alcohol	Butanol
$C_5H_{11}OH$	Pentanol	Amyl alcohol
$C_{16}H_{33}OH$	Hexadecan-1-ol	Cetyl alcohol
Poly hydric alcohols		
$C_2H_4(OH)_2$	Ethane -1,2-diol	Ethylene glycol
$C_3H_6(OH)_2$	Propane -1,2-diol	Propylene Glycol
$C_3H_5(OH)_3$	Propane -1,2,3-triol	Glycerol
$C_4H_6(OH)_4$	Butane -1,2,3,4-tetraol	Erythritol , Threitol

$C_5H_7(OH)_5$	Pentane -1,2,3,4,5-pentol	Xylitol
$C_6H_8(OH)_6$	Hexane -1,2,3,4,5,6-hexol	Mannitol, Sorbitol
$C_7H_9(OH)_7$	Heptane -1,2,3,4,5,6,7-heptol	Volemitol
Unsaturated aliphatic alcohols		
C_3H_5OH	Prop-2-ene-1-ol	Allyl alcohol
$C_{10}H_{17}OH$	3,7-Dimethylocta-2,6-dien-1-ol	Geraniol
C_3H_3OH	Prop-2-in-1-ol	Propargyl alcohol
Alicyclic alcohols		
$C_6H_6(OH)_6$	Cyclohexane-1,2,3,4,5,6-hexol	Inositol
$C_{10}H_{19}OH$	2 - (2-propyl) - 5 - methyl - cyclo hexane -1-ol	Menthol

4 – 2 - 1 – Short - medium- long- and very long-chained alcohols

Short-chain alcohols have alkyl chains of 1- 3 carbons.

Medium-chain alcohols have alkyl chains of 4 -7 carbons.

Long-chain alcohols (also known as fatty alcohols) have alkyl chains of 8 -21 carbons.

Very long-chain alcohols have alkyl chains of 22 carbons or longer.

4 – 2 – 2 - 1 – Simple and higher alcohols

4 – 2 – 2 - 1 – Simple alcohols

"Simple alcohols" appears to be a completely undefined term. However, simple alcohols are often referred to by common names derived by adding the word "alcohol" to the name of the appropriate alkyl group. For instance, a chain consisting of one carbon (a methyl group, CH_3) with an OH group attached to the carbon is called "methyl alcohol" while a chain of two carbons (an ethyl group, CH_2CH_3) with an OH group connected to the CH_2 is called "ethyl alcohol." For more complex alcohols, the IUPAC nomenclature must be used.

Simple alcohols, in particular, ethanol and methanol, possess denaturing and inert rendering properties, leading to their use as anti-microbial agents in medicine, pharmacy, and industry .

4 – 2 – 2 - 2 – Higher alcohols

Encyclopædia Britannica states, "The higher alcohols—those containing 4 to 10 carbon atoms — are somewhat viscous, or oily, and they have heavier fruity odours . Some of the highly branched alcohols and many alcohols containing more than 12 carbon atoms are solids at room temperature."

Like ethanol, butanol can be produced by fermentation processes. (However, the fermenting agent is a bacterium, *Clostridium acetobutylicum*, that feeds on cellulose, not sugars like the Saccharomyces yeast that produces ethanol.) Saccharomyces yeast are known to produce these higher alcohols at temperatures above 24 °C .

4 – 3 - History and etymology

The first alcohol (today known as ethyl alcohol) was discovered by the tenth-century Persian alchemist al - Razi.

kuḥl (kohl) was originally the name given to the very fine powder produced by the sublimation of the natural mineral stibnite to form antimony sulfide Sb_2S_3 (hence the essence or "spirit" of the substance), which was used as an antiseptic, eyeliner and cosmetic (see kohl (cosmetics)). Bartholomew Traheron in his 1543 translation of John of Vigo introduces the word as a term used by "barbarous" (Moorish) authors for "fine powder":

the barbarous auctours use alcohol, or (as I fynde it sometymes wryten) alcofoll, for moost fine poudre.

The word *alcohol* appears in English, as a term for a very fine powder, in the 16th century, loaned via French from medical Latin, ultimately from the Arabic الكحل (*al-kuḥl,* "the kohl, a powder used as an eyeliner"). Al- is the Arabic definitive article, equivalent to *the* in English.

William Johnson in his 1657 *Lexicon Chymicum* glosses the word as *antimonium sive stibium*. By extension, the word came to refer to any fluid obtained by distillation, including "alcohol of wine", the distilled essence of wine.

Libavius in *Alchymia* (1594) has *vini alcohol vel vinum alcalisatum.*

Johnson (1657) glosses *alcohol vini* as *quando omnis superfluitas vini a vino separatur, ita ut accensum ardeat donec totum consumatur, nihilque fæcum aut phlegmatis in fundo remaneat.*

The word's meaning became restricted to "spirit of wine" (the chemical known today as ethanol) in the 18th century, and was extended to the class of substances so-called as "alcohols" in modern chemistry, after 1850.

The current Arabic name for alcohol in The Qur'an, in verse 37:47, uses the word الغول al-ġawl —properly meaning "spirit" or "demon"—with the sense "the thing that gives the wine its headiness." Also, the term *ethanol* was invented 1838, modeled on German äthyl (Liebig), from Greek aither (see ether) + hyle "stuff.". *Ether* in late 14c. meant "upper regions of space," from Old French ether and directly from Latin aether "the upper pure, bright air," from Greek aither "upper air; bright, purer air; the sky," from aithein "to burn, shine," from PIE root *aidh- "to burn" .

5 - Physical and chemical properties

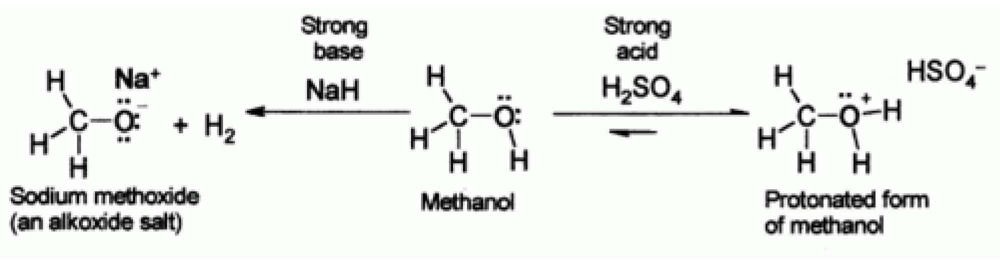
Alcohols have an odor that is often described as “biting” and as “hanging” in the nasal passages. Ethanol has a slightly sweeter (or more fruit - like) odor than the other alcohols.

In general, the hydroxyl group makes the alcohol molecule polar. Those groups can form hydrogen bonds to one another and to other compounds (except in certain large molecules where the hydroxyl is protected by steric hindrance of adjacent groups). This hydrogen bonding means that alcohols can be used as protic solvents. Two opposing solubility trends in alcohols are: the tendency of the polar OH to promote solubility in water, and the tendency of the carbon chain to resist it. Thus, methanol, ethanol, and propanol are miscible in water because the hydroxyl group wins out over the short carbon chain. Butanol, with a four-carbon chain, is moderately soluble because of a balance between the two trends. Alcohols of five or more carbons (pentanol and higher) are effectively insoluble in water because of the hydrocarbon chain's dominance. All simple alcohols are miscible in organic solvents.

Because of hydrogen bonding, alcohols tend to have higher boiling points than comparable hydrocarbons and ethers. The boiling point of the alcohol ethanol is 78.29 °C, compared to 69 °C for the hydrocarbon hexane (a common constituent of gasoline), and 34.6 °C for diethyl ether.

Alcohols, like water, can show either acidic or basic properties at the - OH group. With a pK_a of around 16-19, they are, in general, slightly weaker acids than water, but they are still able to react with strong bases such as sodium hydride or reactive metals such as sodium. The salts that result are called **alkoxides**, with the general formula $RO^- M^+$.

Meanwhile, the oxygen atom has lone pairs of nonbonded electrons that render it weakly basic in the presence of strong acids such as sulfuric acid. For example, with methanol :



Alcohols can also undergo oxidation to give aldehydes, ketones, or carboxylic acids, or they can be dehydrated to alkenes. They can react to form ester compounds, and they can (if activated first) undergo nucleophilic substitution reactions. The lone pairs of electrons on the oxygen of the hydroxyl group also makes alcohols nucleophiles. For more details, see the reactions of alcohols section below.

As one moves from primary to secondary to tertiary alcohols with the same backbone, the hydrogen bond strength, the boiling point, and the acidity typically decrease.

6 - Applications

Alcohol has a long history of several uses worldwide. It is found in beverages for adults, as fuel, and also has many scientific, medical, and industrial uses. The term **alcohol-free** is often used to describe a product that does not contain alcohol. Some consumers of some commercially prepared products may view alcohol as an undesirable ingredient, particularly in products intended for children.

6 – 1 – Alcoholic beverages

Alcoholic beverages, typically containing 5 % to 40 % ethanol by volume, have been produced and consumed by humans since prehistoric times.

6 – 2 – Antifreeze

A 50 % v / v (by volume) solution of ethylene glycol in water is commonly used as an antifreeze.

6 – 3 – Antiseptics

Ethanol can be used as an antiseptic to disinfect the skin before injections are given, often along with iodine. Ethanol-based soaps are becoming common in restaurants and are convenient because they do not require drying due to the volatility of the compound. Alcohol based gels have become common as hand sanitizers.

6 – 4 – Fuels

Some alcohols, mainly ethanol and methanol, can be used as an alcohol fuel. Fuel performance can be increased in forced induction internal combustion engines by injecting alcohol into the air intake after the turbocharger or supercharger has pressurized the air. This cools the pressurized air, providing a denser air charge, which allows for more fuel, and therefore more power.

6 – 5 – Preservative

Alcohol is often used as a preservative for specimens in the fields of science and medicine.

6 – 6 – Solvents

Alcohols have applications in industry and science as reagents or solvents. Because of its relatively low toxicity compared with other alcohols and ability to dissolve non-polar substances, ethanol can be used as a solvent in medical drugs, perfumes, and vegetable essences such as vanilla. In organic synthesis, alcohols serve as versatile intermediates.

7 - Production

In industry, alcohols are produced in several ways:

By fermentation using glucose produced from sugar from the hydrolysis of starch, in the presence of yeast and temperature of less than 37 °C to produce ethanol. For instance, such a process might proceed by the conversion of sucrose by the enzyme invertase into glucose and fructose, then the conversion of glucose by the enzyme zymase into ethanol (and carbon dioxide).

By direct hydration using ethylene (ethylene hydration) or other alkenes from cracking of fractions of distilled crude oil.

7 – 1 – Endogenous

Several of the benign bacteria in the intestine use fermentation as a form of anaerobic metabolism. This metabolic reaction produces ethanol as a waste product, just like aerobic respiration produces carbon dioxide and water. Thus, human bodies contain some quantity of alcohol endogenously produced by these bacteria.

8 - Laboratory synthesis

Several methods exist for the preparation of alcohols in the laboratory.

8 – 1 – Substitution

Primary alkyl halides react with aqueous NaOH or KOH mainly to primary alcohols in nucleophilic aliphatic substitution. (Secondary and especially tertiary alkyl halides will give the elimination (alkene) product instead). Grignard reagents react with carbonyl groups to secondary and tertiary alcohols. Related reactions are the Barbier reaction and the Nozaki - Hiyama reaction.

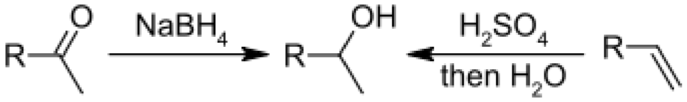
8 – 2 – Reduction

Aldehydes or ketones are reduced with sodium borohydride or lithium aluminium hydride (after an acidic workup). Another reduction by aluminium iso propylates is the Meerwein – Ponndorf - Verley reduction. Noyori asymmetric hydrogenation is the asymmetric reduction of β - keto - esters.

8 – 3 – Hydrolysis

Alkenes engage in an acid catalysed hydration reaction using concentrated sulfuric acid as a catalyst that gives usually secondary or tertiary alcohols. The hydroboration-oxidation and oxymercuration-reduction of alkenes are more reliable in organic synthesis. Alkenes react with NBS and water in halohydrin formation reaction. Amines can be converted to diazonium salts, which are then hydrolyzed.

The formation of a secondary alcohol via reduction and hydration is shown :



9 – Reactions

9 – 1 – Deprotonation

Alcohols can behave as weak acids, undergoing deprotonation. The deprotonation reaction to produce an alkoxide salt is performed either with a strong base such as sodium hydride or *n*-butyllithium or with sodium or potassium metal.

$2\ R\text{-}OH + 2\ NaH \rightarrow 2\ R\text{-}O^{-}Na^{+} + 2H_2\uparrow$
$2\ R\text{-}OH + 2\ Na \rightarrow 2\ R\text{-}O^{-}Na^{+} + H_2$
$2\ CH_3CH_2\text{-}OH + 2\ Na \rightarrow 2\ CH_3\text{-}CH_2\text{-}O^{-+} + H_2\uparrow$

Water is similar in pK_a to many alcohols, so with sodium hydroxide there is an equilibrium set-up, which usually lies to the left:
$R\text{-}OH + Na\ OH \rightleftharpoons R\text{-}O^{-}Na^{+} + H_2O$ (equilibrium to the left)

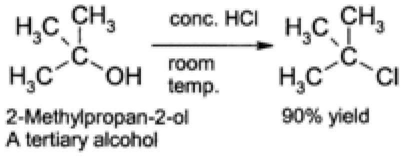
It should be noted, however, that the bases used to deprotonate alcohols are strong themselves. The bases used and the alkoxides created are both highly moisture-sensitive chemical reagents.

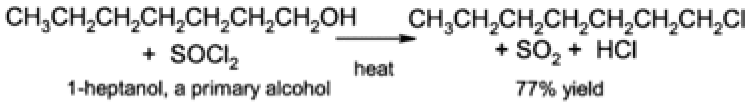
The acidity of alcohols is also affected by the overall stability of the alkoxide ion. Electron - withdrawing groups attached to the carbon containing the hydroxyl group will serve to stabilize the alkoxide when formed, thus resulting in greater acidity. On the other hand, the presence of electron - donating group will result in a less stable alkoxide ion formed. This will result in a scenario whereby the unstable alkoxide ion formed will tend to accept a proton to reform the original alcohol.

With alkyl halides alkoxides give rise to ethers in the Williamson ether synthesis.

9 – 2 – Nucleophilic substitution

The OH group is not a good leaving group in nucleophilic substitution reactions, so neutral alcohols do not react in such reactions. However, if the oxygen is first protonated to give $R{-}OH_2^{+}$, the leaving group (water) is much more stable, and the nucleophilic substitution can take place. For instance, tertiary alcohols react with hydrochloric acid to produce tertiary alkyl halides, where the hydroxyl group is replaced by a chlorine atom by unimolecular nucleophilic substitution. If primary or secondary alcohols are to be reacted with hydrochloric acid, an activator such as zinc chloride is needed. In alternative fashion, the conversion may be performed directly using thionyl chloride .





Alcohols may, likewise, be converted to alkyl bromides using hydro bromic acid or phosphorus tri bromide , for example:

$3\ R\text{-}OH + PBr_3 \rightarrow 3\ RBr + H_3PO_3$

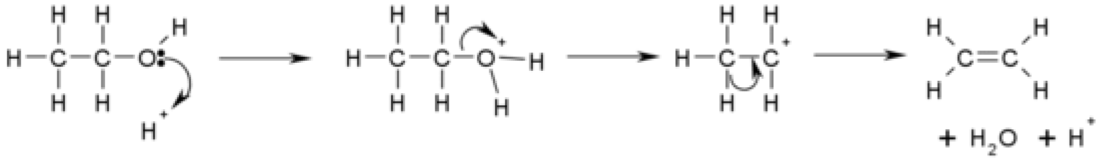
In the Barton – Mc Combie deoxygenation an alcohol is deoxygenated to an alkane with tri butyltin hydride or a tri methyl borane - water complex in a radical substitution reaction.

9 – 3 – Dehydration

Alcohols are themselves nucleophilic, so $R{-}OH_2^+$ can react with ROH to produce ethers and water in a dehydration reaction, although this reaction is rarely used except in the manufacture of diethyl ether.

More useful is the E1 elimination reaction of alcohols to produce alkenes. The reaction, in general, obeys Zaitsev's Rule, which states that the most stable (usually the most substituted) alkene is formed. Tertiary alcohols eliminate easily at just above room temperature, but primary alcohols require a higher temperature.

This is a diagram of acid catalysed dehydration of ethanol to produce ethene:



A more controlled elimination reaction is the Chugaev elimination with carbon disulfide and iodo methane.

9 – 4 – Esterification

To form an ester from an alcohol and a carboxylic acid the reaction, known as Fischer esterification, is usually performed at reflux with a catalyst of concentrated sulfuric acid:

$R\text{-}OH + R'\text{-}COOH \rightarrow R'\text{-}COOR + H_2O$

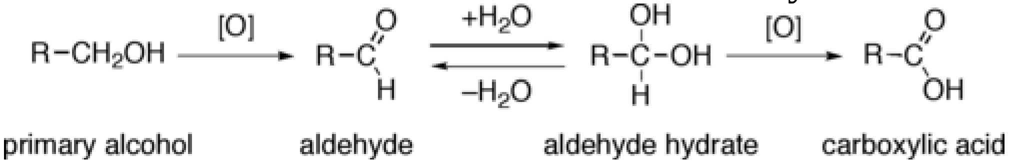
In order to drive the equilibrium to the right and produce a good yield of ester, water is usually removed, either by an excess of H_2SO_4 or by using a Dean-Stark apparatus. Esters may also be prepared by reaction of the alcohol with an acid chloride in the presence of a base such as pyridine.

Other types of ester are prepared in a similar manner — for example, tosyl (tosylate) esters are made by reaction of the alcohol with p-toluene sulfonyl chloride in pyridine.

9 – 5 – Oxidation

Primary alcohols (R-CH_2-OH) can be oxidized either to aldehydes (R-CHO) or to carboxylic acids (R- CO_2H), while the oxidation of secondary alcohols (R^1 R^2 CH-OH) normally terminates at the ketone (R^1 R^2 C= O) stage. Tertiary alcohols ($R^1R^2R^3$C-OH) are resistant to oxidation.

The direct oxidation of primary alcohols to carboxylic acids normally proceeds via the corresponding aldehyde, which is transformed via an *aldehyde hydrate* (R-CH$(OH)_2$) by reaction with water before it can be further oxidized to the carboxylic acid.



Mechanism of oxidation of primary alcohols to carboxylic acids via aldehydes and aldehyde hydrates

Reagents useful for the transformation of primary alcohols to aldehydes are normally also suitable for the oxidation of secondary alcohols to ketones. These include Collins reagent and Dess - Martin periodinane . The direct oxidation of primary alcohols to carboxylic acids can be carried out using potassium permanganate or the Jones reagent.

10 - Occurrence in nature

Alcohol has been found outside the Solar System. It can be found in low densities in star and planetary-system-forming regions of space.

Alcohols by Structure and Preferred IUPAC Name (PIN)

Primary alcohols

Methanol (C_1)
Ethanol (C_2)
Propan-1-ol (C_3)
Butan-1-ol (C_4)
2-methyl-1-propanol (C_4)
Pentan-1-ol (C_5)
3-methyl-1-butanol (C_5)
Hexan-1-ol (C_6)
Heptan-1-ol (C_7)
Octan-1-ol (C_8)
1-Nonanol (C_9)
Decan-1-ol (C_{10})
Undecan-1-ol (C_{11})
Dodecan-1-ol (C_{12})
Tetradecan-1-ol (C_{14})
Hexadecan-1-ol (C_{16})
Octadecan-1-ol (C_{18})
1-Icosanol (C_{20})
Docosan-1-ol (C_{22})
Tetracosan-1-ol (C_{24})
Hexacosan-1-ol (C_{26})
Octacosan-1-ol (C_{28})
Triacontan-1-ol (C_{30})
Polycosanol

Secondary (*sec*) alcohols (2°)

Propan-2-ol (C_3)
Butan-2-ol (C_4)
2-Methyl-1-butanol (C_5)
2-Pentanol (C_5)
Cyclo hexanol (C_6)
Hexan-2-ol (C_6)
Heptan-2-ol (C_7)

Tertiary (*tert*) alcohols (3°)

2-Methylpropan-2-ol (C_4)
2-Methyl-2-butanol (C_5)
2-Methyl-2-pentanol (C_6)
2-Methyl-2-hexanol (C_7)
2-Methyl-2-heptanol (C_8)
3-Methyl-3-pentanol (C_6)

Sugar Alcohols

2-carbon

Ethylene glycol

3-carbon

Glycerol

4-carbon

Erythritol
Threitol

5-carbon

Arabitol
Ribitol
Xylitol

6-carbon

Mannitol
Sorbitol
Galactitol
Iditol

7- carbon

Volemitol

Deoxy sugar alcohols

Fucitol

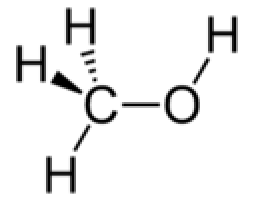
Cyclic sugar alcohols

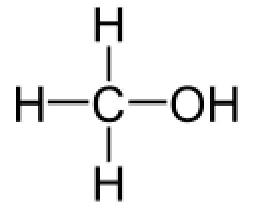
Inositol

Glycylglycitols

Maltitol
Lactitol
Isomalt
Maltotriitol
Maltotetraitol
Polyglycitol

Methanol





Contents

1 - Introduction

Methanol, also known as **methyl alcohol**, **wood alcohol**, **wood naphtha** or **wood spirits**, is a chemical with the formula CH_3OH (often abbreviated Me OH). Methanol acquired the name "wood alcohol" because it was once produced chiefly as a byproduct of the destructive distillation of wood. Modern methanol is produced in a catalytic industrial process directly from carbon monoxide, carbon dioxide, and hydrogen.

Systematic Name ; Methanol
Other Names ;
Hydroxy methane
Methyl alcohol
Methyl hydrate
Methyl hydroxide
Methylic alcohol
Methylol
Wood alcohol

Molecular Formula	CH_4O
Molar Mass	32 g mol^{-1}
Appearance	Colorless liquid
Density	0.7918 g / cm^3
Melting Point	-97.6 °C
Boiling Point	64.7 °C
Vapor Pressure	13.02 kPa (at 20 °C)
Acidity (pK_a)	15.5
Viscosity	5.9×10^{-4} Pa s (at 20 °C)
EU Classification	🔥 F ☠ T
Flash Point	11–12 °C
Auto ignition temperature	385 °C
Explosive limits	36 %
Thermo dynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

Methanol is the simplest alcohol, and is a light, volatile, colorless, flammable liquid with a distinctive odor very similar to, but slightly sweeter than ethanol (drinking alcohol). At room temperature, it is a polar liquid, and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. It is also used for producing biodiesel via trans esterification reaction.

Methanol is produced naturally in the anaerobic metabolism of many varieties of bacteria, and is ubiquitous in small amounts in the environment. As a result, there is a small fraction of methanol vapor in the atmosphere. Over the course of several days, atmospheric methanol is oxidized with the help of sunlight to carbon dioxide and water.

Methanol burns in oxygen (including open air), forming carbon dioxide and water :

$$2\ CH_3OH + 3\ O_2 \rightarrow 2\ CO_2 + 4\ H_2O$$

Methanol ingested in large quantities is metabolized to formic acid or formate salts, which is poisonous to the central nervous system, and may cause blindness, coma, and death. Because of these toxic properties, methanol is frequently used as a denaturant additive for ethanol manufactured for industrial uses. This addition of methanol exempts industrial ethanol (commonly known as "denatured alcohol" or "methylated spirit") from liquor excise taxation in the USA and some other nations.

2 - History

In their embalming process, the ancient Egyptians used a mixture of substances, including methanol, which they obtained from the pyrolysis of wood. Pure methanol, however, was first isolated in 1661 by Robert Boyle, when he produced it via the distillation of buxus (box wood). It later became known as "pyroxylic spirit". In 1834, the French chemists Jean - Baptiste Dumas and Eugene Peligot determined its elemental composition.

They also introduced the word "methylene" to organic chemistry, forming it from Greek *methy* = "wine" + *hȳlē* = wood (patch of trees), with Greek language errors: "wood (substance)" (Greek *xylon*) was intended, and the components are in the wrong order for Greek. The term "methyl" was derived in about 1840 by back-formation from "methylene", and was then applied to describe "methyl alcohol". This was shortened to "methanol" in 1892 by the International Conference on

Chemical Nomenclature. The suffix -yl used in organic chemistry to form names of carbon groups, was extracted from the word "methyl".

In 1923, the German chemists Alwin Mittasch and Mathias Pier, working for BASF, developed a means to convert synthesis gas (a mixture of carbon monoxide, carbon dioxide, and hydrogen) into methanol. A patent was filed Jan 12 1926 (reference no. 1,569,775). This process used a chromium and manganese oxide catalyst, and required extremely vigorous conditions — pressures ranging from 50 to 220 atm, and temperatures up to 450 °C. Modern methanol production has been made more efficient through use of catalysts (commonly copper) capable of operating at lower pressures, the modern low pressure methanol (LPM) was developed by ICI in the late 1960s with the technology now owned by Johnson Matthey, which is a leading licensor of methanol technology.

Methanol is one of the most heavily traded chemical commodities in the world, with an estimated global demand of around 27 to 29 million metric tons. In recent years, production capacity has expanded considerably, with new plants coming on-stream in South America, China and the Middle East, the latter based on access to abundant supplies of methane gas. Even though nameplate production capacity (coal-based) in China has grown significantly, operating rates are estimated to be as low as 50 to 60 %. No new production capacity is scheduled to come on-stream until 2015.

The main applications for methanol are the production of formaldehyde (used in construction and wooden boarding), acetic acid (basis for a.o. PET-bottles), MTBE (fuel component and replacement for the very volatile diethyl ether) and more recently for the formation of methyl esters in the production of bio - diesel. In China, demand is expected to grow exponentially, not only caused by a growing internal market of the traditional applications, but accelerated by new applications, such as direct blending (with gasoline), Methanol-To-Olefins (e.g. propylene) and DME. Methanol can also be used to produce gasoline.

The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability, low cost, and environmental benefits. By the mid-1990s, over 20,000 methanol "flexible fuel vehicles" capable of operating on methanol or gasoline were introduced in the U.S. In addition, low levels of methanol were blended in gasoline fuels sold in Europe during much of the 1980s and early-1990s. Automakers stopped building methanol FFVs by the late-1990s, switching their attention to ethanol-fueled vehicles. While the methanol FFV program was a technical success, rising methanol pricing in the mid- to late-1990s during a period of slumping gasoline pump prices diminished the interest in methanol fuels.

In 2006, astronomers using the MERLIN array of radio telescopes at Jodrell Bank Observatory discovered a large cloud of methanol in space, 288 billion miles across.

3 - Production

3 - 1 - Production of methanol from synthesis gas

Carbon monoxide and hydrogen react over a catalyst to produce methanol. Today, the most widely used catalyst is a mixture of copper, zinc oxide, and alumina first used by ICI in 1966. At 5 –10 MPa (50 –100 atm) and 250 °C, it can catalyze the production of methanol from carbon monoxide and hydrogen with high selectivity (> 99.8 %) :

$$CO + 2\ H_2 \rightarrow CH_3OH$$

It is worth noting that the production of synthesis gas from methane produces three moles of hydrogen gas for every mole of carbon monoxide, while the methanol synthesis consumes only two moles of hydrogen gas per mole of carbon monoxide. One way of dealing with the excess hydrogen is to inject carbon dioxide into the methanol synthesis reactor, where it, too, reacts to form methanol according to the equation:

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$

Some chemists believe that the certain catalysts synthesize methanol using CO_2 as an intermediary, and consuming CO only indirectly.

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$

where the H_2O byproduct is recycled via the water-gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2,$$

This gives an over all reaction, which is the same as listed above.

$$CO + 2\ H_2 \rightarrow CH_3OH$$

3 - 2 - Production of methanol from methane

The direct catalytic conversion of methane to methanol using Cu-zeolites or other catalysts is an alternative process for the efficient production of methanol.

3 - 3 - Feed stocks for methanol production

3 - 3 - 1 - Production of synthesis gas

Originally, synthesis gas for the production of methanol came from coal. Today, synthesis gas is most commonly produced from the methane component in natural gas, because natural gas contains hydrogen. Three processes are commercially practiced. At moderate pressures of 4 MPa (40 atm) and high temperatures (around 850 °C), methane reacts with steam on a nickel catalyst to produce syngas according to the chemical equation:

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

This reaction, commonly called steam-methane reforming or SMR, is endothermic, and the heat transfer limitations place limits on the size of and pressure in the catalytic reactors used. Methane can also undergo partial oxidation with molecular oxygen (at atmospheric pressure) to produce syngas, as the following equation shows:

$$2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2$$

This reaction is exothermic, and the heat given off can be used *in-situ* to drive the steam-methane reforming reaction. When the two processes are combined, it is referred to as *autothermal reforming*. The high pressures and high temperatures needed for steam-reforming require a greater capital investment in equipment than is needed for a simple partial-oxidation process; however, the energy-efficiency of steam-reforming is higher than for partial-oxidation, unless the waste-heat from partial-oxidation is used.

3 - 3 - 1 – 1 - Stoichiometry adjustment

Stoichiometry for methanol production requires the ratio of H_2 / CO to equal 2. The *partial oxidation* process yields a ratio of 2, and the *steam reforming* process yields a ratio of 3. The H_2 / CO ratio can be adjusted to some extent by the water-gas shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2,$$

to provide the appropriate stoichiometry for methanol synthesis.

3 - 3 - 1 – 2 - Alternate feedstock materials

Although natural gas is the most economical and widely used feedstock for methanol production, many other feedstocks can be used to produce syngas via steam reforming. Steam-reformed coal is sometimes used as a feedstock for methanol production, particularly in China. In addition, mature technologies available for biomass gasification are being used for methanol production. For instance, woody biomass can be gasified to water gas (a hydrogen-rich syngas), by introducing a blast of steam in a blast furnace. The water-gas / syngas can then be synthesized to methanol using standard methods. The net process is carbon neutral, since the CO_2 byproduct is required to produce biomass via photosynthesis.

$$2\ C_{16}H_{23}O_{11} + 19\ H_2O + O_2 \rightarrow$$
$$42\ H_2 + 21\ CO + 11\ CO_2 \rightarrow 21\ CH_3OH + 11\ CO_2$$

4 - Applications

Methanol, a common laboratory solvent, is especially useful for HPLC, UV/VIS spectroscopy, and LCMS due to its low UV cutoff.

4 – 1 - Feed stock

The largest use of methanol by far is in making other chemicals. About 40% of methanol is converted to formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles.

Also in the early 1970s, a methanol to gasoline process was developed by Mobil for producing gasoline ready for use in vehicles. One such industrial facility was built at Motunui in New Zealand in the 1980s. In the 1990s, large amounts of methanol were used in the United States to produce the gasoline additive methyl tert-butyl ether (MTBE). While MTBE is no longer marketed in the U.S., it is still widely used in other parts of the world. In addition to direct use as a fuel, methanol (or less commonly, ethanol) is used as a component in the trans esterification of triglycerides to yield a form of biodiesel.

Other chemical derivatives of methanol include dimethyl ether, which has replaced chlorofluorocarbons as an aerosol spray propellant, and acetic acid. Dimethyl ether (DME) also can be blended with liquified petroleum gas (LPG) for home heating and cooking, and can be used as a diesel replacement for transportation fuel.

Methanol-to-Olefins/Methanol - to - Propylene (MTO / MTP), among others processes such as: Metathesis, Propane Dehydrogenation (PDH), High Severity FCC, and Olefins Cracking, is a new and novel lower-cost chemical process for on-purpose propylene production technology of high interest to the petrochemical marketplace, to supply the tight propylene market.

The market became tight because of the ethane prices falling in the USA, due to the exploration of shale gas reserves. The low price ethylene produced from this raw material has given chemical producers in North America a feedstock advantage. Such change has put naphtha-fed steam crackers at a disadvantageous position, with many of them shutting down or revamping to use ethane as feedstock. Nevertheless, the propylene output rates from ethane-fed crackers are negligible.

4 – 2 - Fuel for vehicles

Methanol is used on a limited basis to fuel internal combustion engines. Pure methanol is required by rule to be used in Champcars, Monster Trucks, USAC sprint cars (as well as midgets, modifieds, etc.), and other dirt track series, such as World of Outlaws, and Motorcycle Speedway. Methanol is also used, as the primary fuel ingredient since the late 1940s, in the powerplants for radio control, control line and free flight airplanes (as methanol is required in the engines that primarily power them), cars and trucks, from such an engine's use of a platinum filament glow plug being able to ignite the methanol vapor through a catalytic reaction. Drag racers and mud racers, as well as heavily modified tractor pullers, also use methanol as their primary fuel source. Methanol is required with a supercharged engine in a Top Alcohol dragster and, until the end of the 2006 season, all vehicles in the Indianapolis 500 had to run methanol. Mud racers have mixed methanol with gasoline with nitrous oxide to produce more power than mixing gasoline and nitrous oxide alone.

One of the potential drawbacks of using high concentrations of methanol (and other alcohols, such as ethanol) in fuel is the corrosivity to some metals of methanol, particularly to aluminium. Methanol, although a weak acid, attacks the oxide coating that normally protects the aluminum from corrosion:

$$6\ CH_3OH + Al_2O_3 \rightarrow 2\ Al(OCH_3)_3 + 3\ H_2O$$

The resulting methoxide salts are soluble in methanol, resulting in a clean aluminium surface, which is readily oxidized by dissolved oxygen. Also, the methanol can act as an oxidizer:

$$6\ CH_3OH + 2\ Al \rightarrow 2\ Al(OCH_3)_3 + 3\ H_2$$

This reciprocal process effectively fuels corrosion until either the metal is eaten away or the concentration of CH_3OH is negligible. Concerns with methanol's corrosivity have been addressed by using methanol-compatible materials, and fuel additives that serve as corrosion inhibitors.

When produced from wood or other organic materials, the resulting organic methanol (bioalcohol) has been suggested as renewable alternative to petroleum-based hydrocarbons. Low levels of methanol can be used in existing vehicles, with the use of proper cosolvents and corrosion inhibitors. The European Fuel Quality Directive allows up to 3 % methanol with an equal amount of co solvent to be blending in gasoline sold in Europe. Today, China uses more than one billion gallons of methanol per year as a transportation fuel in both low level blends used in existing vehicles, and as high level blends in vehicles designed to accommodate the use of methanol fuels.

Because of climate change, alternatives to fossil fuels have been sought to run ground vehicles. Various alternatives have been proposed. Biofuels are carbon-neutral, but they require a great deal of fresh water to produce and are not practical in most climates. If a source of renewable or sustainable energy becomes widely available (such as wind, solar or nuclear power), various chemical alternatives have been proposed to power ground vehicles in places of batteries. An example is a hydrogen economy. However, various alcohol-based economies, including a methanol based economy has been proposed in which artificially produced methanol stores all power which cannot be directly used from sustainable sources, and also is used for ground transportation. The chief advantage of a methanol economy is that it could be adapted to present internal combustion engines with a minimum of modification in both engines and infrastructure to store and deliver liquid fuel.

In 2011, the Open Fuel Standard Act of 2011 was introduced into Congress to encourage car manufacturers to warrant their cars to burn methanol as a fuel in addition to gasoline and ethanol. The bill is being championed by the Open Fuel Standard Coalition .

4 – 3 - Other applications

Methanol is a traditional denaturant for ethanol, the product being known as "denatured alcohol" or "methylated spirit". This was commonly used during the Prohibition to discourage consumption of bootlegged liquor, and ended up causing several deaths

Methanol is also used as a solvent, and as an antifreeze in pipelines and windshield washer fluid.

In some wastewater treatment plants, a small amount of methanol is added to wastewater to provide a carbon food source for the denitrifying bacteria, which convert nitrates to nitrogen to reduce the nitrification of sensitive aquifers.

During World War II, methanol was used as a fuel in several German military rocket designs, under the name M-Stoff, and in a roughly 50 / 50 mixture with hydrazine, known as C-Stoff.

Methanol was used as an automobile coolant antifreeze in the early 1900s.

Methanol is used as a denaturing agent in poly acryl amide gel electro phoresis.

Direct-methanol fuel cells are unique in their low temperature, atmospheric pressure operation, allowing them to be miniaturized to an unprecedented degree. This, combined with the relatively easy and safe storage and handling of methanol, may open the possibility of fuel cell-powered consumer electronics, such as for laptop computers and mobile phones.

Methanol is also a widely used fuel in camping and boating stoves. Methanol burns well in an unpressurized burner, so alcohol stoves are often very simple, sometimes little more than a cup to hold fuel. This lack of complexity makes them a favorite of hikers who spend extended time in the wilderness. Similarly, the alcohol can also be gelled to reduce risk of leaking or spilling, as with the brand "Sterno".

Methanol is mixed with water and injected into high performance diesel and gasoline engines for an increase of power and a decrease in exhaust gas temperature in a process known as water methanol injection.

4 – 4 - Energy carrier

Methanol is also useful as an energy carrier. It is easier to store than hydrogen, burns cleaner than fossil fuels, and is biodegradable.

5 - Health and safety

5 – 1 - Toxicity

Methanol has a high toxicity in humans. If as little as 10 mL of pure methanol is ingested, for example, it can break down into formic acid, which can cause permanent blindness by destruction of the optic nerve, and 30 mL is potentially fatal, although the median lethal dose is typically 100 mL (i.e. 1–2 mL / kg body weight of pure methanol). Reference dose for methanol is 0,5 mg / kg / day. Toxic effects take hours to start, and effective antidotes can often prevent permanent damage. Because of its similarities in both appearance and odor to ethanol (the alcohol in beverages), it is difficult to differentiate between the two (such is also the case with denatured alcohol). However, there are cases of methanol resistance, such as that of Mike Malloy, who was the victim of a failed murder attempt by methanol in the early 1930s.

Methanol is toxic by two mechanisms. First, methanol (whether it enters the body by ingestion, inhalation, or absorption through the skin) can be fatal due to its CNS depressant properties in the same manner as ethanol poisoning. Second, in a process of toxication, it is metabolized to formic acid (which is present as the formate ion) via formaldehyde in a process initiated by the enzyme alcohol dehydrogenase in the liver. Methanol is converted to formaldehyde via alcohol dehydrogenase (ADH) and formaldehyde is converted to formic acid (formate) via aldehyde dehydrogenase (ALDH). The conversion to formate via ALDH proceeds completely, with no detectable formaldehyde remaining. Formate is toxic because it inhibits mitochondrial cytochrome c oxidase, causing the symptoms of hypoxia at the cellular level, and also causing metabolic acidosis, among a variety of other metabolic disturbances.

Methanol poisoning can be treated with the antidotes ethanol or fomepizole . Both drugs act to reduce the action of alcohol dehydrogenase on methanol by means of competitive inhibition, so it is excreted by the kidneys rather than being transformed into toxic metabolites. Further treatment may include giving sodium bicarbonate for metabolic acidosis, and hemodialysis or hemodiafiltration can be used to remove methanol and formate from the blood. Folinic acid or folic acid is also administered to enhance the metabolism of formate.

The initial symptoms of methanol intoxication include central nervous system depression, headache, dizziness, nausea, lack of coordination, and confusion. Sufficiently large doses can cause unconsciousness and death. The initial symptoms of methanol exposure are usually less severe than the symptoms resulting from the ingestion of a similar quantity of ethanol . Once the initial symptoms have passed, a second set of symptoms arises, 10 to as many as 30 hours after the initial exposure to methanol, including blurring or complete loss of vision and acidosis. These symptoms result from the accumulation of toxic levels of formate in the blood, and may progress to death by respiratory failure. Physical examination may show tachypnea, and opthalmologic examination may show dilated pupils with hyperemia of the optic disc and retinal edema. Small amounts of methanol are produced by the metabolism of food and are generally harmless, being metabolized quickly and completely.

Ethanol is sometimes denatured (adulterated), and made poisonous, by the addition of methanol. The result is known as methylated spirit, "meths" (British use) or "metho" (Australian slang). These are not to be confused with "meth", a common U.S. abbreviation for methamphetamine, and British abbreviation for methadone.

The formic acid and formaldehyde produced as metabolites of methanol are responsible for the optic nerve damage, causing blindness seen in methanol poisoning.

5 – 2 - Safety in automotive fuels

Pure methanol has been used in open wheel auto racing since the mid-1960s. Unlike petroleum fires, methanol fires can be extinguished with plain water. A methanol-based fire burns invisibly, unlike gasoline, which burns with a visible flame. If a fire occurs on the track, there is no flame or smoke to obstruct the view of fast approaching drivers, but this can also delay visual detection of the fire and the initiation of fire suppression.

The decision to permanently switch to methanol in American IndyCar racing was a result of the devastating crash and explosion at the 1964 Indianapolis 500, which killed drivers Eddie Sachs and Dave MacDonald.[26] In 2007 IndyCars switched to ethanol.

Methanol is readily biodegradable in both aerobic (oxygen present) and anaerobic (oxygen absent) environments. Methanol will not persist in the environment. The half-life for methanol in groundwater is just one to seven days, while many common gasoline components have half-lives in the hundreds of days (such as benzene at 10–730 days). Since methanol is miscible with water and biodegradable, it is unlikely to accumulate in groundwater, surface water, air or soil.

6 - Occurrence in freeze distillation

Freeze distillation can concentrate methanol and fusel alcohols (by-products of fermentation which true distillation separates out) in applejack to unhealthy levels. As a result, many countries prohibit such applejack as a health measure.

Methanol Economy

Contents

1 - Introduction

The **methanol economy** is a suggested future economy in which methanol replaces fossil fuels as a means of energy storage, ground transportation fuel, and raw material for synthetic hydrocarbons and their products. It offers an alternative to the proposed hydrogen economy or ethanol economy.

In the 1990s Nobel prize winner George A. Olah started to advocate the methanol economy and in 2006 he and two co-authors (G. K. Surya Prakash and Alain Goeppert) published a book around this theme. In these publications, they summarize the state of our fossil fuel and alternative energy sources, their availability and limitations before suggesting a new approach in the so-called methanol economy.

Methanol is a fuel for heat engines and fuel cells. Due to its high octane rating it can be used directly as a fuel in flex-fuel cars (including hybrid and plug-in hybrid vehicles) using existing internal combustion engines (ICE) . Methanol can also be used as a fuel in fuel cells, either directly in Direct Methanol Fuel Cells (DMFC) or indirectly (after conversion into hydrogen by reforming).

Methanol is a liquid under normal conditions, allowing it to be stored, transported and dispensed easily, much like gasoline and diesel fuel is currently. It can also be readily transformed by dehydration into di methyl ether, a diesel fuel substitute with a cetane number of 55 .

Methanol is already used today on a large scale (about 37 million tones per year) as a raw material to produce numerous chemical products and materials. In addition, it can be readily converted in the methanol - to - olefin (MTO) process into ethylene and propylene, which can be used to produce synthetic hydrocarbons and their products, currently obtained from oil and natural gas.

Methanol can be efficiently produced from a wide variety of sources including still-abundant fossil fuels (natural gas, coal, oil shale, tar sands, etc.), but also agricultural products and municipal waste, wood and varied biomass. More importantly, it can also be made from chemical recycling of carbon dioxide, which Carbon Recycling International has demonstrated with its first commercial scale plant . Initially the major source will be the CO_2 rich flue gases of fossil – fuel - burning power plants or exhaust from cement and other factories. In the longer range however, considering diminishing fossil fuel resources and the effect of their utilization on earth's atmosphere, even the low concentration of atmospheric CO_2 itself could be captured and recycled via methanol, thus supplementing nature’s own photosynthetic cycle. Efficient new absorbents to capture atmospheric CO_2 are being developed, mimicking plants' ability. Chemical recycling of CO_2 to new fuels and materials could thus become feasible, making them renewable on the human timescale.

Methanol may be viewed as a compact way of storing hydrogen. One m^3 of methanol at ambient pressure and temperature contains 1660 Nm^3 (normal cubic metres) of hydrogen gas (H_2). This may be compared to liquid hydrogen where one m^3 of liquid hydrogen (LH2) at -253°C contains only 788 Nm^3 of hydrogen gas

2 - Uses of methanol in a methanol economy

2 -1 - Fuel uses

In an economy based on methanol, methanol could be used as a fuel :

In internal combustion engines (ICEs)

Methanol has a high octane rating (RON of 107 and MON of 92), making it a suitable gasoline substitute. It has a higher flame speed than gasoline, leading to higher efficiency as well as a higher latent heat of vaporization (3.7 times higher than gasoline), meaning that the heat generated by the engine can be removed more effectively, making it possible to use air cooled engines. Methanol burns cleaner than gasoline and is safer in the case of a fire, but has only half the volumetric energy content of gasoline (15.6 MJ/L vs. 32.4 MJ/L).

In compression ignition engines (diesel engine)

Methanol itself is not a good substitute for diesel fuels. Methanol can, however, be converted by dehydration to dimethyl ether, which is a good diesel fuel with a cetane number of 55-60 as compared to 45-55 for regular diesel fuel. This improves its cold-start ability in winters and reduces its noise. Compared to diesel fuel, DME has much lower emissions of NO_x and CO and emits no particulate matter, SO_x. Methanol can also be, and is in fact already, used to produce biodiesel via transesterification of vegetable oil (SVO).

In advanced methanol - powered vehicles

The use of methanol and dimethyl ether can be combined with hybrid and plug-in vehicle technologies allowing higher gas mileage and lower emissions. These fuels can also be used in fuel cells either via onboard reforming to hydrogen or directly in Direct Methanol Fuel Cells (DMFC).

For electricity production

Methanol and DME can be used in existing gas turbines to generate electricity. Fuel cells (PAFC, MCFC, SOFC) can also be used for electricity generation.

As a domestic fuel

Methanol and DME can be used in commercial buildings and homes to generate heat and/or electricity. DME can be used in a commercial gas stove without modifications. DME can also be blended with LPG and used as a cooking or heating fuel as is already the case in China. In developing countries methanol could be used as a cooking fuel, burning much cleaner than wood and thus mitigating indoor air quality problems.

2 – 2 - Raw material for chemicals and materials

Methanol is already used today on a large scale as raw material to produce a variety of chemicals and products. Through the methanol-to-gasoline (MTG) process, it can be transformed into gasoline. Using the methanol-to-olefin (MTO) process, methanol can also be converted to ethylene and propylene, the two chemicals produced in largest amounts by the petrochemical industry.[8] These are important building blocks for the production of essential polymers (LDPE, HDPE, PP) and like other chemical intermediates are currently produced mainly from petroleum feedstock. Their production from methanol could therefore reduce our dependency on petroleum. It would also make it possible to continue producing these chemicals when fossil fuels reserves are depleted.

3 - Methanol production for a methanol economy

The methanol needed in the methanol economy can be synthesized not only from a wide array of carbon sources including still available fossil fuels and biomass but also CO_2 emitted from fossil fuel burning power plants and other industries and eventually even the CO_2 contained in the air.

Today methanol is produced exclusively from methane through syngas. Although conventional natural gas resources are currently the preferred feedstock for the production of methanol, unconventional gas resources such as coalbed methane, tight sand gas and eventually the very large methane hydrate resources present under the continental shelves of the seas and Siberian and Canadian tundra could also be used. Besides methane all other conventional or unconventional (tar sands, oil shale,etc.) fossil fuels could be utilized to produce methanol.

Besides the conventional route to methanol from methane passing through syngas generation by steam reforming combined (or not) with partial oxidation, new and more efficient ways to produce methanol from methane are being developed. These include:

Methane oxidation with homogeneous catalysts in sulfuric acid media

Methane bromination followed by hydrolysis of the obtained bromo methane

Direct oxidation of methane with oxygen

Microbial or photochemical conversion of methane

The use of methane or another fossil fuel for the production of methanol using all the above mentioned synthetic routes has a potential drawback: the emission of the greenhouse gas carbon dioxide CO_2. To mitigate this, methanol can be made through ways minimizing the emission of CO_2. One solution is to produce it from syngas obtained by biomass gasification. For this purpose any biomass can be used including wood, wood wastes, grass, agricultural crops and their by-products, animal waste, aquatic plants and municipal waste. There is no need to use food crops as in the case of ethanol from corn, sugar cane and wheat.

Biomass → Syngas (CO, CO_2, H_2) → CH_3OH

More importantly, methanol can also be produced from CO_2 by catalytic hydrogenation of CO_2 with H_2 where the hydrogen has been obtained from water electrolysis. Methanol may also be produced through CO_2 electrochemical reduction, if electrical power is available. The energy needed for these reactions in order to be carbon neutral would come from renewable energy sources such as wind, hydroelectricity and solar as well as nuclear power. In effect, all of them allow free energy to be stored in easily transportable methanol, which is made immediately from hydrogen and carbon dioxide, rather than attempting to store energy in free hydrogen.

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

$CO_2 + 2H_2O + \text{electrons} \rightarrow CO + 2H_2\ (+ 3/2\ O_2) \rightarrow CH_3OH$

The necessary CO_2 would be captured from fossil fuel burning power plants and other industrial flue gases including cement factories. With diminishing fossil fuel resources and therefore CO_2 emissions, the CO_2 content in the air could also be used. Considering the low concentration of CO_2 in air (0.037%) improved and economically viable technologies to absorb CO_2 will have to be developed. This would allow the chemical recycling of CO_2, thus mimicking nature's photosynthesis.

4 - Advantages over other energy storage media

In the process of photosynthesis, green plants use the energy of sunlight to split water into free oxygen (which is released) and free hydrogen. Rather than attempt to store the hydrogen, plants immediately capture carbon dioxide from the air to allow the hydrogen to reduce it to storable fuels such as hydrocarbons (plant oils and terpenes) and poly alcohols (glycerol, sugars and starches). In the methanol economy, any process which similarly produces free hydrogen, proposes to immediately use it "captively" to reduce carbon dioxide into methanol, which, like plant products from photosynthesis, has great advantages in storage and transport over free hydrogen itself.

4 – 1 - Advantages over hydrogen

Methanol economy advantages compared to a hydrogen economy:

Efficient energy storage by volume, as compared with compressed hydrogen [9]. And when hydrogen pressure-confinement vessel is taken into account, an advantage in energy storage by weight can also be realized. The volumetric energy density of methanol is considerably higher than liquid hydrogen, in part because of the low density of liquid hydrogen of 71 grams/litre. Hence there is actually more hydrogen in a liter of methanol (99 grams/litre) than in a litre of liquid hydrogen, and methanol needs no cryogenic container maintained at a temperature of -253°C .

A liquid hydrogen infrastructure would be prohibitively expensive. Methanol can use existing gasoline infrastructure with only limited modifications.

Can be blended with gasoline (for example in M85, a mixture containing 85% methanol and 15% gasoline).

User friendly. Hydrogen is volatile and requires high pressure or cryogenic system confinement.

4 – 2 - Methanol economy advantages compared to ethanol

Can be made from any organic material using proven technology going through syngas. There is no need to use food crops and compete with food production. The amount of methanol that can be generated from biomass is much greater than ethanol.

Can compete with and complement ethanol in a diversified energy marketplace. Methanol obtained from fossil fuels has a lower price than ethanol.

Can be blended in gasoline like ethanol. In 2007, China blended more than 1 billion US gallons (3,800,000 m^3) of methanol into fuel and will introduce methanol fuel standard by mid-2008.[10] M85, a mixture of 85% methanol and 15 % gasoline can be used much like E85 sold in some gas stations today.

5 - Methanol economy disadvantages

High energy costs associated with generating hydrogen (when needed to synthesize methanol)

Depending on the feedstock the generation in itself may be not clean

Presently generated from syngas still dependent on fossil fuels (although in theory any energy source can be used).

Energy density (by weight or volume) one half of that of gasoline and 24 % less than ethanol

Corrosive to some metals including aluminum, zinc and manganese. Parts of the engine fuel - intake systems are made from aluminum. Similar to ethanol, compatible material for fuel tanks, gasket and engine intake have to be used.

As with similarly corrosive and hydrophilic ethanol, existing pipelines designed for petroleum products cannot handle methanol. Thus methanol requires shipment at higher energy cost in trucks and trains, until a whole new pipeline infrastructure can be built.

Methanol, as an alcohol, increases the permeability of some plastics to fuel vapors (e.g. high-density polyethylene).[12] This property of methanol has the possibility of increasing emissions of volatile organic compounds (VOCs) from fuel, which contributes to increased tropospheric ozone and possibly human exposure.

Low volatility in cold weather: pure methanol-fueled engines can be difficult to start, and they run inefficiently until warmed up. This is why a mixture containing 85% methanol and 15% gasoline called M85 is generally used in ICEs. The gasoline allows the engine to start even at lower temperatures.

Methanol is generally considered toxic. Methanol is in fact toxic and eventually lethal when ingested in larger amounts (30 to 100 mL).[14] But so are most motor fuels, including gasoline (120 to 300 mL) and diesel fuel. Gasoline also contains many compounds known to be carcinogenic (e.g. benzene). Methanol is not a carcinogen, nor does it contain any carcinogens. However, methanol may be metabolized in the body to formaldehyde, which is both toxic and carcinogenic. Methanol occurs naturally in small quantities in the human body and in edible fruits.

Methanol is a liquid: this creates a greater fire risk compared to hydrogen in open spaces. Methanol leaks do not dissipate. A methanol-based fire burns invisibly unlike gasoline. Compared to gasoline, however, methanol is much safer. It is more difficult to ignite and releases less heat when it burns. Methanol fires can be extinguished with plain water, whereas gasoline floats on water and continues to burn. The EPA has estimated that switching fuels from gasoline to methanol would reduce the incidence of fuel related fires by 90 %.

Methanol accidentally released from leaking underground fuel storage tanks may undergo relatively rapid groundwater transport and contaminate well water, although this risk has not been thoroughly studied. The history of the fuel additive methyl t-butyl ether (MTBE) as a groundwater contaminant has highlighted the importance of assessing the potential impacts of fuel and fuel additives on multiple environmental media . An accidental release of methanol in the environment would, however, cause much less damage than a comparable gasoline or crude oil spill. Unlike these fuels, methanol, being totally soluble in water, would be rapidly diluted to a concentration low enough for microorganism to start bio degradation. Methanol is in fact used for de nitrification in water treatment plant as a nutrient for bacteria.

Methanol Fuel

Contents

1 - Introduction

Methanol is an alternative fuel for internal combustion and other engines, either in combination with gasoline or directly ("neat"). It is used in racing cars in many countries and in China. In the U.S., methanol fuel has received less attention than ethanol fuel as an alternative to petroleum-based fuels, because in the 2000s particularly, the support of corn-based ethanol offered certain political advantages. In general, ethanol is less toxic and has higher energy density, although methanol is less expensive to produce sustainably and is a less expensive way to reduce the carbon footprint. However, for optimizing engine performance, fuel availability, toxicity and political advantage, a blend of ethanol, methanol and petroleum is likely to be preferable to using any of these individual substances alone. Methanol may be made from hydrocarbon or renewable resources, in particular natural gas and biomass respectively. It can also be synthesized from CO_2 (carbon dioxide) and hydrogen.

2 - History and production

Historically, methanol was first produced by destructive distillation (pyrolysis) of wood, resulting in its common English name of wood alcohol.

At present, methanol is usually produced using methane (the chief constituent of natural gas) as a raw material. In China, methanol is made for fuel from coal.

"Bio methanol" may be produced by gasification of organic materials to synthesis gas followed by conventional methanol synthesis. This route can offer methanol production from biomass at efficiencies up to 75 %. [Widespread production by this route has a proposed potential (see Hagen, SABD & Olah references below) to offer methanol fuel at a low cost and with benefits to the environment. These production methods, however, are not suitable for small-scale production.

Recently, methanol fuel has been produced using renewable energy and carbon dioxide as a feedstock. Carbon Recycling International, an Icelandic-American company, completed the first commercial scale renewable methanol plant in 2011.

3 - Major fuel use

During the OPEC 1973 oil crisis, Reed and Lerner (1973) proposed methanol from coal as a proven fuel with well-established manufacturing technology and sufficient resources to replace gasoline.[3] Hagen (1976) reviewed prospects for synthesizing methanol from renewable resources and its use as a fuel.[4] Then in 1986, the Swedish Motor Fuel Technology Co. (SBAD) extensively reviewed the use of alcohols and alcohol blends as motor fuels . It reviewed the potential for methanol production from natural gas, very heavy oils, bituminous shales, coals, peat and biomass. In 2005 , 2006 Nobel prize winner George A. Olah and colleagues advocated an entire methanol economy based on energy storage in synthetically produced methanol . The Methanol Institute, the methanol trade industry organization, posts reports and presentations on methanol. Director Gregory Dolan presented the 2008 global methanol fuel industry in China.

On January 26, 2011, the European Union's Directorate-General for Competition approved the Swedish Energy Agency's award of 500 million Swedish kronor (approx. €56M as at January 2011) toward the construction of a 3 billion Swedish kronor (approx. €335M) industrial scale experimental development biofuels plant for production of Biomethanol and BioDME at the Domsjö Fabriker biorefinery complex in Örnsköldsvik, Sweden, using Chemrec's black liquor gasification technology.

4 - Uses

4 – 1 - Internal combustion engine fuel

Both methanol and ethanol burn at lower temperatures than gasoline, and both are less volatile, making engine starting in cold weather more difficult. Using methanol as a fuel in spark-ignition engines can offer an increased thermal efficiency and increased power output (as compared to gasoline) due to its high octane rating (114) and high heat of vaporization. However, its low energy content of 19.7 MJ/kg and stoichiometric air-to-fuel ratio of 6.42:1 mean that fuel consumption (on volume or mass bases) will be higher than hydrocarbon fuels. The extra water produced also makes the charge rather wet (similar to hydrogen/oxygen combustion engines) and with the formation of acidic products during combustion, the wearing of valves, valve seats and cylinder might be higher than with hydrocarbon burning. Certain additives may be added to the fuel in order to neutralize these acids.

Methanol, just like ethanol, contains soluble and insoluble contaminants. These soluble contaminants, halide ions such as chloride ions, have a large effect on the corrosivity of alcohol fuels. Halide ions increase corrosion in two ways; they chemically attack passivating oxide films on several metals causing pitting corrosion, and they increase the conductivity of the fuel. Increased electrical conductivity promotes electric, galvanic, and ordinary corrosion in the fuel system. Soluble contaminants, such as aluminum hydroxide, itself a product of corrosion by halide ions, clog the fuel system over time.

Methanol is hygroscopic, meaning it will absorb water vapor directly from the atmosphere.[2] Because absorbed water dilutes the fuel value of the methanol (although it suppresses engine knock), and may cause phase separation of methanol-gasoline blends, containers of methanol fuels must be kept tightly sealed.

4 – 2 - Racing

Beginning in 1965, pure methanol was used wide spread in USAC Indy car competition, which at the time included the Indiana polis 500.

A seven-car crash on the second lap of the 1964 Indianapolis 500 resulted in USAC's decision to encourage, and later mandate, the use of methanol. Eddie Sachs and Dave MacDonald died in the crash when their gasoline-fueled cars exploded. The gasoline-triggered fire created a dangerous cloud of thick black smoke that completely blocked the view of the track for oncoming cars. Johnny Rutherford, one of the other drivers involved, drove a methanol-fueled car, which also leaked following the crash. While this car burned from the impact of the first fireball, it formed a much smaller inferno than the gasoline cars, and one that burned invisibly. That testimony, and pressure from **Indianapolis Star** writer George Moore, led to the switch to alcohol fuel in 1965.

Methanol was used by the CART circuit during its entire campaign (1979–2007). It is also used by many-short track organizations, especially midget, sprint cars and speedway bikes. Pure methanol was used by the IRL from 1996-2006.

In 2006, in partnership with the ethanol industry, the IRL used a mixture of 10% ethanol and 90% methanol as its fuel. Starting in 2007, the IRL switched to "pure" ethanol, E100.

Methanol fuel is also used extensively in drag racing, primarily in the Top Alcohol category, while between 10 % and 20 % methanol may be used in Top Fuel classes in addition to Nitromethane.

Formula One racing continues to use gasoline as its fuel, but in prewar grand prix racing methanol was often used in the fuel.

Methanol is also used in Monster Truck racing.

4 – 3 - Fuel for model engines

The earliest model engines for free-flight model aircraft flown before the end of World War II used a 3:1 mix of white gas and motor oil for the two-stroke spark ignition engines used for the hobby at that time. By 1948, the new glow plug-ignition model engines began to take over the market, requiring the use of methanol fuel to react in a catalytic reaction with the coiled platinum filament in a glow plug for the engine to run. The glow-ignition variety of model engine, because it no longer required an onboard battery, ignition coil, ignition points and capacitor that a spark ignition model engine required, saved valuable weight and allowed model aircraft to have better flight performance. In their current two - and four-stroke forms, methanol-fueled glow engines are the usual choice for radio controlled aircraft for recreational use, for engine sizes that can range from 0.8 cm3 (0.049 cu.in.) to as large as 25 to 32 cm3 (1.5-2.0 cu.in) displacement, and significantly larger displacements for twin and multi-cylinder opposed-cylinder and radial configuration model aircraft engines, many of which are of four-stroke configuration.

5 - Toxicity

Methanol occurs naturally in the human body and in some fruits, but is poisonous in sufficient concentration. Ingestion of 10 ml can cause blindness and 60-100 ml can be fatal if the condition is untreated.[13] Like many volatile chemicals, methanol does not have to be swallowed to be dangerous since the liquid can be absorbed through the skin, and the vapors through the lungs. Methanol fuel is much safer when blended with ethanol, even at relatively low ethanol percentages.

US maximum allowed exposure in air (40 h / week) is 1900 mg / m^3 for ethanol, 900 mg/m^3 for gasoline, and 1260 mg/m^3 for methanol. However, it is much less volatile than gasoline, and therefore has lower evaporative emissions, producing a lower exposure risk for an equivalent spill. While methanol offers somewhat different toxicity exposure pathways, the effective toxicity is no worse than those of benzene or gasoline, and methanol poisoning is far easier to treat successfully. One substantial concern is that methanol poisoning generally must be treated while it is still asymptomatic for full recovery.

Inhalation risk is mitigated by a characteristic pungent odor. At concentrations greater than 2,000 ppm (0.2%) it is generally quite noticeable, however lower concentrations may remain undetected while still being potentially toxic over longer exposures, and may still present a fire/explosion hazard. Again, this is similar to gasoline and ethanol; standard safety protocols exist for methanol and are very similar to those for gasoline and ethanol.

Use of methanol fuel reduces the exhaust emissions of certain hydrocarbon-related toxins such as benzene and 1,3 butadiene, and dramatically reduces long term groundwater pollution caused by fuel spills. Unlike benzene - family fuels, methanol will rapidly and non-toxically biodegrade with no long - term harm to the environment as long as it is sufficiently diluted.

6 - Fire safety

Methanol is far more difficult to ignite than gasoline and burns about 60 % slower. A methanol fire releases energy at around 20% of the rate of a gasoline fire, resulting in a much cooler flame. This results in a much less dangerous fire that is easier to contain with proper protocols. Unlike gasoline, water is acceptable and even preferred as a fire suppressant, since this both cools the fire and rapidly dilutes the fuel below the concentration where it will maintain self-flammability. These facts mean that, as a vehicle fuel, methanol has great safety advantages over gasoline. Ethanol shares many of these same advantages.

Since methanol vapor is heavier than air, it will linger close to the ground or in a pit unless there is good ventilation, and if the concentration of methanol is above 6.7 % in air it can be lit by a spark and will explode above 54 F / 12 C. Once ablaze, an undiluted methanol fire gives off very little visible light, making it potentially very hard to see the fire or even estimate its size in bright daylight, although in the vast majority of cases, existing pollutants or flammables in the fire (such as tires or asphalt) will color and enhance the visibility of the fire. Ethanol, natural gas, hydrogen, and other existing fuels offer similar fire-safety challenges, and standard safety and firefighting protocols exist for all such fuels.

Post-accident environmental damage mitigation is facilitated by the fact that low-concentration methanol is biodegradable, of low toxicity, and non-persistent in the environment. Post-fire cleanup often merely requires large additional amounts of water to dilute the spilled methanol followed by vacuuming or absorption recovery of the fluid. Any methanol that unavoidably escapes into the environment will have little long-term impact, and with sufficient dilution will rapidly biodegrade with little to no environmental damage due to toxicity. A methanol spill that combines with an existing gasoline spill can cause the mixed methanol/gasoline spill to persist about 30% to 35% longer than the gasoline alone would have done.

7 - Use

7 – 1 - United States

The State of California ran an experimental program from 1980 to 1990 that allowed anyone to convert a gasoline vehicle to 85% methanol with 15% additives of choice. Over 500 vehicles were converted to high compression and dedicated use of the 85/15 methanol and ethanol, with great results. Detroit was not willing to produce any methanol or ethanol vehicles without government subsidy.

In 1982 the big three were each given $5,000,000 for design and contracts for 5,000 vehicles to be bought by the State. That was the beginning of the low-compression flexible-fuel vehicles that we can still buy today.

In 2005, California's Governor, Arnold Schwarzenegger, stopped the use of methanol after 25 years and 200,000,000 miles of success, to join the expanding use of ethanol driven by producers of corn. In spite of this, he was optimistic about the future of the program, claiming "it will be back." Ethanol is currently (as of 2007) priced at 3 to 4 dollars per gallon at the pump, while methanol made from natural gas remains at 47 cents per gallon in bulk, not at the pump.

Presently there are zero operating gas stations in California supplying methanol in their pumps. Rep. Eliot Engel [D-NY17] has introduced "An Open Fuel Standard" Act in Congress: "To require automobile manufacturers to ensure that not less than 80 percent of the automobiles manufactured or sold in the United States by each such manufacturer to operate on fuel mixtures containing 85 percent ethanol, 85 percent methanol, or biodiesel."

7 – 2 - European Union

The amended Fuel Quality Directive adopted in 2009 allows up to 3 % v / v blend-in of methanol in petrol.

7 – 2 - Brazil

A drive to add an appreciable percentage of methanol to gasoline got very close to implementation in Brazil, following a pilot test set up by a group of scientists involving blending gasoline with methanol between 1989 and 1992. The larger-scale pilot experiment that was to be conducted in São Paulo was vetoed at the last minute by the city's mayor, out of concern for the health of gas station workers, who are mostly illiterate and could not be expected to follow safety precautions. As of 2006 , the idea has not resurfaced.

Air – Auel Ratio

Contents

1 - Introduction

Air – fuel ratio (**AFR**) is the mass ratio of air to fuel present in an internal combustion engine. If exactly enough air is provided to completely burn all of the fuel, the ratio is known as the stoichiometric mixture, often abbreviated to **stoich**. AFR is an important measure for anti-pollution and performance-tuning reasons. The lower the excess air, the "richer" the flame.

2 - Synopsis

In theory a stoichiometric mixture has just enough air to completely burn the available fuel. In practice this is never quite achieved, due primarily to the very short time available in an internal combustion engine for each combustion cycle. Most of the combustion process completes in approximately 4 – 5 milliseconds at an engine speed of 6000 rpm. This is the time that elapses from when the spark is fired until the burning of the fuel air mix is essentially complete after some 80 degrees of crankshaft rotation. Catalytic converters are designed to work best when the exhaust gases passing through them are the result of nearly perfect combustion.

A stoichiometric mixture unfortunately burns very hot and can damage engine components if the engine is placed under high load at this fuel–air mixture. Due to the high temperatures at this mixture, detonation of the fuel air mix shortly after maximum cylinder pressure is possible under high load (referred to as knocking or pinging). Detonation can cause serious engine damage as the uncontrolled burning of the fuel air mix can create very high pressures in the cylinder. As a consequence stoichiometric mixtures are only used under light load conditions. For acceleration and high load conditions, a richer mixture (lower air-fuel ratio) is used to produce cooler combustion products and thereby prevent detonation and overheating of the cylinder head.

3 - Engine management systems

A stoichiometric mixture is the working point that modern engine management systems employing fuel injection attempt to achieve in light load cruise situations. For gasoline fuel, the stoichiometric air–fuel mixture is approximately 13:1 but E.P.A. regulations raised the ratio to 14:1 to allow the use of catalytic converters i.e. for every one gram of fuel, 14.7 grams of air are required (the fuel oxydation reaction is: $25 / 2\ O_2 + C_8H_{18} \rightarrow 8\ CO_2 + 9\ H_2O$). Any mixture less than 14.7 to 1 is considered to be a rich mixture; any more than 14.7 to 1 is a lean mixture – given perfect (ideal) "test" fuel (gasoline consisting of solely n-heptane and iso-octane). In reality, most fuels consist of a combination of heptane, octane, a handful of other alkanes, plus additives including detergents, and possibly oxygenators such as MTBE (methyl tert-butyl ether) or ethanol / methanol. These compounds all alter the stoichiometric ratio, with most of the additives pushing the ratio downward (oxygenators bring extra oxygen to the combustion event in liquid form that is released at time of combustions; for MTBE- laden fuel, a stoichiometric ratio can be as low as 14.1:1). Vehicles using an oxygen sensor(s) or other feedback-loop to control fuel to air ratios (usually by controlling fuel volume) will usually compensate automatically for this change in the fuel's stoichiometric rate by measuring the exhaust gas composition, while vehicles without such controls (such as most motorcycles until recently, and cars predating the mid-1980s) may have difficulties running certain boutique blends of fuels (esp. winter fuels used in some areas) and may need to be rejetted (or otherwise have the fueling ratios altered) to compensate for special boutique fuel mixes. Vehicles using oxygen sensors enable the air-fuel ratio to be monitored by means of an air–fuel ratio meter.

4 - Other types of engine

In the typical air to natural gas combustion burner, a double cross limit strategy is employed to ensure ratio control. (This method was used in World War 2). The strategy involves adding the opposite flow feedback into the limiting control of the respective gas (air or fuel).This assures ratio control within an acceptable margin.

5 - Other terms used

There are other terms commonly used when discussing the mixture of air and fuel in internal combustion engines.

5 – 1 - Mixture

Mixture is the predominant word that appears in training texts, operation manuals and maintenance manuals in the aviation world.

5 – 2 - Air–fuel ratio (AFR)

The **air–fuel ratio** is the most common reference term used for mixtures in internal combustion engines.

$$AFR = \frac{m_{air}}{m_{fuel}}$$

It is the ratio between the *mass* of air and the mass of fuel in the fuel–air mix at any given moment. The mass used is the mass of all constituents that compose the fuel and air whether the constituents are combustible or not. For example, if calculating the mass of natural gas which often contains carbon dioxide (CO_2) and nitrogen (N_2) as well as various alkanes, the mass of the carbon dioxide and nitrogen are included in addition to all alkanes to determine the value of m_{fuel}.[1]

For pure octane the stoichiometric mixture is approximately 14.7:1, or λ of 1.00 exactly.

In naturally aspirated engines powered by octane, maximum power is frequently reached at AFRs ranging from 12.5 to 13.3:1 or λ of 0.850 to 0.901.

5 – 3 - Fuel–air ratio (FAR)

Fuel–air ratio is commonly used in the gas turbine industry as well as in government studies of internal combustion engine, and refers to the ratio of fuel to the air.

$$FAR = \frac{1}{AFR}$$

5 – 4 - Air-Fuel Equivalence Ratio

Air-Fuel equivalence ratio, λ, is the ratio of actual AFR to stoichiometry for a given mixture. λ= 1.0 is at stoichiometry, rich mixtures λ < 1.0, and lean mixtures λ > 1.0.

There is a direct relationship between λ and AFR. To calculate AFR from a given λ, multiply the measured λ by the stoichiometric AFR for that fuel. Alternatively, to recover λ from an AFR, divide AFR by the stoichiometric AFR for that fuel. This last equation is often used as the definition of λ:

$$\lambda = \frac{AFR}{AFR_{stoich}}$$

Because the composition of common fuels varies seasonally, and because many modern vehicles can handle different fuels, when tuning, it makes more sense to talk about λ values rather than AFR.

Most practical AFR devices actually measure the amount of residual oxygen (for lean mixes) or unburnt hydrocarbons (for rich mixtures) in the exhaust gas as know in PPCHS.

5 – 5 - Fuel-Air Equivalence ratio

The **fuel-air equivalence ratio** of a system is defined as the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio. Mathematically,

$$\phi = \frac{\text{fuel-to-oxidizer ratio}}{(\text{fuel-to-oxidizer ratio})_{st}} = \frac{m_{fuel}/m_{ox}}{(m_{fuel}/m_{ox})_{st}} = \frac{n_{fuel}/n_{ox}}{(n_{fuel}/n_{ox})_{st}}$$

where, *m* represents the mass, *n* represents number of moles, suffix *st* stands for stoichiometric conditions.

The advantage of using equivalence ratio over fuel–oxidizer ratio is that it takes into account, and therefore is independent, both mass and molar values for the fuel and the oxidizer. Consider a mixture of one mole of ethane (C_2H_6) and one mole of oxygen (O_2).

Fuel –oxidizer ratio of this mixture based on the mass of fuel and air is

$$\frac{m_{\mathrm{C_2H_6}}}{m_{\mathrm{O_2}}} = \frac{1\cdot(2\cdot 12+6\cdot 1)}{1\cdot(2\cdot 16)} = \frac{30}{32} = 0.938$$

Clearly the two values are not equal. To compare it with the equivalence ratio, we need to determine the fuel–oxidizer ratio of ethane and oxygen mixture. For this we need to consider the stoichiometric reaction of ethane and oxygen,

Another advantage of using the equivalence ratio is that ratios greater than one always represent excess fuel in the fuel–oxidizer mixture than would be required for complete combustion (stoichiometric reaction) irrespective of the fuel and oxidizer being used, while ratios less than one represent a deficiency of fuel or equivalently excess oxidizer in the mixture.

This is not the case if one uses fuel–oxidizer ratio, which will take different values for different mixtures.

The fuel-air equivalence ratio is related to the air-fuel equivalence ratio (defined previously) as follows:

6 - Stoichiometric mixture fraction

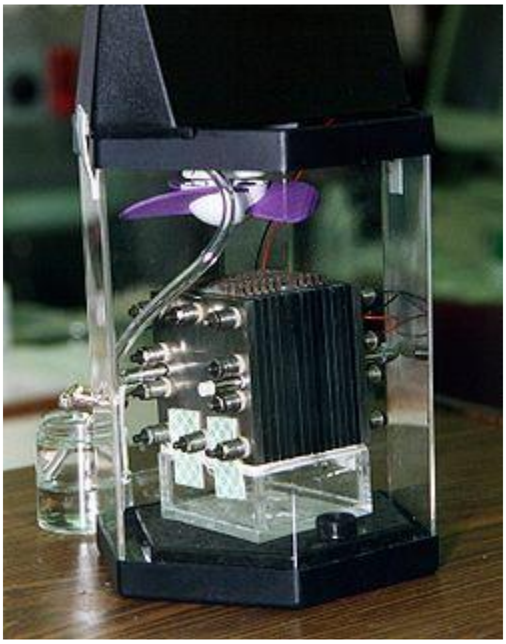
The relative amounts of oxygen enrichment and fuel dilution can be quantified by the stoichiometric mixture fraction, Z_{st}, defined as, where and represent the fuel and oxidizer mass fractions at the inlet, and are the species molecular weights, and and are the fuel and oxygen stoichiometric coefficients, respectively.

Z_{st} is related to lambda and AFR by the equations:

7 - Percent excess combustion air

In industrial fired heaters, power plant steam generators, and large gas-fired turbines, the more common term is percent excess combustion air. For example, excess combustion air of 15 percent means that 15 percent more than the required stoichiometric air is being used.

Direct Methanol Fuel Cell



Direct-methanol fuel cell

Contents

1 - Introduction

Direct-methanol fuel cells or **DMFCs** are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel. Their main advantage is the ease of transport of methanol, an energy-dense yet reasonably stable liquid at all environmental conditions.

Efficiency is quite low for these cells, so they are targeted especially to portable applications, where energy and power density are more important than efficiency.

A more efficient version of a direct fuel cell would play a key role in the theoretical use of methanol as a general energy transport medium, in the hypothesized methanol economy.

2 - The cell

In contrast to indirect methanol fuel cells, where methanol is reacted to hydrogen by steam reforming, DMFCs use a methanol solution (usually around 1M, i.e. about 3 % in mass) to carry the reactant into the cell; common operating temperatures are in the range 50 – 120 °C , where high temperatures are usually pressurized. DMFCs themselves are more efficient at high temperatures and pressures, but these conditions end up causing so many losses in the complete system that the advantage is lost ; therefore, atmospheric-pressure configurations are currently preferred.

Because of the methanol cross-over, a phenomenon by which methanol diffuses through the membrane without reacting, methanol is fed as a weak solution: this decreases efficiency significantly, since crossed - over methanol, after reaching the air side (the cathode), immediately reacts with air; though the exact kinetics are debated, the end result is a reduction of the cell voltage. Cross-over remains a major factor in inefficiencies, and often half of the methanol is lost to cross - over.

Other issues include the management of carbon dioxide created at the anode, the sluggish dynamic behavior, and the ability to maintain the solution water.

The only waste products with these types of fuel cells are carbon dioxide and water.

3 - History

In 1990 superacid specialist Dr. Surya Prakash, and Nobel laureate Dr. George A. Olah, both of the University of Southern California's Loker Hydrocarbon Research Institute, invented a fuel cell that would directly convert methanol to electricity. USC, in a collaborative effort with Jet Propulsion Laboratory (JPL) proceeded to invent the direct oxidation of liquid hydrocarbons subsequently coined as DMFC, Direct Methanol Fuel Cell Technology. Others were involved in the invention, including California Institute of Technology (Caltech) and DTI Energy, Inc. Some advances in DMFC have been: bringing down the fuel crossover, miniaturizing the cell for consumer and military products, ceramic plates, carbon nanotubes, porous silicon layers and oxidation reduction.

4 - Application

Current DMFCs are limited in the power they can produce, but can still store a high energy content in a small space. This means they can produce a small amount of power over a long period of time. This makes them ill-suited for powering large vehicles (at least directly), but ideal for smaller vehicles such as forklifts and tuggers[2] and consumer goods such as mobile phones, digital cameras or laptops. Military applications of DMFCs are an emerging application since they have low noise and thermal signatures and no toxic effluent. These applications include power for man-portable tactical equipment, battery chargers, and autonomous power for test and training instrumentation. Units are available with power outputs between 25 watts and 5 kilowatts with durations up to 100 hours between refuelings.

5 - Methanol

Methanol is a liquid from - 97.0 °C to 64.7 °C at atmospheric pressure. The energy density of methanol is an order of magnitude greater than even highly compressed hydrogen, and 15 times higher than Lithium - ion batteries.

Methanol is toxic and flammable. However, the International Civil Aviation Organization's (ICAO) Dangerous Goods Panel (DGP) voted in November 2005 to allow passengers to carry and use micro fuel cells and methanol fuel cartridges when aboard airplanes to power laptop computers and other consumer electronic devices. On September 24, 2007, the US Department of Transportation issued a proposal to allow airline passengers to carry fuel cell cartridges on board.[3] The Department of Transportation issued a final ruling on

April 30, 2008, permitting passengers and crew to carry an approved fuel cell with an installed methanol cartridge and up to two additional spare cartridges . It is worth noting that 200 ml maximum methanol cartridge volume allowed in the final ruling is double the 100 ml limit on liquids allowed by the Transportation Security Administration in carry-on bags.

6 - Reaction

The DMFC relies upon the oxidation of methanol on a catalyst layer to form carbon dioxide. Water is consumed at the anode and is produced at the cathode. Protons (H^+) are transported across the proton exchange membrane - often made from Nafion - to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing power to connected devices.

The half-reactions are :

	Equation
Anode	$CH_3OH + H_2O \rightarrow 6\ H^+ + 6\ e^- + CO_2$ Oxidation
Cathode	$\frac{3}{2}O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$ Reduction
Overall reaction	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2\ H_2O + CO_2$ Redox Reaction

Methanol and water are adsorbed on a catalyst usually made of platinum and ruthenium particles, and lose protons until carbon dioxide is formed. As water is consumed at the anode in the reaction, pure methanol cannot be used without provision of water via either passive transport such as back diffusion (osmosis), or active transport such as pumping. The need for water limits the energy density of the fuel.

Platinum is used as a catalyst for both half-reactions. This contributes to the loss of cell voltage potential, as any methanol that is present in the cathode chamber will oxidize. If another catalyst could be found for the reduction of oxygen, the problem of methanol crossover would likely be significantly lessened. Furthermore, platinum is very expensive and contributes to the high cost per kilowatt of these cells.

During the methanol oxidation reaction carbon monoxide (CO) is formed, which strongly adsorbs onto the platinum catalyst, reducing the surface area and thus the performance of the cell. The addition of another components, such as ruthenium or gold, to the catalyst tends to ameliorate this problem because, according to the most well-established theory in the field, these catalysts oxidize water to yield OH radicals: $H_2O \rightarrow OH\bullet + H^+ + e^-$. The OH species from the oxidized water molecule oxidizes CO to produce CO_2 which can then be released as a gas: $CO + OH\bullet \rightarrow CO_2 + H^+ + e^-$.

Using these OH groups in the half reactions, they are also expressed as :

	Equation
Anode	$CH_3OH + 6\ OH^- \rightarrow 5\ H_2O + 6\ e^- + CO_2$ Oxidation
Cathode	$\frac{3}{2}O_2 + 3\ H_2O + 6\ e^- \rightarrow 6\ OH^-$ Reduction
Overall reaction	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2\ H_2O + CO_2$ Redox Reaction

6 -1 – Cross - over current

Methanol on the anodic side is usually in a weak solution (from 1M to 3M), because methanol in high concentrations has the tendency to diffuse through the membrane to the cathode, where its concentration is about zero because it is rapidly consumed by oxygen. Low concentrations help in reducing the cross - over, but also limit the maximum attainable current.

The practical realization is usually that a solution loop enters the anode, exits, is refilled with methanol, and returns to the anode again.

6 – 2 -Water drag

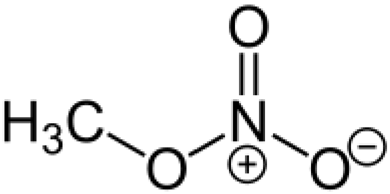
The water in the anodic loop is lost because of the anodic reaction, but mostly because of the associated water drag: every proton formed at the anode drags a number of water molecules to the cathode. Depending on temperature and membrane type, this number can be between 2 and 6.

7 - Ancillary units

A direct methanol fuel cell is usually part of a larger system including all the ancillary units that permit its operation. Compared to most other types of fuel cells, the ancillary system of DMFCs is relatively complex. The main reasons for its complexity are:

providing water along with methanol would make the fuel supply more cumbersome, so water has to be recycled in a loop;

Methyl Nitrate



Contents

1 - Introduction

Methyl nitrate is the methyl ester of nitric acid and has the chemical formula CH_3NO_3. It is a colourless volatile liquid that is explosive.

2 - Synthesis

It can be produced by the condensation of nitric acid and methanol :

$$CH_3OH + HNO_3 \rightarrow CH_3NO_3 + H_2O$$

Methyl nitrate can be produced on a laboratory or industrial scale either through the distillation of a mixture of methanol and nitric acid, or by the nitration of methanol by a mixture of sulfuric and nitric acids. The first procedure is not preferred due to the great explosion danger presented by the methyl nitrate vapour. The second procedure is essentially identical to that of making nitroglycerin. However, the process is usually run at a slightly higher temperature and the mixture is stirred mechanically on an industrial scale instead of with compressed air.

IUPAC name : methyl nitrate	
Other names : nitric acid methyl ester	
Molecular formula	CH_3NO_3
Molar mass	77 g / mol
Appearance	Liquid

Density	1.203 g / cm³, liquid
Melting point	- 82.3 °C
Boiling point	64.6 °C (explodes)[1]
Explosive data	
Explosive velocity	6300 m s^{-1}
Main hazards	Toxic, High Explosive

3 - Explosive properties

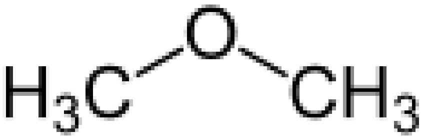
Methyl nitrate is a sensitive explosive. When ignited it burns extremely fiercely with a gray-blue flame. It is one of the most brisant explosives known . The sensitivity of methyl nitrate to initiation by detonation is among the greatest known, with even a number one blasting cap, the lowest power available, producing a near full detonation of the explosive .

Despite the superior explosive properties of methyl nitrate, it has not received application as an explosive due mostly to its high volatility, which prevents it from being stored or handled safely. It was used as a rocket fuel by Germany in World War II, in a mixture containing 25 % methanol, which was named "myrol". This mixture would evaporate at a constant rate and so its composition would not change over time. It presents a slight explosive danger (it is somewhat difficult to detonate) and does not detonate easily via shock .

4 - Safety

As well as being an explosive, methyl nitrate is toxic and causes headaches when inhaled.

Di Methyl Ether

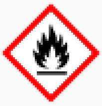


Contents

1 – Introduction

Dimethyl ether (DME), also known as **methoxymethane**, is the organic compound with the formula CH_3OCH_3. The simplest ether, it is a colourless gas that is a useful precursor to other organic compounds and an aerosol propellant.

Systematic name : Methoxy methane	
Other names : Demeon , Dimethyl oxide , Dymel , Methyl ether , Wood ether	
Molecular formula	C_2H_6O
Molar mass	46 g mol^{-1}
Appearance	Colourless gas
Odor	Typical
Density	1.97 g L^{-1}
Melting point	-141 °C
Boiling point	-24 °C

Solubility in water	71 g dm^{-3} (at 20 °C)
log P	0.022
GHS pictograms	
GHS signal word	Danger
EU classification	 F+
Flash point	- 41 °C
Autoignition temperature	350 °C
Explosive limits	27 %
Structure and properties	n, ε_r, etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

2 - Production

Today, DME is primarily produced by converting hydrocarbons sourced from natural gas or coal via gasification to synthesis gas (syngas). Synthesis gas is then converted into methanol in the presence of catalyst (usually copper-based), with subsequent methanol dehydration in the presence of a different catalyst (for example, silica-alumina) resulting in the production of DME. As described, this is a two-step (indirect synthesis) process that starts with methanol synthesis and ends with DME synthesis (methanol dehydration) . The same process can be conducted using organic waste or biomass. Approximately 50,000 tons were produced in 1985 in Western Europe by using the methanol dehydration process.[3] Alternatively, DME can be produced through direct synthesis, using a dual catalyst system that permits both methanol synthesis and dehydration in the same process unit, with no methanol isolation and purification, a procedure that by eliminating the intermediate methanol synthesis stage, the licensors claim promises efficiency advantages and cost benefits.

Both the one-step and two-step processes above are commercially available. Currently, there is more widespread application of the two-step process since it is relatively simple and start-up costs are relatively low. It is worth mentioning that there is a developing one-step liquid-phase process.

3 - Applications

The largest use of DME is currently (2010) as substitute for propane in LPG used as fuel in household and industry . The largest use of DME for this purpose is in China. DME has two other primary applications: as a propellant in aerosol canisters, and as a precursor to dimethyl sulfate. As an aerosol propellant, DME is useful as a some what polar solvent. It can also be used as a refrigerant.

3 – 1 - Feed stock

Several thousand tons of DME are consumed annually for the production of the methylating agent, dimethyl sulfate, which entails its reaction with sulfur trioxide:

$$CH_3OCH_3 + SO_3 \rightarrow (CH_3O)_2SO_2$$

DME can also be converted into acetic acid using carbonylation technology related to the Monsanto acetic acid process:

$$(CH_3)_2O + 2\ CO + H_2O \rightarrow 2\ CH_3CO_2H$$

3 – 2 - Laboratory reagent and solvent

DME is a low- temperature solvent and extraction agent, applicable to specialized laboratory procedures. Its usefulness is limited by its low boiling point (−23 °C), but the same property facilitates its removal from reaction mixtures. DME is the precursor to the useful alkylating agent, trimethy loxonium tetra fluoro borate.

3 – 3 - Fuel

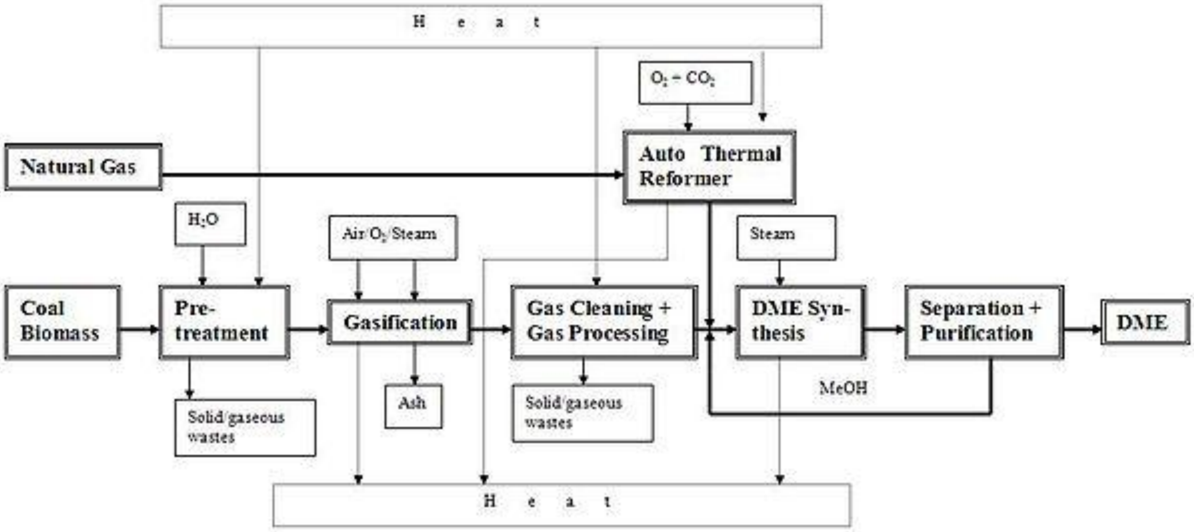
DME is a promising fuel in diesel engines , petrol engines (30% DME / 70 % LPG) , and gas turbines owing to its high cetane number, which is 55, compared to diesel's, which is 40 – 53. Only moderate modification are needed to convert a diesel engine to burn

DME. The simplicity of this short carbon chain compound leads during combustion to very low emissions of particulate matter, NO_x, and CO. For these reasons as well as being sulfur-free, DME meets even the most stringent emission regulations in Europe (EURO5), U.S. (U.S. 2010), and Japan (2009 Japan). Mobil is using DME in their methanol to gasoline process.

Installation of Bio DME synthesis towers at Chemrec's pilot facility

DME is being developed as a synthetic second generation biofuel (Bio DME), which can be manufactured from ligno cellulosic biomass. Currently the EU is considering Bio DME in its potential biofuel mix in 2030; the Volvo Group is the coordinator for the European Community Seventh Framework Programme project Bio DME where Chemrec's Bio DME pilot plant based on black liquor gasification is nearing completion in Piteå, Sweden.

The image below illustrates some of processes from various raw materials to DME.



In 2009 a team of university students from Denmark won the Urban Concept/Internal Combustion class at the European Shell Eco Marathon (The Shell Eco Marathon is an unofficial World Championship for mileage) with a vehicle running on 100 % DME. The vehicle drove 589 km/liter, fuel equivalent to gasoline with a 50 ccm 2-stroke engine operating by the Diesel principle. As well as winning they beat the old standing record of 306 km/liter, set by the same team in 2007

3 – 4 - Refrigerant

DME is also gaining popularity as a refrigerant with ASHRAE refrigerant designation R- E170 . DME is also used in refrigerant blends with e.g. butane and propene .

4 - 5 - Treating warts

A mixture of DME and propane is used in an over-the-counter device to treat warts, by freezing them.

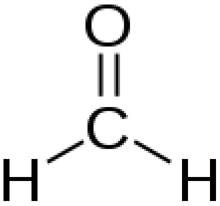
3 - 6 - Freezer spray

DME is the main constituent of freezer spray, used as a low temperature source in field testing of electronic components.

4 - Safety

Unlike other alkyl ethers, DME resists autoxidation. DME is also relatively non-toxic, although it is highly flammable.

Formaldehyde



Contents

1 - Introduction

Formaldehyde is an organic compound with the formula CH_2O. It is the simplest aldehyde, hence its systematic name **methanal**. The common name of the substance comes from its similarity and relation to formic acid.

A gas at room temperature, formaldehyde is colorless and has a characteristic pungent, irritating odor. It is an important precursor to many other materials and chemical compounds. In 2005, annual world production of formaldehyde was estimated to be 8.7 million tonnes.[3] Commercial solutions of formaldehyde in water, commonly called **formalin**, were formerly used as disinfectants and for preservation of biological specimens.

In view of its widespread use, toxicity and volatility, exposure to formaldehyde is a significant consideration for human health . In 2011, the US National Toxicology Program described formaldehyde as "known to be a human carcinogen".

IUPAC name : Methanal	
Systematic name : Methanal	
ther names :Methyl aldehyde , Methylene glycol , Methylene oxide , Formalin , Formol	
Molecular formula	CH_2O
Molar mass	30 g mol^{-1}
Appearance	Colorless gas
Density	0.8153 g /cm^3 (−20 °C)
Melting point	- 92 °C
Boiling point	-19 °C
Solubility in water	400 g dm^{-3}
Molecular shape	Trigonal planar
EU classification	Toxic (T) Corrosive (C)
Flash point	64 °C
Auto ignition temperature	430 °C
Explosive limits	7–73%
LD_{50}	100 mg / kg (oral, rat)

2 - Forms of formaldehyde

Formaldehyde is more complicated than many simple carbon compounds because it adopts different forms. One important derivative is the cyclic trimer meta formaldehyde or trioxane with the formula $(CH_2O)_3$. There is also an infinite polymer called para formaldehyde. These compounds behave, in a chemical sense, similarly to the molecule CH_2O.

When dissolved in water, formaldehyde forms a hydrate methanediol with the formula $H_2C(OH)_2$. This diol also exists in equilibrium with a series of oligomers (short polymers), depending on the concentration and temperature. A saturated water solution, that contains about 40 % formaldehyde by volume or 37 % by mass, is called "100 % formalin". A small amount of stabilizer, such as methanol, is usually added to suppress oxidation and polymerization. A typical commercial grade formalin may contain 10 –12 % methanol in addition to various metallic impurities.

3 - Occurrence

Processes in the upper atmosphere contribute up to 90 percent of the total formaldehyde in the environment. Formaldehyde is an intermediate in the oxidation (or combustion) of methane as well as other carbon compounds, e.g. forest fires, in automobile exhaust, and in tobacco smoke. When produced in the atmosphere by the action of sunlight and oxygen on atmospheric methane and other hydrocarbons, it becomes part of smog. Formaldehyde has also been detected in outer space (see below).

Formaldehyde, as well as its oligomers and hydrates, are rarely encountered in living organisms. Methanogenesis proceeds via the equivalent of formaldehyde, but this one-carbon species is masked as a methylene group in methanopterin. Formaldehyde is the primary cause of methanol's toxicity, since methanol is metabolized into formaldehyde by alcohol dehydrogenase . Formaldehyde does not accumulate in the environment, because it is broken down within a few hours by sunlight or by bacteria present in soil or water. Humans metabolize formaldehyde quickly, so it does not accumulate, and is converted to formic acid in the body.

3 – 1 - Interstellar formaldehyde

Formaldehyde was the first polyatomic organic molecule detected in the interstellar medium[8] and since its initial detection has been observed in many regions of the galaxy. Because of the widespread interest in interstellar formaldehyde it has recently been extensively studied, yielding new extragalactic sources . A proposed mechanism for the formation is the hydrogenation of CO ice, shown below.

$H + CO \rightarrow HCO$

$HCO + H \rightarrow H_2CO$ (rate constant = $9.2\times10^{-3}\ s^{-1}$)

Formaldehyde appears to be a useful probe for astrochemists due to its low reactivity in the gas phase and to the fact that the $1_{10}\leftarrow1_{11}$ and $2_{11}\leftarrow2_{12}$ K-doublet transitions are rather clear.

4 - Synthesis and industrial production

Formaldehyde was first reported in 1859 by the Russian chemist Aleksandr Butlerov (1828 – 86) and was conclusively identified in 1869 by August Wilhelm von Hofmann.

Formaldehyde is produced industrially by the catalytic oxidation of methanol. The most common catalysts are silver metal or a mixture of an iron and molybdenum or vanadium oxides. In the commonly used formox process, methanol and oxygen react at ca. 250–400 °C in presence of iron oxide in combination with molybdenum and/or vanadium to produce formaldehyde according to the chemical equation:

$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O$$

The silver-based catalyst usually operates at a higher temperature, about 650 °C. Two chemical reactions on it simultaneously produce formaldehyde: that shown above and the dehydrogenation reaction:

$$CH_3OH \rightarrow H_2CO + H_2$$

In principle formaldehyde could be generated by oxidation of methane, but this route is not industrially viable because the formaldehyde is more easily oxidized than methane.

5 - Organic chemistry

Formaldehyde is a building block in the synthesis of many other compounds of specialised and industrial significance. It exhibits most of the chemical properties of other aldehydes but is more reactive. For example it is more readily oxidized by atmospheric oxygen to formic acid (formic acid is found in ppm levels in commercial formaldehyde). Formaldehyde is a good electrophile, participating in electrophilic aromatic substitution reactions with aromatic compounds , and can undergo electrophilic addition reactions with alkenes and aromatics. Formaldehyde undergoes a Cannizzaro reaction in the presence of basic catalysts to produce formic acid and methanol.

5 – 1 - Examples of organic synthetic applications

Condensation with acetaldehyde affords penta erythritol, a chemical necessary in synthesizing PETN, a high explosive. Condensation with phenols gives phenol - formaldehyde resins. With 4-substituted phenols one obtains calixarenes.

When combined with hydrogen sulfide it forms trithiane.

$$3CH_2O + 3H_2S \rightarrow (CH_2S)_3 + 3H_2O$$

6 - Uses

6 – 1 - Industrial applications

Formaldehyde is a common precursor to more complex compounds and materials. In approximate order of decreasing consumption, products generated from formaldehyde include urea formaldehyde resin, melamine resin, phenol formaldehyde resin, poly oxy methylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate. The textile industry uses formaldehyde-based resins as finishers to make fabrics crease-resistant. Formaldehyde-based materials are key to the manufacture of automobiles, and used to make components for the transmission, electrical system, engine block, door panels, axles and brake shoes. The value of sales of formaldehyde and derivative products was over $ 145 billion in 2003, about 1.2 % of the Gross Domestic Product (GDP) of the United States and Canada. Including indirect employment, over 4 million work in the formaldehyde industry across approximately 11,900 plants in the U.S. and Canada.

When treated with phenol, urea, or melamine, formaldehyde produces, respectively, hard thermo set phenol formaldehyde resin, urea formaldehyde resin, and melamine resin. These polymers are common permanent adhesives used in plywood and carpeting. It is used as the wet-strength resin added to sanitary paper products such as (listed in increasing concentrations injected into the paper machine headstock chest) facial tissue, table napkins, and roll towels. They are also foamed to make insulation, or cast into moulded products. Production of formaldehyde resins accounts for more than half of formaldehyde consumption.

Formaldehyde is also a precursor to poly functional alcohols such as penta erythritol, which is used to make paints and explosives. Other formaldehyde derivatives include methylene diphenyl diisocyanate, an important component in poly urethane paints and foams, and hexamine, which is used in phenol-formaldehyde resins as well as the explosive RDX. Formaldehyde has been found as a contaminant in several bath products, at levels from 54–610 ppm: it is thought to arise from the breakdown of preservatives in the products, most frequently diazolidinyl urea.

6 – 2 - Disinfectant and biocide

An aqueous solution of formaldehyde can be useful as a disinfectant as it kills most bacteria and fungi (including their spores). Formaldehyde solutions are applied topically in medicine to dry the skin, such as in the treatment of warts. Many aquarists use formaldehyde as a treatment for the parasites *Ichthyophthirius multifiliis* and *Cryptocaryon irritans*.

Formaldehyde is used to inactivate bacterial products for toxoid vaccines (vaccines that use an inactive bacterial toxin to produce immunity). It is also used to kill unwanted viruses and bacteria that might contaminate the vaccine during production . Urinary tract infections are also often treated using a derivative of formaldehyde (methenamine), a method often chosen because it prevents overuse of antibiotics and the resultant development of bacterial resistance to them. In an acid environment methenamine is converted in the kidneys to formaldehyde, which then has an antibacterial effect in the urinary tract. This is not safe for long term use due to the carcinogenic effect of formaldehyde. Some topical creams, cosmetics and personal hygiene products also contain derivatives of formaldehyde as the active ingredients that prevent the growth of potentially harmful bacteria.

6 – 3 - Tissue fixative and embalming agent

Formaldehyde preserves or fixes tissue or cells by a mixture of reversible (short exposure time and low temperatures) and irreversible (long exposure time and higher temperatures) cross-linking of primary amino groups in proteins with other nearby nitrogen atoms in protein or DNA through a - CH_2 - linkage. This is exploited in ChIP-on - chip transcriptomics experiments, where nucleotide-binding proteins are cross-linked to their cognate binding sites on the chromosome and analyzed to determine what genes are regulated by the proteins. Formaldehyde is also used as a denaturing agent in RNA gel electrophoresis, preventing RNA from forming secondary structures. A solution of 4 % formaldehyde fixes pathology tissue specimens at about one mm per hour at room temperature.

Formaldehyde solutions are used as a fixative for microscopy and histology, although the percentage formaldehyde used may vary based on the method of analysis. Additionally, the methanol used to stabilize formaldehyde may interfere with the ability to properly fix tissue or cells, and therefore commercial formaldehyde preparations are available that are packaged in glass ampules under an inert gas to prevent the use of contaminating methanol for stabilization. Formaldehyde-based solutions are also used in embalming to disinfect and temporarily preserve human and animal remains. It is the ability of formaldehyde to fix the tissue that produces the tell-tale firmness of flesh in an embalmed body. In post mortem examinations a procedure known as the "sink test" involves placing the lungs of an animal in an aqueous solution of formaldehyde; if the lungs float it suggests the animal was probably breathing or able to breathe at the time of death.

Although formaldehyde solutions are commonly used as a biological preserving medium, usually for smaller specimens, it delays, but does not prevent, decay.

Several European countries restrict the use of formaldehyde, including the import of formaldehyde-treated products and embalming. Starting September 2007, the European Union banned the use of formaldehyde due to its carcinogenic properties as a biocide (including embalming) under the Biocidal Products Directive (98/8/EC) . Countries with a strong tradition of embalming corpses, such as Ireland and other colder - weather countries, have raised concerns. Despite reports to the contrary, no decision on the inclusion of formaldehyde on Annex I of the Biocidal Products Directive for product-type 22 (embalming and taxidermist fluids) had been made as of September 2009.

6 – 4 - Drug testing

Formaldehyde, along with 18 M (concentrated) sulfuric acid makes Marquis reagent which can be used to identify alkaloids and other compounds.

6 – 5 - Hobbies

In photography, formaldehyde is used in low concentrations for process C- 41 (color negative film) stabilizer in the final wash step,[26] as well as in the process E- 6 pre - bleach step, to obviate the need for it in the final wash.

7 - Safety

Formaldehyde is highly toxic to all animals, regardless of method of intake. Ingestion of as little as 30 mL of a solution containing 37 % formaldehyde has been reported to cause death in an adult human. Water solution of formaldehyde is very corrosive and its ingestion can cause severe injury to the upper gastrointestinal tract.

Occupational exposure to formaldehyde by inhalation is mainly from three types of sources: thermal or chemical decomposition of formaldehyde-based resins, formaldehyde emission from aqueous solutions (for example, embalming fluids), and the production of formaldehyde resulting from the combustion of a variety of organic compounds (for example, exhaust gases). Formaldehyde can be toxic, allergenic, and carcinogenic. Because formaldehyde resins are used in many construction materials it is one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. Formaldehyde inhaled at this concentration may cause headaches, a burning sensation in the throat, and difficulty breathing, and can trigger or aggravate asthma symptoms.

A 1988 Canadian study of houses with urea-formaldehyde foam insulation found that formaldehyde levels as low as 0.046 ppm were positively correlated with eye and nasal irritation. Although many studies have failed to show a relationship between formaldehyde and asthma, a recent review of studies has shown a strong association between exposure to formaldehyde and the development of childhood asthma. Chronic exposure at higher levels, starting at around 1.9 ppm, has been shown to result in significant damage to pulmonary function, resulting in reduced maximum mid-expiratory flow and forced vital capacity. There is also research that supports the theory that formaldehyde exposure contributes to reproductive problems in women. A study on Finnish women working in laboratories at least 3 days a week found a significant correlation between spontaneous abortion and formaldehyde exposure, and a study of Chinese women found abnormal menstrual cycles in 70 % of the women occupationally exposed to formaldehyde compared to only 17 % in the control group. There have been no studies done on the effect of formaldehyde exposure on reproduction in men.

The primary exposure concern is for the workers in the industries producing or using formaldehyde. As far back as 1987, the U.S. EPA classified it as a *probable human carcinogen* and after more studies the WHO International Agency for Research on Cancer (IARC), in 1995, also classified it as a *probable human carcinogen*. Further information and evaluation of all known data led the IARC to reclassify formaldehyde as a *known human carcinogen* associated with nasal sinus cancer and nasopharyngeal cancer. Recent studies have also shown a positive correlation between exposure to formaldehyde and the development of leukemia, particularly myeloid leukemia. The formaldehyde theory of carcinogenesis was proposed in 1978 . In the residential environment, formaldehyde exposure comes from a number of different routes; formaldehyde can off-gas from wood products, such as plywood or particle board, but it is produced by paints, varnishes, floor finishes, and cigarette smoking as well.

The United States Environmental Protection Agency (EPA) allows no more than 0.016 ppm formaldehyde in the air in new buildings constructed for that agency. A U.S. Environmental Protection Agency study found a new home measured 0.076 ppm when brand new and 0.045 ppm after 30 days. The Federal Emergency Management Agency (FEMA) has also announced limits on the formaldehyde levels in trailers purchased by that agency. The EPA recommends the use of “exterior-grade” pressed-wood products with phenol instead of urea resin to limit formaldehyde exposure, since pressed-wood products containing formaldehyde resins are often a significant source of formaldehyde in homes.

For most people, irritation from formaldehyde is temporary and reversible, though formaldehyde can cause allergies and is part of the standard patch test series. People with formaldehyde allergy are advised to avoid formaldehyde releasers as well (*e.g.*, Quaternium-15, imidazolidinyl urea, and diazolidinyl urea). People who suffer allergic reactions to formaldehyde tend to display lesions on the skin in the areas that have had direct contact with the substance, such as the neck or thighs (often due to formaldehyde released from permanent press finished clothing) or dermatitis on the face (typically from cosmetics). Formaldehyde has been banned in cosmetics in both Sweden and Japan. The eyes are most sensitive to formaldehyde exposure: The lowest level at which many people can begin to smell formaldehyde is about 0.05 ppm and the highest level is 1 ppm. The maximum concentration value at the workplace is 0.3 ppm. In controlled chamber studies, individuals begin to sense eye irritation at about 0.5 ppm; 5 to 20 percent report eye irritation at 0.5 to 1 ppm; and greater certainty for sensory irritation occurred at 1 ppm and above. While some agencies have used a level as low as 0.1 ppm as a threshold for irritation, the expert panel found that a level of 0.3 ppm would protect against nearly all irritation. In fact, the expert panel found that a level of 1.0 ppm would avoid eye irritation — the most sensitive endpoint — in 75 – 95 % of all people exposed.

Formaldehyde levels in building environments are affected by a number of factors. These include the potency of formaldehyde-emitting products present, the ratio of the surface area of emitting materials to volume of space, environmental factors, product age, interactions with other materials, and ventilation condition. Formaldehyde emits from a variety of construction materials, furnishings, and consumer products. The three products that emit the highest concentrations are medium density fiberboard, hardwood plywood, and particle board. Environmental factors such as temperature and relative humidity can elevate levels because formaldehyde has a high vapor pressure. Formaldehyde levels from building materials are the highest when a building first opens because materials would have less time to off-gas. Formaldehyde levels decrease over time as the sources suppress.

Formaldehyde levels in air can be sampled and tested in several ways, including impinger , treated sorbent, and passive monitors.[48] The National Institute for Occupational Safety and Health (NIOSH) has measurement methods numbered 2016, 2541, 3500, and 3800.

Studies on the interactions between formaldehyde and proteins at the molecular level have been reported on the effects of the body's carrier protein, serum albumin. The binding of formaldehyde loosens the skeletal structure of albumin and exposure of aromatic ring amino acids in the internal hydrophobic region. Symptoms may affect personal awareness, making one feel tired or fatigue .

Formaldehyde inhalation has also shown to cause oxidative stress and inflammation in animals. Mice studied over an exposure to a high dose of formaldehyde (3ppm), showed increased levels of NO−3 levels in plasma. This result suggests that FA inhalation either decreased NO production or increased NO scavenging, which may be an anti - stress mechanism in the body. Formaldehyde inhalation changes the sensitivity of immune system, which influences oxidative stress.

In June 2011, the twelfth edition of the National Toxicology Program (NTP) Report on Carcinogens (RoC) changed the listing status of formaldehyde from "reasonably anticipated to be a human carcinogen" to "known to be a human carcinogen".[5][6][7] Concurrently, a National Academy of Sciences (NAS) committee was convened and issued an independent review of the draft United States Environmental Protection Agency IRIS assessment of formaldehyde, providing a comprehensive health effects assessment and quantitative estimates of human risks of adverse effects.

7 – 1 - International bans

There are several web articles claiming that formaldehyde has been banned from manufacture or import into the European Union (EU) under REACH (Registration, Evaluation, Authorization, and restriction of Chemical substances) legislation. This appears to be misinformation, as official EU chemical databases contradict these claims as of February 19, 2010. This misconception has gained some ground. Formaldehyde is not listed in the Annex I of Regulation (EC) No 689/2008 (export and import of dangerous chemicals regulation), nor on a priority list for risk assessment. However, formaldehyde is banned from use in certain applications (preservatives for liquid-cooling and processing systems, slimicides, metalworking-fluid preservatives, and antifouling products) under the Biocidal Products Directive. In the EU, the maximum allowed concentration of formaldehyde in finished products is 0.2%, and any product that exceeds 0.05 % has to include a warning that the product contains formaldehyde.

In the United States, a bill was passed in congress on July 7, 2010 regarding the use of formaldehyde in hardwood plywood, particle board, and medium density fiberboard. The bill limited the allowable amount of formaldehyde emissions from these wood products to .09 ppm, a standard which companies will have to meet by January 2013. Formaldehyde was declared a toxic substance by the 1999 Canadian Environmental Protection Act.

7 – 2 - FEMA trailer incidents

7 – 2 - 1 - Hurricanes Katrina and Rita

In the U.S. the Federal Emergency Management Agency (FEMA) provided travel trailers, recreational park trailers and manufactured homes starting in 2006 for habitation by residents of the U.S. gulf coast displaced by Hurricane Katrina and Hurricane Rita. Some of the people who moved into the trailers complained of breathing difficulties, nosebleeds, and persistent headaches. Formaldehyde - catalyzed resins were used in the production of these homes.

The United States Centers For Disease Control and Prevention (CDC) performed indoor air quality testing for formaldehyde[55] in some of the units. On February 14, 2008 the CDC announced that potentially hazardous levels of formaldehyde were found in many of the travel trailers and manufactured homes provided by the agency. The CDC's preliminary evaluation of a scientifically established random sample of 519 travel trailers and manufactured homes tested between December 21, 2007 and January 23, 2008 (2+ years after manufacture) showed average levels of formaldehyde in all units of about 0.077 parts per million (ppm). Long-term exposure to levels in this range can be linked to an increased risk of cancer and, at levels above this range, there can also be a risk of respiratory illness. These levels are higher than expected in indoor air, where levels are commonly in the range of 0.01–0.02 ppm, and are higher than the Agency for Toxic Substance Disease Registry (ATSDR, division of he CDC) Minimal Risk Level (MRL) of 0.008 ppm. Levels measured ranged from 0.003 ppm to 0.59 ppm.

FEMA, which requested the testing by the CDC, said it would work aggressively to relocate all residents of the temporary housing as soon as possible. Lawsuits are being filed against FEMA as a result of the exposures.

7 – 2 – 2 - Iowa floods of 2008

Also in the U.S., problems arose in trailers again provided by FEMA to residents displaced by the Iowa floods of 2008. Several months after moving to the trailers, occupants reported violent coughing, headaches, as well as asthma, bronchitis, and other problems. Tests showed that in some trailers, levels of formaldehyde exceeded the limits recommended by the U.S. Environmental rotection Agency and American Lung Association. The associated publicity has resulted in additional testing to begin in November.

7 – 2 – 3 - 2008 Sichuan earthquake

After an earthquake hit Sichuan, China, a large number of survivors were housed in trailers made with medium-density fiberboard that emitted up to 5 times China's maximum allowable formaldehyde levels. In April 2009, 100 miscarriages were recorded in this community, which may have been linked to exposure to high levels of formaldehyde found in the trailers used for housing after the disaster.

8 - Contaminant in food

Scandals have broken in both the 2005 Indonesia food scare and 2007 Vietnam food scare regarding the addition of formaldehyde to foods to extend shelf life. After a four-year absence, in 2011 Indonesian authorities have again found some foods with formaldehyde being sold in markets in a number of regions across the country. Besides using formaldehyde, they also use borax, but not combined together . In August 2011, at least at 2 Carrefour supermarkets, the Central Jakarta Livestock and Fishery Sub-Department found a sweet glutinous rice drink (cendol) contained 10 parts per million of formaldehyde . Foods known to be contaminated include noodles, salted fish, tofu, and rumors of chicken and beer. In some places, such as China, formaldehyde is still used illegally as a preservative in foods, which exposes people to formaldehyde ingestion . In humans, the ingestion of formaldehyde has been shown to cause vomiting, abdominal pain, dizziness, and in extreme cases can cause death; in addition, there is limited evidence of a carcinogenic effect . Testing for formaldehyde is by blood and/or urine by gas chromatography - mass spectrometry. Other methods include infrared detection, gas detector tubes, etc., of which HPLC is the most sensitive In the early 1900s, it was frequently added by US milk plants to milk bottles as a method of pasteurization due to the lack of knowledge regarding formaldehyde's toxicity.

In 2011 in Nakhon Ratchasima, Thailand, truckloads of rotten chicken were exposed to formaldehyde in which "a large network" including 11 slaughterhouses run by a criminal gang were implicated. In 2012, 1 billion Rupiah (almost 1 million USD) of fish were imported from Pakistan to Batam, Indonesia were found laced with formaldehyde.

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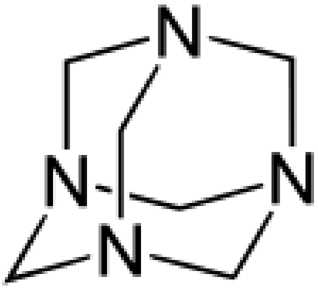
Hexa Methylene Tetramine



Contents

1 - Introduction

Hexa methylene tetramine is a heterocyclic organic compound with the formula $(CH_2)_6N_4$. This white crystalline compound is highly soluble in water and polar organic solvents. It has a cage-like structure similar to adamantane. It is useful in the synthesis of other chemical compounds, e.g. plastics, pharmaceuticals, rubber additives. It sublimes in a vacuum at 280 °C.

The compound was discovered by Aleksandr Butlerov in 1859.

IUPAC name :
1,3,5,7-Tetra aza tri cyclo [3.3.1.1] decane
Other names :
Hexamine ; Methen amine ; Urotropine;
1,3,5,7- tetra aza adamantane , Formin, Aminoform
Molecular formula $C_6H_{12}N_4$

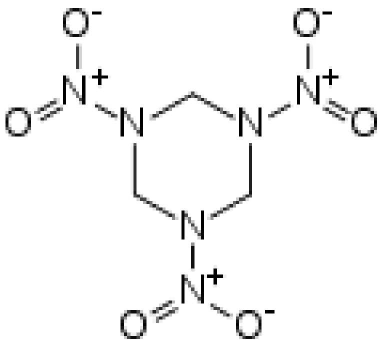
Molar mass	140 g / mol
Density	1.33 g / cm³ (at 20 °C)
Boiling point	280 °C (sublimes)
Solubility in water	85.3 g/100 mL
Main hazards	Highly flammable , harmful
Autoignition temperature	410 °C

2 - Synthesis, structure, reactivity

Hexamethylenetetramine is prepared by the reaction of formaldehyde and ammonia. The reaction can be conducted in gas-phase and in solution.

The molecule has a symmetric tetrahedral cage-like structure, similar to adamantane, whose four "corners" are nitrogen atoms and "edges" are methylene bridges. Although the molecular shape defines a cage, no void space is available at the interior for binding other atoms or molecules, unlike crown ethers or larger cryptand structures.

The molecule behaves like an amine base, undergoing protonation and *N*- alkylation .



RDX

When reacted with nitric acid, hexamine forms cyclo tri methylene tri nitramine (**RDX**). It can also be reacted with hydrogen peroxide, with a catalyst of citric acid, or dilute sulfuric acid, to form Hexa methylene tri peroxide diamine , or **HMTD**.

3 - Applications

The main use of hexamethylenetetramine is in the production of powdery or liquid preparations of phenolic resins and phenolic resin moulding compounds, where it is added as a hardening component. These products are used as binders, e.g. in brake and clutch linings, abrasive products, non-woven textiles, formed parts produced by moulding processes, and fireproof materials. It is also used to produce RDX and consequently, C- 4

3 – 1 - Medical uses

As the mandelic acid salt (generic methen amine mandelate tablets, **USP**) it is used for the treatment of urinary tract infection: hexa methyl tetra mine ("methen amine") decomposes at an acid pH to formaldehyde and ammonia, and the formaldehyde is bactericidal; the mandelic acid adds to this effect. Urinary acidity is typically ensured by co-administering vitamin C (ascorbic acid) or ammonium chloride. Its use had temporarily been reduced in the late 1990s, due to adverse effects (notably chemically-induced hemorrhagic cystitis in overdose), but its use has now been reapproved because of the prevalence of antibiotic resistance to more commonly used drugs. This drug is particularly suitable for long-term prophylactic treatment of urinary tract infection, because bacteria do not develop resistance to formaldehyde: however, it should not be used in the presence of renal insufficiency.

3 – 2 - Histological stains

Methen amine silver stains are used for staining in histology, including the following types:

Grocott's methenamine silver stain, used widely as a screen for fungal organisms.

Jones' stain, a methenamine silver-Periodic acid-Schiff that stains for basement membrane, availing to view the "spiked" Glomerular basement membrane associated with membranous glomerulonephritis.

3 – 3 - Solid fuel

Together with 1,3,5- trioxane, hexamethylenetetramine is a component of hexamine fuel tablets used by campers, hobbyists, the military and relief organizations for heating camping food or military rations. It burns smokelessly , has a high energy density (30.0 MJ / kg) , does not liquify while burning, and leaves no ashes.

Standardized 0.149 g tablets of methenamine (hexamine) are used by fire-protection laboratories as a clean and reproducible fire source to test the flammability of carpets and rugs.

3 – 4 - Food additive

Hexa methylene tetra mine or hexamine is also used as a food additive as a preservative (INS number 239). It is approved for usage for this purpose in the EU, where it is listed under E number E239, however it is not approved in the USA, Australia, or New Zealand.

3 – 5 - Reagent in organic chemistry

Hexamethylenetetramine is a versatile reagent in organic synthesis. It is used in the Duff reaction (formylation of arenes), the Sommelet reaction (converting benzyl halides to aldehydes), and in the Delepine reaction (synthesis of amines from alkyl halides).

4 - Producers

Since 1990 the number of European producers has been declining. The French SNPE factory closed in 1990; in 1993, the production of hexamethylenetetramine in Leuna, Germany ceased; in 1996, the Italian facility of Agrolinz closed down; in 2001, the UK producer Borden closed; in 2006, production at Chemko, Slovak Republic, was closed. Remaining producers include INEOS in Germany, Caldic in the Netherlands, and Hexion in Italy. In the US, Eli Lilly and Company stopped producing methenamine tablets in 2002.

Hexamine Fuel Tablet

Several Esbit tablets

Contents

1 - Introduction

A **hexamine fuel tablet** is a form of solid fuel in tablet form. The tablets burn smokelessly, have a high energy density, do not liquify while burning and leave no ashes. Invented in Murrhardt, Germany, in 1936, the main component is hexamine, which was discovered by Aleksandr Butlerov in 1859. Some fuel tablets use 1,3,5-trioxane as another ingredient.

A number of alternative names are in use, including **heat tablet** and **Esbit**. Esbit (which stands for *Erich Schumms Brennstoff in Tablettenform* or *Erich Schumm's Fuel in Tablets*) is a genericized trademark as it is used to refer to similar products made by other companies.

2 - Uses

The tablets are used for cooking by campers, the military and relief organizations. They are often used with disposable metal stoves that are included with field ration packs. Backpackers concerned with ultra light gear tend to buy or make their own much lighter stove. An Esbit beverage-can stove can be made by cutting off the bottom of an aluminum soft drink can, and turning it upside down to support the fuel tablet. A pot can be supported above this with a circle of chicken wire or metal tent pegs. The burning tablets are sensitive to wind, so a simple windscreen should be used, such as a strip of aluminum foil curved in a circle around the pot and stove. If necessary, the fuel tablet can be placed on a rock or on the dirt, with a pot supported above it by rocks, but this is less than ideal.

Another common use is to provide a relatively safe (see disadvantages below) heat source for model steam engines, such as those manufactured by Wilesco and Mamod, and other external combustion engines such as Stirling engines and pop pop boats.

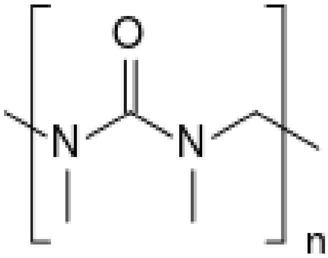
3 - Advantages and disadvantages

Hexamine is prepared by the reaction of formaldehyde and ammonia. In an acid environment hexamine is converted to formaldehyde, which is toxic.

Fuel tablets are simple, ultra-lightweight compared to other stove options, and compact; the entire stove system and fuel can be stored inside a small 850ml cooking pot. As with trioxane, hexamine has an almost infinite shelf life if stored properly. However, the heat given off cannot be easily adjusted, so water can be boiled, but cooking requiring simmering is more difficult. Tablets are not a particularly powerful stove fuel, and are sensitive to wind and dampness. They are expensive and are not as widely available compared to alternatives such as alcohol or petrol.

Esbit's Material Safety Data Sheet states combustion can create formaldehyde, ammonia, nitrogen oxide, hydrogen cyanide and ingestion may cause nausea, vomiting, gastrointestinal disturbances, and kidney damage. [1] When burned, the chemical oxidation of the fuel yields noxious fumes, requiring foods being cooked to be contained in a receptacle such as a pot or pan, and burned tablets will leave a sticky dark residue on the bottom of pots. If they are stored or used under damp conditions then they can break up while burning and shed burning fragments.

Urea - Formaldehyde



Contents

1 - Introduction

Urea-formaldehyde, also known as **urea-methanal**, named so for its common synthesis pathway and overall structure , is a non-transparent thermosetting resin or plastic, made from urea and formaldehyde heated in the presence of a mild base such as ammonia or pyridine. These resins are used in adhesives, finishes, MDF, and molded objects.

It was first synthesized in 1884 by Hölzer, who was working with Bernhard Tollens . In 1919, Hanns John (1891–1942) of Prague, Czechoslovakia obtained the first patent for urea-formaldehyde resin.

2 - Properties

Urea-formaldehyde resin's attributes include high tensile strength, flexural modulus, and heat distortion temperature, low water absorption, mould shrinkage, high surface hardness, elongation at break, and volume resistance.

3 - Chemical structure

The chemical structure of UF resins can be described as that of polymethylene. This description leaves the details of the structure undetermined, which can vary linearly and branched. These are grouped by their average molar mass and the content of different functional groups. Changing synthesis conditions of the resins give good designing possibilities for the structure and resin properties.

4 - Production

There is approximately 1 million metric tons of urea-formaldehyde produced every year. Over 70% of this production is then put into use by the forest industry products. It produces a great resin for bonding particleboard (61%), medium density fiberboard (27%), hardwood plywood (5%), and laminating adhesive (7 %) .

5 - General uses

A range of objects made from urea formaldehyde

Urea-Formaldehyde is everywhere and used in many manufacturing processes due to its useful properties. Examples include decorative laminates, textiles, paper, foundry sand molds, wrinkle resistant fabrics, cotton blends, rayon, corduroy, etc. It is also used to glue wood together. Urea formaldehyde was commonly used when producing electrical appliances casing (e.g. desk lamps).

The product is widely chosen as an adhesive resin due to its high reactivity, good performance, and low price. Urea-formaldehyde resin is a chemical combination of urea and formaldehyde. Amino resins are considered a class of thermosetting resins of which urea-formaldehyde resins make up 80 % produced globally. Examples of amino resins include automobile tires in order to improve the bonding of rubber to tire cord, paper for improving tear strength, molding electrical devices, molding jar caps, etc.

6 - Agricultural use

Urea formaldehyde is also used in agriculture as a controlled release source of nitrogen fertilizer. Urea formaldehyde's rate of decomposition into CO_2 and NH_3 is determined by the action of microbes found naturally in most soils. The activity of these microbes, and, therefore, the rate of nitrogen release, is temperature dependent. The optimum temperature for microbe activity is approximately 20 - 30°C .

7 - Urea-formaldehyde foam insulation

Urea-formaldehyde foam insulation (UFFI) dates back to the 1930s and made a great synthetic insulation with R-values near 5.0 per inch. It is basically a foam, like shaving cream that is easily injected into walls with a hose. It is made by using a pump set and hose with a mixing gun to mix the foaming agent, resin and compressed air. The fully expanded foam is pumped into areas in need of insulation. It becomes firm within minutes but cures within a week. UFFI is generally spotted in homes built before the 1970s; one should look in basements, crawl spaces, attics, and unfinished attics. Visually it looks like oozing liquid that has been hardened. Over time, it tends to vary in shades of butterscotch but new UFFI is a light yellow color. Early forms of UFFI tended to shrink significantly. Modern UF insulation with updated catalysts and foaming technology have reduced shrinkage to minimal levels (between 2-4%). The foam dries with a dull matte color with no shine. When cured, it often has a dry and crumbly texture.

7 – 1 - Safety concerns

Urea-formaldehyde foam insulation (UFFI) was used extensively in the 1970s. Homeowners used UFFI as a wall cavity filler at the time in order to conserve energy. In the 1980s, concerns began to develop about formaldehyde vapor emitted in the curing process, as well as from the breakdown of old foam. Emission rates exceeding 3.0 - 5.0 parts per million (ppm) cause a variety of adverse health effects impacting the eyes, nose, and respiratory system. Consequently, its use was discontinued. The urea-formaldehyde emissions decline over time and significant levels should no longer be present in the homes today. Modern replacement options for UFFI include melamine formaldehyde resin, low-emission UF insulation materials, and polyurethane.

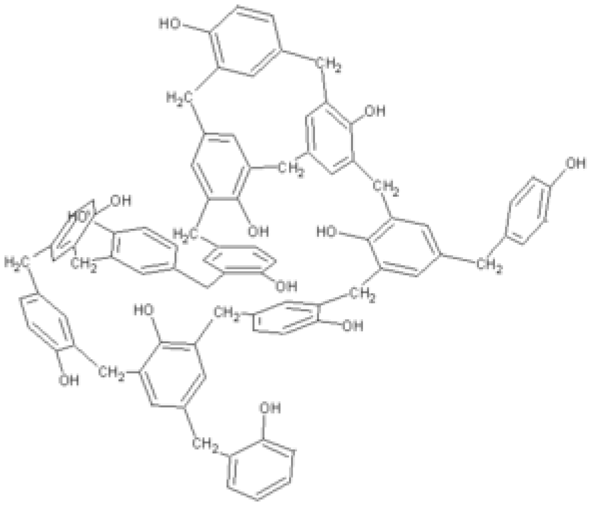
UFFI was usually mixed at the location of use while constructing the home's walls. It was then injected inside the walls, the curing process occurs, and the final product acts as an insulating agent. Because less information was known about the toxic health effects of formaldehyde in the 1970s, extra formaldehyde was often added to the mixture to ensure that the curing process would occur completely. Since the UFFI was not a well-sealed product [open-celled foam], any excess formaldehyde in the insulation would off-gas into the home's living space. The early UFFI materials were also affected by moisture and heat which compounded the offgassing concerns. When temperature rises, residuals of formaldehyde contained in the insulation are released and migrate into indoor air. Remedial actions to take when formaldehyde levels exceed recommended levels include sealing off the any outlets for the vapors; sealing any cracks or openings in interior walls; removing any sources of water or moisture that come in contact with the insulation; applying one or more layers of vapor barrier paint; increasing the air exchange rate with outside air in buildings that are tightly sealed; or covering walls with mylar or vinyl paper. Aluminum foil is a useful alternative for barricading vapors. Generally there is not an off-gassing concern with older UFFI insulation since those materials have already cured. Removal is a costly and tedious option for UFFI and would require a replacement insulation installation.

7 – 2 - Health effects

Health effects occur when urea-formaldehyde based materials and products release formaldehyde into the air. Generally ther are no observable health effects from formaldehyde when air concentrations are below 1.0 ppm. The onset of respiratory irritation and other health effects, and even increased cancer risk begins when air concentrations exceed 3.0-5.0 ppm. This triggers watery eyes, nose irritations, wheezing and coughing, fatigue, skin rash, severe allergic reactions, burning sensations in the eyes and throat, nausea, and difficulty in breathing in some humans (usually > 1.0 ppm). Recent studies have shown that chronic exposure at elevated levels can cause naso-pharyengeal cancer in humans and animals.< / ref > ((cite web url=http://www.iarc.fr/en/media-centre/pr/2004/pr153.html))

Occupants of UFFI insulated homes with elevated formaldehyde levels experienced systemic symptoms such as headache, malaise, insomnia, anorexia, and loss of libido. Irritation of the mucus membrane (specifically eyes, nose, and throat) was a common upper respiratory tract symptom related to formaldehyde exposure. However when compared to control groups, the frequency of symptoms did not exceed the controls expect when it came to wheezing, difficult breathing, and a burning skin sensation. Controlled studies have suggested that tolerance to formaldehydes odor and irritating effects can occur over a prolonged exposure. Tolerance, sensitivity, and idiosyncratic reactions should be considered for further investigation. The effects of cancer or congenital malformations may be too low to assess .

Phenol Formaldehyde



Contents

1 - Introduction

Phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. Phenolic resins are mainly used in the production of circuit boards. They are better known however for the production of molded products including pool balls, laboratory countertops, and as coatings and adhesives. In the form of Bakelite, they are the earliest commercial synthetic resin.

2 - Formation and structure

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalyzed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxy methyl phenol:

$$HOC_6H_5 + CH_2O \rightarrow HOC_6H_4CH_2OH$$

The hydroxy methyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge:

$$HOC_6H_4CH_2OH + HOC_6H_5 \rightarrow (HOC_6H_4)_2CH_2 + H_2O$$

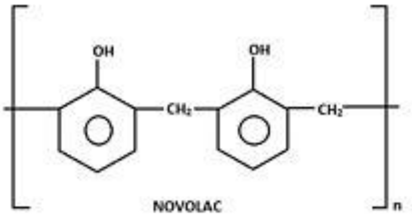
The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is itself an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.

$$2\ HOC_6H_4CH_2OH \rightarrow (HOC_6H_4CH_2)_2O + H_2O$$

3 - Novolacs

Novolacs are phenol-formaldehyde resins with a formaldehyde to phenol molar ratio of less than one. The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids. The phenol units are mainly linked by methylene and/or ether groups. Novolacs are commonly used as photoresists. See also photolithography. The molecular weights are in the low thousands, corresponding to about 10-20 phenol units.

Hexa methylene tetramine or "hexamine" is a hardener added to crosslink novolac. At a temperature >90 °C, it forms methylene and dimethylene amino bridges.



Novolac

4 - Resoles

Base- catalyzed phenol-formaldehyde resins are made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resoles. Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction, at around 70 °C, forms a thick reddish-brown tacky material, which is rich in hydroxy methyl and benzylic ether groups.

The rate of the base - catalyzed reaction initially increases with pH, and reaches a maximum at about pH = 10. The reactive species is the phenoxide anion ($C_6H_5O^-$) formed by deprotonation of phenol. The negative charge is delocalised over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde.

Being thermosets, hydroxy methyl phenols will crosslink on heating to around 120 °C to form methylene and methyl ether bridges through eliminating water molecules. At this point the resin is a 3-dimensional network, which is typical of poly merised phenolic resins. The high cross linking gives this type of phenolic resin its hardness, good thermal stability, and chemical imperviousness. Resols are referred to as "one step" resins as they cure without a cross linker unlike novolacs, a "two step" resin.

Resoles are major polymeric resin materials widely used for gluing and bonding building materials. Exterior plywood, oriented strand boards (OSB), engineered laminated composite lumber (LCL) are typical applications.

5 - Cross linking and the phenol/formaldehyde ratio

When the molar ratio of formaldehyde : phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely cross linked. This is why novolacs (F:P <1) don't harden without the addition of a cross linking agent, and why resoles with the formula F:P >1 will.

6 - Applications

Phenolic resins are found in myriad industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards and household laminates. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control. Snooker balls as well as balls from many table-based ball games are also made from phenol formaldehyde resin. The binding agent in normal (organic) brake pads, brake shoes and clutch disks are phenolic resin.

The Dutch forger Han van Meegeren mixed phenol formaldehyde with his oil paints before baking the finished canvas in order to fake the drying out of the paint over the centuries.

7 - Trade names

Tufnol plate

Bakelaque is a rigid laminate or tube made from phenolic resin on a substrate cotton fabric, paper or glass.

Bakelite is made from phenolic resin and wood flour.

Kooltherm is a rigid closed-cell thermoset insulation

Novotext is cotton fibre-reinforced phenolic, using randomly oriented fibres.

Aquafoam is a phenolic foam developed by Syndicate Sales, Inc. that absorbs and retains water, and is used to grip flowers in the design of floral arrangements.

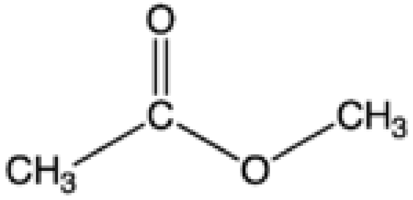
Oasis is "an open-celled phenolic foam that readily absorbs water and is used as a base for flower arrangements."

Paxolin Paper stone and Richlite are made from phenolic resin and paper.

Trymer Green is a rigid cellular phenolic thermal insulation.

Tufnol is made from phenolic resin and woven cotton or linen fabric.

Methyl Acetate



Contents

1 - Introduction

Methyl acetate, also known as **MeOAc**, **acetic acid methyl ester** or **methyl ethanoate**, is a carboxylate ester with the formula CH_3COOCH_3. It is a flammable liquid with a characteristically pleasant smell reminiscent of some glues and nail polish removers. Methyl acetate is occasionally used as a solvent, being weakly polar and lipophilic, but its close relative ethyl acetate is a more common solvent being less toxic and less soluble in water. Methyl acetate has a solubility of 25% in water at room temperature. At elevated temperature its solubility in water is much higher. Methyl acetate is not stable in the presence of strong aqueous bases or aqueous acids. Methyl acetate is VOC exempt.

IUPAC name ; Methyl acetate	
Systematic name : Methyl ethanoate	
Molecular formula	$C_3H_6O_2$
Molar mass	74 g mol^{-1}
Density	0.932 g cm^{-3}
Melting point	-98 °C
Boiling point	56.9 °C
Solubility in water	~25% (20 °C)
Refractive index (n_D)	1.361
Flash point	−9 °C

2 - Preparation and reactions

Methyl acetate is produced industrially via the carbonylation of methanol as a byproduct of the production of acetic acid . Methyl acetate also arises by esterification of acetic acid with methanol in the presence of strong acids such as sulfuric acid, this production process is famous because of Eastman Kodak's intensified process using a reactive distillation.

2 – 1 - Reactions

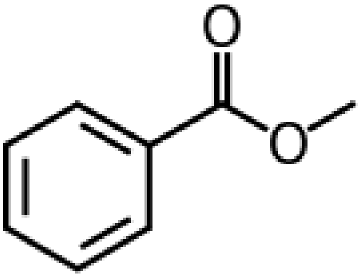
In the presence of strong bases such as sodium hydroxide or strong acids such as hydrochloric acid or sulfuric acid it is hydrolyzed back into methanol and acetic acid, especially at elevated temperature. The conversion of methyl acetate back into its components, by an acid, is a first- order reaction with respect to the ester. The reaction of methyl acetate and a base, for example sodium hydroxide, is a second-order reaction with respect to both reactants.

3 - Applications

A major use of methyl acetate is as a volatile low toxicity solvent in glues, paints, and nail polish removers.

Acetic anhydride is produced by carbonylation of methyl acetate in a process that was inspired by the Monsanto acetic acid synthesis.[4]

Methyl Benzoate



Contents

1 - Introduction

Methyl benzoate is an organic compound. It is an ester with the chemical formula $C_6H_5CO_2CH_3$. It is a colorless liquid that is poorly soluble in water, but miscible with organic solvents. Methyl benzoate has a pleasant smell, strongly reminiscent of the fruit of the feijoa tree, and it is used in perfumery. It also finds use as a solvent and as a pesticide used to attract insects.

IUPAC name : Methyl benzoate	
Molecular formula	$C_8H_8O_2$
Molar mass	136 $g\,mol^{-1}$
Density	1.0837 g / cm^3
Melting point	-12.5 °C
Boiling point	199.6 °C
Refractive index (n_D)	1.5164
Flash point	82 °C

2 Synthesis and reactions

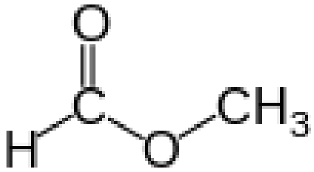
Methyl benzoate is formed by the condensation of methanol and benzoic acid, in presence of a strong acid such as hydrochloric acid.[1] It reacts both at the ring and the ester. Illustrative of its ability to undergo electrophilic substitution, methyl benzoate undergoes acid-catalysed nitration with nitric acid to give methyl 3-nitrobenzoate. It also undergoes hydrolysis with addition of aqueous NaOH to give methanol and sodium benzoate, which can be acidified with aqueous HCl to form benzoic acid.

3 - Occurrence

Methyl benzoate can be isolated from the freshwater fern *Salvinia molesta*. It is one of many compounds that is attractive to males of various species of orchid bees, which apparently gather the chemical to synthesize pheromones; it is commonly used as bait to attract and collect these bees for study.

Cocaine hydrochloride hydrolyzes in moist air to give methyl benzoate; drug-sniffing dogs are thus trained to detect the smell of methyl benzoate.

Methyl Formate



Contents

1 - Introduction

Methyl formate, also called **methyl methanoate**, is the methyl ester of formic acid. The simplest example of an ester, it is a clear liquid with an ethereal odour, high vapor pressure, and low surface tension.

IUPAC name : methyl methanoate	
Other names : R- 611	
Molecular formula	$C_2H_4O_2$
Molar mass	60 g mol^{-1}
Density	0.98 g / cm^3
Melting point	-100 °C
Boiling point	32 °C
EU classification	Highly flammable (F+) ; Harmful (Xn)

2 - Production

In the laboratory, methyl formate can be produced by the condensation reaction of methanol and formic acid, as follows:

$HCOOH + CH_3OH \rightarrow HCOOCH_3 + H_2O$

Industrial methyl formate, however, is usually produced by the combination of methanol and carbon monoxide (carbonylation) in the presence of a strong base, such as sodium methoxide:

$CH_3OH + CO \rightarrow HCOOCH_3$

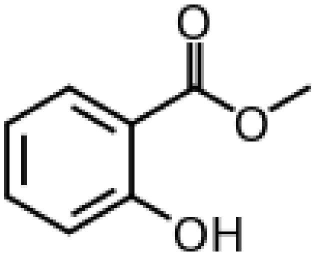
This process, practiced commercially by BASF among other companies gives 96 % selectivity toward methyl formate, although it can suffer from catalyst sensitivity to water, which can be present in the carbon monoxide feedstock, commonly derived from synthesis gas. Very dry carbon monoxide is, therefore, an essential requirement.

3 - Uses

Methyl formate is used primarily to manufacture formamide, di methyl formamide , and formic acid. Because of its high vapor pressure, it is used for quick-drying finishes. It is also used as an insecticide and to manufacture certain pharmaceuticals. Foam Supplies, Inc. has trademarked Ecomate, which is used as a blowing agent for foam insulation, as a replacement for CFC, HCFC, or HFCs, with zero ozone depletion potential and < 25 global warming potential.

A historical use of methyl formate, which sometimes brings it attention, was in refrigeration. Before the introduction of less-toxic refrigerants, methyl formate was used as an alternative to sulfur dioxide in domestic refrigerators, such as some models of the famous GE Monitor Top. Owners of methyl formate refrigerators should keep in mind that, even though they operate below atmospheric pressure, if evidence of a leak develops, they should take measures to avoid exposure to the ether - smelling liquid and vapor.

Methyl Salicylate



Contents

1 - Introduction

Methyl salicylate (**oil of winter green** or **winter green oil**) is an organic ester that is naturally produced by many species of plants. Some of the plants which produce it are called winter greens, hence the common name. This compound is used as a fragrance. It is also found in liniments (rubbing ointments).

IUPAC name : Methyl 2-hydroxy benzoate	
Other names : Salicylic acid methyl ester; Oil of wintergreen; Betula oil; Methyl 2-hydroxybenzoate	
Molecular formula	$C_8H_8O_3$
Molar mass	152. g / mol
Density	1.174 g/cm³
Melting point	- 9 °C
Boiling point	220 - 224 °C
Main hazards	Harmful
Flash point	101 °C

2 - Natural occurrence

Wintergreen plants (*Gaultheria procumbens*)

Numerous plants produce methyl salicylate in very small amounts. Some plants, such as the following, produce more:

some species of the genus *Gaultheria* in the family Ericaceae, including Gaultheria procumbens, the wintergreen or eastern teaberry;

some species of the genus *Betula* in the family Betulaceae, particularly those in the subgenus *Betulenta* such as *B. lenta*, the black birch;

all species of the genus *Spiraea* in the family Rosaceae, also called the meadow sweets.

This compound is produced most likely as an anti-herbivore defense. If the plant is infected with herbivorous insects, the release of methyl salicylate may function as an aid in the recruitment of beneficial insects to kill the herbivorous insects.[1] Aside from its toxicity, methyl salicylate may also be used by plants as a pheromone to warn other plants of pathogens such as tobacco mosaic virus.

3 - Commercial production

Methyl salicylate can be produced by esterifying salicylic acid with methanol. Commercial methyl salicylate is now synthesized, but in the past, it was commonly distilled from the twigs of *Betula lenta* (sweet birch) and *Gaultheria procumbens* (eastern teaberry or wintergreen).

4 - Uses

Methyl salicylate is used in high concentrations as a rubefacient in deep heating liniments (such as Bengay) to treat joint and muscular pain. Randomized double blind trial reviews report evidence of its effectiveness that is weak, but stronger for acute pain than chronic pain, and that effectiveness may be due entirely to counter-irritation. However, in the body it metabolizes into salicylates, including salicylic acid, a known NSAID.

It is used in low concentrations as a flavoring agent (no more than 0.04 %; it is toxic). It is also used to provide fragrance to various products and as an odor-masking agent for some organophosphate pesticides. If used excessively, it can cause stomach and kidney problems.

Methyl salicylate is among the compounds that attract male orchid bees, who apparently gather the chemical to synthesize pheromones; it is commonly used as bait to attract and collect these bees for study.

Methyl salicylate has the ability to clear plant or animal tissue samples of color, and as such is useful for microscopy and immunohisto chemistry when excess pigments obscure structures or block light in the tissue being examined. This clearing generally only takes a few minutes, but the tissue must first be dehydrated in alcohol.

Methyl salicylate, though its source plants are not true mints, is used as a mint in some kinds of chewing gum and candy, as an alternative to the more common peppermint and spearmint oils. It can also be found as a flavoring of root beer. It is also a potentially entertaining source of tri bioluminescence ; when mixed with sugar and dried, it gains the tendency to build up electrical charge when crushed or rubbed. This effect can be observed by crushing wintergreen Life Savers candy in a dark room.

Methyl salicylate can be used as a transfer agent, to produce a manual copy of an image on a surface.

Methyl salicylate is added in small amounts to glacial acetic acid to lower its freezing point for transport in cold countries.

Methyl salicylate is used as a simulant or surrogate for the research of chemical warfare agent sulfur mustard, due to its similar chemical and physical properties.

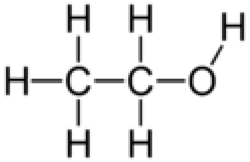
Methyl salicylate is one of several antiseptic ingredients in Listerine mouthwash produced by the Johnson & Johnson company.

5 - Safety and toxicity

In pure form, methyl salicylate is toxic, especially when taken internally. A single teaspoon (5ml) of methyl salicylate contains 7g of salicylate,[13] which is equivalent to more than twenty-three 300 mg aspirin tablets. The lowest published lethal dose is 101 mg/kg body weight in adult humans , (or 7.07 grams for a 70 - kg adult). It has proven fatal to small children in doses as small as 4 ml. A seventeen-year- old cross - country runner at Notre Dame Academy on Staten Island, died in April 2007, after her body absorbed methyl salicylate through excessive use of topical muscle-pain relief products.

Most instances of human toxicity due to methyl salicylate are a result of over-application of topical analgesics, especially involving children. Some people have intentionally ingested large amounts of oil of wintergreen. Salicylate, the major metabolite of methyl salicylate, may be quantitated in blood , plasma or serum to confirm a diagnosis of poisoning in hospitalized patients or to assist in an autopsy.

Ethanol



Contents

1 - Introduction

Ethanol, also called **ethyl alcohol**, **pure alcohol**, **grain alcohol**, or **drinking alcohol**, is a volatile, flammable, colorless liquid. A psychoactive drug and one of the oldest recreational drugs known, ethanol produces a state known as alcohol intoxication when consumed. Best known as the type of alcohol found in alcoholic beverages, it is also used in thermometers, as a solvent, and as a fuel. In common usage, it is often referred to simply as **alcohol** or **spirits**.

Systematic Name ; Ethanol
Other Names ;
Absolute alcohol
Alcohol
Drinking alcohol
Ethyl alcohol
Ethyl hydrate

Ethyl hydroxide	
Ethylic alcohol	
Ethylol	
Grain alcohol	
Hydroxyethane	
Methylcarbinol	
Molecular Formula	C_2H_6O
Molar Mass	46 g mol^{-1}
Appearance	Colorless liquid
Density	0.789 g/cm^3 (at 20°C)
Melting Point	−114 °C
Boiling Point	78.37 °C
Vapor pressure	5.95 kPa (at 20 °C)
Acidity (pK_a)	15.9
Basicity (pK_b)	-1.9
Refractive index (n_D)	1.361
Viscosity	0.0012 Pa s (at 20 °C), 0.001074 Pa s (at 25 °C)
EU classification	F
Flash point	13–14 °C
Autoignition temperature	363 °C
LD_{50}	5628 mg kg^{-1} (oral, rat)
Thermodynamic data	Phase behaviour Solid , liquid , gas
Spectral data	UV, IR, NMR, MS

[edit] Etymology

The term *ethanol* was invented 1838, modeled on German äthyl (Liebig), from Greek aither + hyle "stuff." *Ether* in late 14c. meant "upper regions of space," from Old French ether and directly from Latin aether "the upper pure, bright air," from Greek aither "upper air; bright, purer air; the sky," from aithein "to burn, shine," from PIE root *aidh- "to burn" (see edifice) . The current Arabic name for alcohol in The Qur'an, in verse 37 : 47, uses the word الغول al - ġawl —properly meaning "spirit" or "demon"—with the sense "the thing that gives the wine its headiness."

Ethanol is the systematic name defined by the IUPAC nomenclature of organic chemistry for a molecule with two carbon atoms (prefix "eth-"), having a single bond between them (suffix "-ane"), and an attached - OH group (suffix "-ol").

3 - Chemical formula

Ethanol is a 2- carbon alcohol with the empirical formula C_2H_6O. Its molecular formula is CH_3CH_2OH. An alternative notation is $CH_3–CH_2–OH$, which indicates that the carbon of a methyl group ($CH_3–$) is attached to the carbon of a methylene group ($–CH_2–$), which is attached to the oxygen of a hydroxyl group (–OH). It is a constitutional isomer of dimethyl ether. Ethanol is often abbreviated as **EtOH**, using the common organic chemistry notation of representing the ethyl group (C_2H_5) with **Et**.

4 - History

The fermentation of sugar into ethanol is one of the earliest biotechnologies employed by humans. The intoxicating effects of ethanol consumption have been known since ancient times. Ethanol has been used by humans since prehistory as the intoxicating ingredient of alcoholic beverages. Dried residue on 9,000-year-old pottery found in China imply that Neolithic people consumed alcoholic beverages.

Although distillation was well known by the early Greeks and Arabs, the first recorded production of alcohol from distilled wine was by the School of Salerno alchemists in the 12th century . The first to mention absolute alcohol, in contrast with alcohol - water mixtures, was Raymond Lull.

In 1796, Johann Tobias Lowitz obtained pure ethanol by mixing partially purified ethanol (the alcohol-water azeotrope) with an excess of anhydrous alkali and then distilling the mixture over low heat. Antoine Lavoisier described ethanol as a compound of carbon, hydrogen, and oxygen, and in 1807 Nicolas-Théodore de Saussure determined ethanol's chemical Formula . Fifty years later, Archibald Scott Couper published the structural formula of ethanol. It was one of the first structural formulas determined.

Ethanol was first prepared synthetically in 1825 by Michael Faraday. He found that sulfuric acid could absorb large volumes of coal gas. He gave the resulting solution to Henry Hennell, a British chemist, who found in 1826 that it contained "sulphovinic acid" (ethyl hydrogen sulfate). In 1828, Hennell and the French chemist Georges-Simon Sérullas independently discovered that sulphovinic acid could be decomposed into ethanol. Thus, in 1825 Faraday had unwittingly discovered that ethanol could be produced from ethylene (a component of coal gas) by acid-catalyzed hydration, a process similar to current industrial ethanol synthesis.

Ethanol was used as lamp fuel in the United States as early as 1840, but a tax levied on industrial alcohol during the Civil War made this use uneconomical. The tax was repealed in 1906 . Use as an automotive fuel dates back to 1908, with the Ford Model T able to run on gasoline or ethanol. It remains a common fuel for spirit lamps.

Ethanol intended for industrial use is often produced from ethylene . Ethanol has widespread use as a solvent of substances intended for human contact or consumption, including scents, flavorings, colorings, and medicines. In chemistry, it is both a solvent and a feedstock for the synthesis of other products. It has a long history as a fuel for heat and light, and more recently as a fuel for internal combustion engines.

5 - Properties

5 – 1 - Physical properties

Ethanol is a volatile, colorless liquid that has a slight odor. It burns with a smokeless blue flame that is not always visible in normal light.

The physical properties of ethanol stem primarily from the presence of its hydroxyl group and the shortness of its carbon chain. Ethanol's hydroxyl group is able to participate in hydrogen bonding, rendering it more viscous and less volatile than less polar organic compounds of similar molecular weight, such as propane.

Ethanol burning with its spectrum depicted

Ethanol is slightly more refractive than water, having a refractive index of 1.36242 (at λ=589.3 nm and 18.35 °C).

The triple point for ethanol is 150K at a pressure of 4.3×10^{-4} Pa.

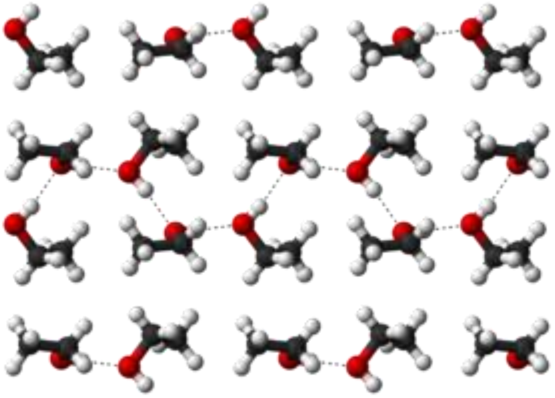
5 – 2 - Solvent properties

Ethanol is a versatile solvent, miscible with water and with many organic solvents, including acetic acid, acetone, benzene, carbon tetrachloride, chloroform, diethyl ether , ethylene glycol, glycerol, nitromethane, pyridine, and toluene . It is also miscible with light aliphatic hydrocarbons, such as pentane and hexane, and with aliphatic chlorides such as tri chloro ethane and tetra chloro ethylene.

Ethanol's miscibility with water contrasts with the immiscibility of longer-chain alcohols (five or more carbon atoms), whose water miscibility decreases sharply as the number of carbons increases. The miscibility of ethanol with alkanes is limited to alkanes up to undecane, mixtures with dodecane and higher alkanes show a miscibility gap below a certain temperature (about 13 °C for dodecane). The miscibility gap tends to get wider with higher alkanes and the temperature for complete miscibility increases.

Ethanol-water mixtures have less volume than the sum of their individual components at the given fractions. Mixing equal volumes of ethanol and water results in only 1.92 volumes of mixture. Mixing ethanol and water is exothermic, with up to 777 J/mol being released at 298 K.

Mixtures of ethanol and water form an azeotrope at about 89 mole-% ethanol and 11 mole-% water or a mixture of about 96 volume percent ethanol and 4% water at normal pressure and T = 351 K. This azeotropic composition is strongly temperature - and pressure-dependent and vanishes at temperatures below 303 K.



Hydrogen bonding in solid ethanol at −186 °C

Hydrogen bonding causes pure ethanol to be hygroscopic to the extent that it readily absorbs water from the air. The polar nature of the hydroxyl group causes ethanol to dissolve many ionic compounds, notably sodium and potassium hydroxides, magnesium chloride, calcium chloride, ammonium chloride, ammonium bromide, and sodium bromide.[26] Sodium and potassium chlorides are slightly soluble in ethanol.[26] Because the ethanol molecule also has a nonpolar end, it will also dissolve nonpolar substances, including most essential oils and numerous flavoring, coloring, and medicinal agents.

The addition of even a few percent of ethanol to water sharply reduces the surface tension of water. This property partially explains the "tears of wine" phenomenon. When wine is swirled in a glass, ethanol evaporates quickly from the thin film of wine on the wall of the glass. As the wine's ethanol content decreases, its surface tension increases and the thin film "beads up" and runs down the glass in channels rather than as a smooth sheet.

5 – 3 - Flammability

An ethanol - water solution that contains 40 % ABV (alcohol by volume) will catch fire if heated to about 26 °C and if an ignition source is applied to it. This is called its flash point. The flash point of pure ethanol is 16.60 °C , less than average room temperature.[35]

The flash points of ethanol concentrations from 10 % ABV to 96 % ABV are shown below :

concentrations %	**°C**
10	49
12.5	52
20	36
30	29
40	26
50	24
60	22
70	21
80	20
90	17
96	17

Alcoholic beverages that have a low concentration of ethanol will burn if sufficiently heated and an ignition source (such as an electric spark or a match) is applied to them. For example, the flash point of ordinary wine containing 12.5 % ethanol is about 52 °C .

6 - Production

Ethanol is produced both as a petrochemical, through the hydration of ethylene and, via biological processes, by fermenting sugars with yeast. Which process is more economical depends on prevailing prices of petroleum and grain feed stocks.

6 - 1 - Ethylene hydration

Ethanol for use as an industrial feedstock or solvent (sometimes referred to as synthetic ethanol) is made from petrochemical feed stocks, primarily by the acid - catalyzed hydration of ethylene, represented by the chemical equation

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

The catalyst is most commonly phosphoric acid, adsorbed onto a porous support such as silica gel or diatomaceous earth. This catalyst was first used for large-scale ethanol production by the Shell Oil Company in 1947. The reaction is carried out with an excess of high pressure steam at 300 °C. In the U.S., this process was used on an industrial scale by Union Carbide Corporation and others; but now only LyondellBasell uses it commercially.

In an older process, first practiced on the industrial scale in 1930 by Union Carbide, but now almost entirely obsolete, ethylene was hydrated indirectly by reacting it with concentrated sulfuric acid to produce ethyl sulfate, which was hydrolysed to yield ethanol and regenerate the sulfuric acid :

$$C_2H_4 + H_2SO_4 \rightarrow CH_3CH_2SO_4H$$
$$CH_3CH_2SO_4H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

6 - 2 - Fermentation

Ethanol for use in alcoholic beverages, and the vast majority of ethanol for use as fuel is produced by fermentation. When certain species of yeast (e.g., *Saccharomyces cerevisiae*) metabolize sugar in reduced-oxygen conditions they produce ethanol and carbon dioxide. The chemical equations below summarize the conversion :

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$
$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4\ CH_3CH_2OH + 4\ CO_2$$

Fermentation is the process of culturing yeast under favorable thermal conditions to produce alcohol. This process is carried out at around 35 – 40 °C. Toxicity of ethanol to yeast limits the ethanol concentration obtainable by brewing; higher concentrations, therefore, are usually obtained by fortification or distillation. The most ethanol-tolerant strains of yeast can survive up to approximately 15% ethanol by volume.

To produce ethanol from starchy materials such as cereal grains, the starch must first be converted into sugars. In brewing beer, this has traditionally been accomplished by allowing the grain to germinate, or malt, which produces the enzyme amylase. When the malted grain is mashed, the amylase converts the remaining starches into sugars. For fuel ethanol, the hydrolysis of starch into glucose can be accomplished more rapidly by treatment with dilute sulfuric acid, fungally produced amylase, or some combination of the two.

6 - 2 - 1 - Cellulosic ethanol

Sugars for ethanol fermentation can be obtained from cellulose. Until recently, however, the cost of the cellulase enzymes capable of hydrolyzing cellulose has been prohibitive. The Canadian firm Iogen brought the first cellulose-based ethanol plant on-stream in 2004 . Its primary consumer so far has been the Canadian government, which, along with the United States Department of Energy, has invested heavily in the commercialization of cellulosic ethanol. Deployment of this technology could turn a number of cellulose - containing agricultural by-products, such as corncobs, straw, and saw dust, into renewable energy resources. Other enzyme companies are developing genetically engineered fungi that produce large volumes of cellulose , xylanase , and hemi cellulose enzymes.

These would convert agricultural residues such as corn stover, wheat straw, and sugar cane bagasse and energy crops such as switch grass into fermentable sugars.

Cellulose-bearing materials typically contain other poly saccharides, including hemi cellulose. Hydrolysis of hemicellulose gives mostly five-carbon sugars such as xylose. *S. cerevisiae*, the yeast most commonly used for ethanol production, cannot metabolize xylose. Other yeasts and bacteria are under investigation to ferment xylose and other pentoses into ethanol.

6 - 2 - 32 - Hydrocarbon - based ethanol production

A process developed and marketed by Celanese Corporation under the name TCX Technology uses hydrocarbons such as natural gas or coal for ethanol production rather than using fermented crops such as corn or sugarcane.

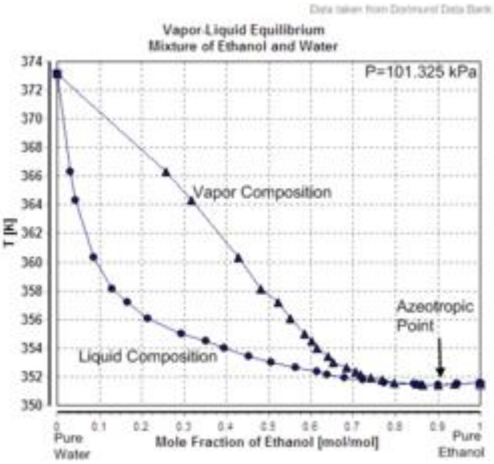
6 - 3 - Testing

Breweries and bio fuel plants employ two methods for measuring ethanol concentration. Infrared ethanol sensors measure the vibrational frequency of dissolved ethanol using the CH band at 2900 cm^{-1}. This method uses a relatively inexpensive solid state sensor that compares the CH band with a reference band to calculate the ethanol content. The calculation makes use of the Beer-Lambert law. Alternatively, by measuring the density of the starting material and the density of the product, using a hydrometer, the change in specific gravity during fermentation indicates the alcohol content. This inexpensive and indirect method has a long history in the beer brewing industry.

7 - Purification

7 – 1 - Distillation

Ethylene hydration or brewing produces an ethanol–water mixture. For most industrial and fuel uses, the ethanol must be purified. Fractional distillation can concentrate ethanol to 95.6% by volume (89.5 mole%). This mixture is an azeotrope with a boiling point of 78.1 °C, and *cannot* be further purified by distillation. Addition of an entraining agent, such as benzene, cyclo hexane, or heptane, allows a new ternary azeotrope comprising the ethanol, water, and the entraining agent to be formed. This lower-boiling ternary azeotrope is removed preferentially, leading to water-free ethanol.



Vapor-liquid equilibrium of the mixture of Ethanol and Water (incl. azeotrope), composition given in molefractions

At pressures less than atmospheric pressure, the composition of the ethanol-water azeotrope shifts to more ethanol-rich mixtures, and at pressures less than 70 torr (9.333 kPa), there is no azeotrope, and it is possible to distill absolute ethanol from an ethanol-water mixture. While vacuum distillation of ethanol is not presently economical, pressure-swing distillation is a topic of current research. In this technique, a reduced - pressure distillation first yields an ethanol-water mixture of more than 95.6 % ethanol. Then, fractional distillation of this mixture at atmospheric pressure distills off the 95.6% azeotrope, leaving anhydrous ethanol at the bottoms.

7 – 2 - Molecular sieves and desiccants

Molecular sieves can be used to selectively absorb the water from the 95.6 % ethanol solution. Synthetic zeolite in pellet form can be used, as well as a variety of plant-derived absorbents, including corn meal, straw, and sawdust. The zeolite bed can be regenerated essentially an unlimited number of times by drying it with a blast of hot carbon dioxide. Cornmeal and other plant-derived absorbents cannot readily be regenerated, but where ethanol is made from grain, they are often available at low cost. Absolute ethanol produced this way has no residual benzene, and can be used to fortify port and sherry in traditional winery operations.

Apart from distillation, ethanol may be dried by addition of a desiccant, such as molecular sieves, cellulose, and cornmeal. The desiccants can be dried and reused.

7 – 2 - Membranes and reverse osmosis

Membranes can also be used to separate ethanol and water. Membrane-based separations are not subject to the limitations water-ethanol azeotrope because separation is not based on vapor-liquid equilibria. Membranes are often used in the so-called hybrid membrane distillation process. This process uses a pre-concentration distillation column as first separating step. The further separation is then accomplished with a membrane operated either in vapor permeation or per evaporation mode. Vapor permeation uses a vapor membrane feed and pervaporation uses a liquid membrane feed.

7 – 4 - Other techniques

A variety of other techniques have been discussed, including the following :

Liquid-liquid extraction of ethanol from an aqueous solution

Extraction of ethanol from grain mash by supercritical carbon dioxide

Per evaporation

Pressure swing adsorption

8 - Grades of ethanol

Ethanol is available in a range of purities that result from its production or, in the case of denatured alcohol, are introduced intentionally.

8 – 1 - Denatured alcohol

Pure ethanol and alcoholic beverages are heavily taxed as a psychoactive drug, but ethanol has many uses that do not involve consumption by humans. To relieve the tax burden on these uses, most jurisdictions waive the tax when an agent has been added to the ethanol to render it unfit to drink. These include bittering agents such as denatonium benzoate and toxins such as methanol, naphtha, and pyridine. Products of this kind are called *denatured alcohol*.

8 – 2 - Absolute alcohol

Absolute or anhydrous alcohol refers to ethanol with a low water content. There are various grades with maximum water contents ranging from 1 % to ppm levels. Absolute alcohol is not intended for human consumption. If azeotropic distillation is used to remove water, it will contain trace amounts of the material separation agent (e.g. benzene). Absolute ethanol is used as a solvent for laboratory and industrial applications, where water will react with other chemicals, and as fuel alcohol. Spectroscopic ethanol is an absolute ethanol with a low absorbance in ultraviolet and visible light, fit for use as a solvent in ultraviolet-visible spectroscopy.

Pure ethanol is classed as 200 proof in the USA, equivalent to 175 degrees proof in the UK system.

8 – 3 - Rectified spirits

Rectified spirit, an azeotropic composition of 96% ethanol containing 4 % water, is used instead of anhydrous ethanol for various purposes. Wine spirits are about 94% ethanol (188 proof). The impurities are different from those in 95% (190 proof) laboratory ethanol.

9 - Reactions

For more details on this topic, see Alcohol.

Ethanol is classified as a primary alcohol, meaning that the carbon its hydroxyl group attaches to has at least two hydrogen atoms attached to it as well. Many ethanol reactions occur at its hydroxyl group.

9 – 1 - Ester formation

In the presence of acid catalysts, ethanol reacts with carboxylic acids to produce ethyl esters and water:

$$RCOOH + HOCH_2CH_3 \rightarrow RCOOCH_2CH_3 + H_2O$$

This reaction, which is conducted on large scale industrially, requires the removal of the water from the reaction mixture as it is formed. Esters react in the presence of an acid or base to give back the alcohol and a salt. This reaction is known as saponification because it is used in the preparation of soap. Ethanol can also form esters with inorganic acids. Diethyl sulfate and triethyl phosphate are prepared by treating ethanol with sulfur trioxide and phosphorus pentoxide respectively. Diethyl sulfate is a useful ethylating agent in organic synthesis. Ethyl nitrite, prepared from the reaction of ethanol with sodium nitrite and sulfuric acid, was formerly a widely used diuretic.

9 – 2 - Dehydration

Strong acid desiccants cause the dehydration of ethanol to form diethyl ether and other byproducts. If the dehydration temperature exceeds around 160 °C, ethylene will be the main product. Millions of kilograms of diethyl ether are produced annually using sulfuric acid catalyst:

$$2\ CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O \text{ (on 120 °C)}$$

9 – 3 - Combustion

Complete combustion of ethanol forms carbon dioxide and water vapor :

$$C_2H_5OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (g)\ ;$$

$$(\Delta H_c = -1371 \text{ kJ / mol}) \text{ specific heat} = 2.44 \text{ kJ / (kg}\cdot\text{K)}$$

9 – 4 - Acid - base chemistry

Ethanol is a neutral molecule and the pH of a solution of ethanol in water is nearly 7.00. Ethanol can be quantitatively converted to its conjugate base, the ethoxide ion ($CH_3CH_2O^-$), by reaction with an alkali metal such as sodium :

$$2\ CH_3CH_2OH + 2\ Na \rightarrow 2\ CH_3CH_2ONa + H_2$$

or a very strong base such as sodium hydride:

$$CH_3CH_2OH + NaH \rightarrow CH_3CH_2ONa + H_2$$

The acidity of water and ethanol are nearly the same, as indicated by their pKa of 15.7 and 16 respectively. Thus, sodium ethoxide and sodium hydroxide exist in an equilbrium that is closely balanced:

$$CH_3CH_2OH + NaOH \rightleftharpoons CH_3CH_2ONa + H_2O$$

9 – 5 - Halogenation

Ethanol is not used industrially as a precursor to ethyl halides, but the reactions are illustrative. Ethanol reacts with hydrogen halides to produce ethyl halides such as ethyl chloride and ethyl bromide via an S_N2 reaction:

$$CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$$

These reactions require a catalyst such as zinc chloride.[43] HBr requires refluxing with a sulfuric acid catalyst.[43] Ethyl halides can, in principle, also be produced by treating ethanol with more specialized halogenating agents, such as thionyl chloride or phosphorus tri bromide.

$$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$$

Upon treatment with halogens in the presence of base, ethanol gives the corresponding haloform (CHX_3, where X = Cl, Br, I). This conversion is called the haloform reaction.[59] " An intermediate in the reaction with chlorine is the aldehyde called chloral:

$$4\ Cl_2 + CH_3CH_2OH \rightarrow CCl_3CHO + 5\ HCl$$

9 – 6 - Oxidation

Ethanol can be oxidized to acetaldehyde and further oxidized to acetic acid, depending on the reagents and conditions.[43] This oxidation is of no importance industrially, but in the human body, these oxidation reactions are catalyzed by the enzyme liver alcohol dehydrogenase. The oxidation product of ethanol, acetic acid, is a nutrient for humans, being a precursor to acetyl CoA, where the acetyl group can be spent as energy or used for biosynthesis.

10 - Uses

10 – 1 - As a fuel

Energy content of some fuels compared with ethanol :

Fuel type	MJ/L	MJ/kg	Research octane number
Dry wood (20 % moisture)		~19.5	
Methanol	17.9	19.9	108.7
Ethanol	21.2	26.8	108.6
E85 (85% ethanol, 15% gasoline)	25.2	33.2	105
Liquefied natural gas	25.3	~55	
Autogas (LPG) (60 % propane + 40 % butane)	26.8	50.	
Aviation gasoline (high-octane gasoline, not jet fuel)	33.5	46.8	100/130 (lean/rich)
Gasohol (90 % gasoline + 10 % ethanol)	33.7	47.1	93/94
Regular gasoline/petrol	34.8	44.4	min. 91
Premium gasoline/petrol			max. 104
Diesel	38.6	45.4	25
Charcoal, extruded	50	23	

The largest single use of ethanol is as a motor fuel and fuel additive. More than any other major country, Brazil relies on ethanol as a motor fuel. Gasoline sold in Brazil contains at least 25% anhydrous ethanol. Hydrous ethanol (about 95 % ethanol and 5% water) can be used as fuel in more than 90% of new cars sold in the country. Brazilian ethanol is produced from sugar cane and noted for high carbon sequestration . The US uses Gasohol (max 10% ethanol) and E85 (85 % ethanol) ethanol / gasoline mixtures.

Ethanol may also be utilized as a rocket fuel, and is currently in lightweight rocket - powered racing aircraft.

Australian law limits of the use of pure ethanol sourced from sugarcane waste to up to 10% in automobiles. It has been recommended that older cars (and vintage cars designed to use a slower burning fuel) have their valves upgraded or replaced.

According to an industry advocacy group for promoting ethanol called the American Coalition for Ethanol, ethanol as a fuel reduces harmful tailpipe emissions of carbon monoxide, particulate matter, oxides of nitrogen, and other ozone-forming pollutants. Argonne National Laboratory analyzed the greenhouse gas emissions of many different engine and fuel combinations. Comparing ethanol blends with gasoline alone, they showed reductions of 8% with the biodiesel / petro diesel blend known as B20, 17 % with the conventional E85 ethanol blend, and that using cellulosic ethanol lowers emissions 64 % .

Ethanol combustion in an internal combustion engine yields many of the products of incomplete combustion produced by gasoline and significantly larger amounts of formaldehyde and related species such as acetaldehyde . This leads to a significantly larger photochemical reactivity that generates much more ground level ozone . These data have been assembled into The Clean Fuels Report comparison of fuel emissions[71] and show that ethanol exhaust generates 2.14 times as much ozone as does gasoline exhaust When this is added into the custom *Localised Pollution Index (LPI)* of The Clean Fuels Report the local pollution (pollution that contributes to smog) is 1.7 on a scale where gasoline is 1.0 and higher numbers signify greater pollution The California Air Resources Board formalized this issue in 2008 by recognizing control standards for formaldehydes as an emissions control group, much like the conventional NOx and Reactive Organic Gases (ROGs).

Ethanol pump station in São Paulo, Brazil where the fuel is available commercially.

World production of ethanol in 2006 was 51 gigalitres (1.3×10^{10} US gal), with 69 % of the world supply coming from Brazil and the United States. More than 20 % of Brazilian cars are able to use 100 % ethanol as fuel, which includes ethanol-only engines and flex-fuel engines. Flex-fuel engines in Brazil are able to work with all ethanol, all gasoline or any mixture of both. In the US flex-fuel vehicles can run on 0 % to 85 % ethanol (15 % gasoline) since higher ethanol blends are not yet allowed or efficient. Brazil supports this population of ethanol-burning automobiles with large national infrastructure that produces ethanol from domestically grown sugar cane. Sugar cane not only has a greater concentration of sucrose than corn (by about 30 %), but is also much easier to extract. The bagasse generated by the process is not wasted, but is used in power plants to produce electricity.

A Ford Taurus "fueled by clean burning ethanol" owned by New York City.

The United States fuel ethanol industry is based largely on corn. According to the Renewable Fuels Association, as of October 30, 2007, 131 grain ethanol bio-refineries in the United States have the capacity to produce 7.0 billion US gallons (26,000,000 m^3) of ethanol per year. An additional 72 construction projects underway (in the U.S.) can add 6.4 billion US gallons (24,000,000 m^3) of new capacity in the next 18 months. Over time, it is believed that a material portion of the ≈150-billion-US-gallon (570,000,000 m^3) per year market for gasoline will begin to be replaced with fuel ethanol.

United States Postal Service vehicle running on E85, a "flex-fuel" blend in Saint Paul, Minnesota.

ne problem with ethanol is its high miscibility with water, which means that it cannot be efficiently shipped through modern pipelines, like liquid hydrocarbons, over long distances. Mechanics also have seen increased cases of damage to small engines, in particular, the carburetor, attributable to the increased water retention by ethanol in fuel.

In 2011, the Open Fuel Standard Coalition introduced a bill into Congress that would mandate most cars sold in the United States to be warranted to run on ethanol, as well as methanol and gasoline. The bill aims to provide enough financial incentive to find better ways to make ethanol fuel so it could compete economically against gasoline.

10 – 2 - Alcoholic beverages

Ethanol is the principal psychoactive constituent in alcoholic beverages, with depressant effects on the central nervous system. It has a complex mode of action and affects multiple systems in the brain, the most notable one being its agonistic action on the GABA receptors . Similar psychoactives include those that also interact with GABA receptors, such as benzodiazepines, barbiturates, gamma-hydroxybutyric acid (GHB). Ethanol is metabolized by the body as an energy-providing nutrient, as it metabolizes into acetyl CoA, an intermediate common with glucose and fatty acid metabolism that can be used for energy in the citric acid cycle or for bio synthesis.

Alcoholic beverages vary considerably in ethanol content and in foodstuffs they are produced from. Most alcoholic beverages can be broadly classified as fermented beverages, beverages made by the action of yeast on sugary foodstuffs, or distilled beverages, beverages whose preparation involves concentrating the ethanol in fermented beverages by distillation. The ethanol content of a beverage is usually measured in terms of the volume fraction of ethanol in the beverage, expressed either as a percentage or in alcoholic proof units.

Fermented beverages can be broadly classified by the foodstuff they are fermented from. Beers are made from cereal grains or other starchy materials, wines and ciders from fruit juices, and meads from honey. Cultures around the world have made fermented beverages from numerous other foodstuffs, and local and national classifications for various fermented beverages abound.

Distilled beverages are made by distilling fermented beverages. Broad categories of distilled beverages include whiskeys, distilled from fermented cereal grains; brandies, distilled from fermented fruit juices; and rum, distilled from fermented molasses or sugarcane juice. Vodka and similar neutral grain spirits can be distilled from any fermented material (grain and potatoes are most common); these spirits are so thoroughly distilled that no tastes from the particular starting material remain. Numerous other spirits and liqueurs are prepared by infusing flavors from fruits, herbs, and spices into distilled spirits. A traditional example is gin, which is created by infusing juniper berries into a neutral grain alcohol.

The ethanol content in alcoholic beverages can be increased by means other than distillation. Applejack is traditionally made by freeze distillation, by which water is frozen out of fermented apple cider, leaving a more ethanol - rich liquid behind. Ice beer (also known by the German term *Eisbier* or *Eisbock*) is also freeze-distilled, with beer as the base beverage. Fortified wines are prepared by adding brandy or some other distilled spirit to partially fermented wine. This kills the yeast and conserves a portion of the sugar in grape juice; such beverages are not only more ethanol-rich but are often sweeter than other wines.

Alcoholic beverages are used in cooking for their flavors and because alcohol dissolves hydrophobic flavor compounds.

Just as industrial ethanol is used as feedstock for the production of industrial acetic acid, alcoholic beverages are made into vinegar. Wine and cider vinegar are both named for their respective source alcohols, whereas malt vinegar is derived from beer.

10 – 3 - Feed stock

Ethanol is an important industrial ingredient and has widespread use as a base chemical for other organic compounds. These include ethyl halides, ethyl esters, diethyl ether, acetic acid, ethyl amines, and, to a lesser extent, butadiene.

10 – 4 - Antiseptic

Ethanol is used in medical wipes and in most common antibacterial hand sanitizer gels at a concentration of about 62 % v / v as an antiseptic. Ethanol kills organisms by denaturing their proteins and dissolving their lipids and is effective against most bacteria and fungi, and many viruses, but is ineffective against bacterial spores.

10 – 5 - Treatment for poisoning by other alcohols

Ethanol is sometimes used to treat poisoning by other, more toxic alcohols, in particular methanol[81] and ethylene glycol. Ethanol competes with other alcohols for the alcohol dehydrogenase enzyme, lessening metabolism into toxic aldehyde and carboxylic acid derivatives , and reducing one of the more serious toxic effect of the glycols to crystallize in the kidneys.

10 – 6 - Solvent

Ethanol is miscible with water and is a good general purpose solvent. It is found in paints, tinctures, markers, and personal care products such as perfumes and deodorants. It may also be used as a solvent or solute in cooking, such as in vodka sauce.

10 – 7 - Historical uses

Before the development of modern medicines, ethanol was used for a variety of medical purposes. It has been known to be used as a truth drug (as hinted at by the maxim *"in vino veritas"*), as medicine for depression and as an anesthetic.

Ethanol was commonly used as fuel in early bipropellant rocket (liquid propelled) vehicles, in conjunction with an oxidizer such as liquid oxygen. The German V-2 rocket of World War II, credited with beginning the space age, used ethanol, mixed with 25% of water to reduce the combustion chamber temperature. The V-2's design team helped develop U.S. rockets following World War II, including the ethanol-fueled Redstone rocket, which launched the first U.S. satellite. Alcohols fell into general disuse as more efficient rocket fuels were developed.

11 - Pharmacology

Ethanol binds to acetylcholine, GABA, serotonin, and NMDA receptors. It also appears to cause an increase in dopamine through a poorly understood process that may involve inhibiting the enzyme that breaks dopamine down.

The removal of ethanol through oxidation by alcohol dehydrogenase in the liver from the human body is limited. Hence, the removal of a large concentration of alcohol from blood may follow zero - order kinetics. This means that alcohol leaves the body at a constant rate, rather than having an elimination half-life.

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Also, the rate-limiting steps for one substance may be in common with other substances. For instance, the blood alcohol concentration can be used to modify the biochemistry of methanol and ethylene glycol. Methanol itself is not highly toxic, but its metabolites formaldehyde and formic acid are; therefore, to reduce the concentration of these harmful metabolites, ethanol can be ingested to reduce the rate of methanol metabolism due to shared rate-limiting steps. Ethylene glycol poisoning can be treated in the same way.

12 - Drug effects

Pure ethanol will irritate the skin and eyes. Nausea, vomiting and intoxication are symptoms of ingestion. Long-term use by ingestion can result in serious liver damage. Atmospheric concentrations above one in a thousand are above the European Union Occupational exposure limits.

12 – 1 - Short-term

BAC (g / L)	BAC (% v / v)	Symptoms
0.5	0.05 %	Euphoria, talkativeness, relaxation
1	0.1 %	Central nervous system depression, nausea, possible vomiting, impaired

		motor and sensory function, impaired cognition
> 1.4	> 0.14 %	Decreased blood flow to brain
3	0.3 %	Stupefaction, possible unconsciousness
4	0.4 %	Possible death
> 5.5	> 0.55 %	Death

12 – 1 – 1 - Effects on the central nervous system

Ethanol is a central nervous system depressant and has significant psychoactive effects in sub lethal doses; for specifics, see "Effects of alcohol on the body by dose". Based on its abilities to change the human consciousness, ethanol is considered a psychoactive drug. Death from ethanol consumption is possible when blood alcohol level reaches 0.4 %. A blood level of 0.5 % or more is commonly fatal. Levels of even less than 0.1 % can cause intoxication, with unconsciousness often occurring at 0.3 – 0.4 %.

The amount of ethanol in the body is typically quantified by blood alcohol content (BAC), which is here taken as weight of ethanol per unit volume of blood. The table at the right summarizes the symptoms of ethanol consumption. Small doses of ethanol, in general, produce euphoria and relaxation; people experiencing these symptoms tend to become talkative and less inhibited, and may exhibit poor judgment. At higher dosages (BAC > 1 g / L), ethanol acts as a central nervous system depressant, producing at progressively higher dosages, impaired sensory and motor function, slowed cognition, stupefaction, unconsciousness, and possible death.

Ethanol acts in the central nervous system by binding to the GABA-A receptor, increasing the effects of the inhibitory neurotransmitter GABA (i.e., it is a positive allosteric modulator).

Prolonged heavy consumption of alcohol can cause significant permanent damage to the brain and other organs. See Alcohol consumption and health.

According to the US National Highway Traffic Safety Administration, in 2002 about "41 % of people fatally injured in traffic crashes were in alcohol related crashes". The risk of a fatal car accident increases exponentially with the level of alcohol in the driver's blood.[94] Most drunk driving laws governing the acceptable levels in the blood while driving or operating heavy machinery set typical upper limits of blood alcohol content (BAC) between 0.05% and 0.08 %.

Discontinuing consumption of alcohol after several years of heavy drinking can also be fatal. Alcohol withdrawal can cause anxiety, autonomic dysfunction, seizures, and hallucinations. Delirium tremens is a condition that requires people with a long history of heavy drinking to undertake an alcohol detoxification regimen.

The reinforcing effects of alcohol consumption are also mediated by acetaldehyde generated by catalase and other oxidizing enzymes such as cytochrome P- 4502E1 in the brain. Although acetaldehyde has been associated with some of the adverse and toxic effects of ethanol, it appears to play a central role in the activation of the mesolimbic dopamine system.

12 – 1 – 2 - Effects on metabolism

Main articles: Ethanol metabolism and Alcohol dehydrogenase

Ethanol within the human body is converted into acetaldehyde by alcohol dehydrogenase and then into the acetyl in acetyl CoA by acetaldehyde dehydrogenase. Acetyl CoA is the final product of both carbohydrate and fat metabolism, where the acetyl can be further used to produce energy or for biosynthesis. As such, ethanol is a nutrient. However, the product of the first step of this breakdown, acetaldehyde, is more toxic than ethanol. Acetaldehyde is linked to most of the clinical effects of alcohol. It has been shown to increase the risk of developing cirrhosis of the liver and multiple forms of cancer.

During the metabolism of alcohol via the respective dehydrogenases, NAD is converted into reduced NAD. Normally, NAD is used to metabolize fats in the liver, and as such alcohol competes with these fats for the use of NAD. Prolonged exposure to alcohol means that fats accumulate in the liver, leading to the term 'fatty liver'. Continued consumption (such as in alcoholism) then leads to cell death in the hepatocytes as the fat stores reduce the function of the cell to the point of death. These cells are then replaced with scar tissue, leading to the condition called cirrhosis.

12 – 1 – 3 - Drug interactions

Ethanol can intensify the sedation caused by other central nervous system depressant drugs such as barbiturates, benzodiazepines, opioids, phenothiazines, and anti - depressants . It interacts with cocaine in vitro to produce cocaethylene, another psychoactive substance.

12 – 1 – 4 - Magnitude of effects

Some individuals have less effective forms of one or both of the metabolizing enzymes, and can experience more severe symptoms from ethanol consumption than others. However, those having acquired alcohol tolerance have a greater quantity of these enzymes, and metabolize ethanol more rapidly.

12 – 1 – 5 - Other effects

Frequent drinking of alcoholic beverages has been shown to be a major contributing factor in cases of elevated blood levels of triglycerides.

Ethanol is not a carcinogen . However, the first metabolic product of ethanol in the liver, acetaldehyde, is toxic, mutagenic, and carcinogenic.

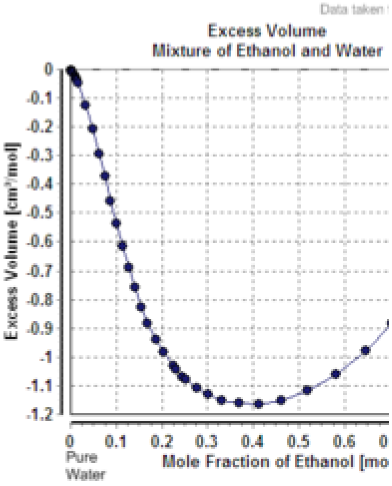
Ethanol is also widely used, clinically and over the counter, as an antitussive agent.

13 - Natural occurrence

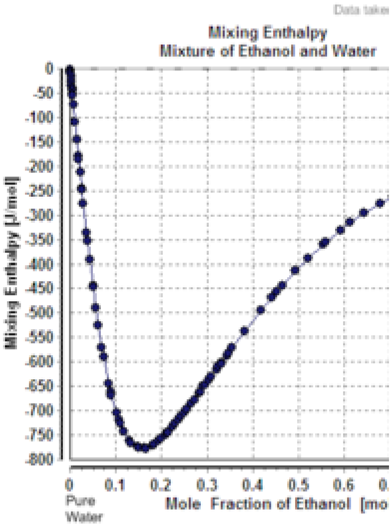
Ethanol is a byproduct of the metabolic process of yeast. As such, ethanol will be present in any yeast habitat. Ethanol can commonly be found in overripe fruit. Ethanol produced by symbiotic yeast can be found in Bertam Palm blossoms. Although some species such as the Pentailed Tree shrew exhibit ethanol seeking behaviors, most show no interest or avoidance of food sources containing ethanol.[105] Ethanol is also produced during the germination of many plants as a result of natural anerobiosis . Ethanol has been detected in outer space, forming an icy coating around dust grains in interstellar clouds.

14 - Charts

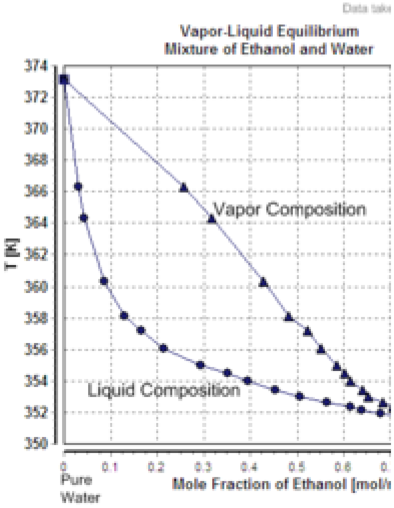
Thermo physical properties of mixtures of ethanol with water and dodecane



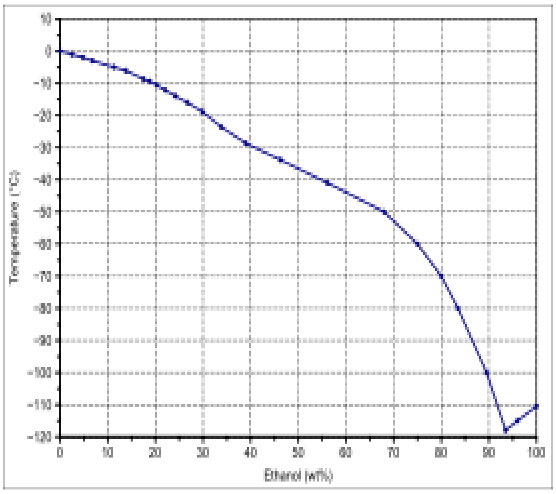
Excess volume of the mixture of ethanol and water (volume contraction)



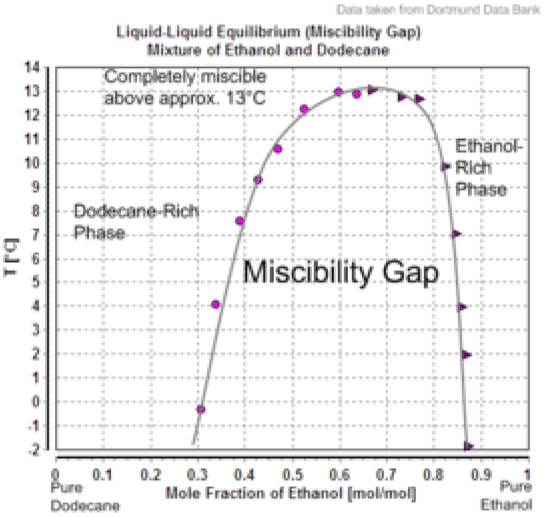
Heat of mixing of the mixture of ethanol and water



Vapor-liquid equilibrium of the mixture of ethanol and water (including azeotrope)



Solid-liquid equilibrium of the mixture of ethanol and water (including eutecticum)



Miscibility gap in the mixture of dodecane and ethanol

Ethanol Fermentation

Contents

1 - Introduction

Alcoholic Fermentation, also referred to as ethanol fermentation, is a biological process in which sugars such as glucose, fructose, and sucrose are converted into cellular energy and thereby produce ethanol and carbon dioxide as metabolic waste products. Because yeasts perform this conversion in the absence of oxygen, alcoholic fermentation is considered an anaerobic process.

Alcoholic fermentation occurs in the production of alcoholic beverages and ethanol fuel, and in the rising of bread dough.

2 - Chemical Process of Fermentation of Glucose

The chemical equations below summarize the fermentation of sucrose ($C_{12}H_{22}O_{11}$) into ethanol (C_2H_5OH). Alcoholic fermentation converts one mole of sucrose into four moles of ethanol and four moles of carbon dioxide, producing two moles of ATP in the process.

The overall chemical formula for alcoholic fermentation is:

$$C_6H_{12}O_6 + \text{Zymase} \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

Sucrose is a dimer of glucose and fructose molecules. In the first step of alcoholic fermentation, the enzyme invertase cleaves the glycosidic linkage between the two glucose molecules.

$$C_{12}H_{22}O_{11} + H_2O + \text{invertase} \rightarrow 2\ C_6H_{12}O_6$$

Next, each glucose molecule is broken down into two pyruvate molecules in a process known as glycolysis . Glycolysis is summarized by the equation:

$$C_6H_{12}O_6 + 2\ ADP + 2\ P_i + 2\ NAD^+ \rightarrow$$
$$2\ CH_3COCOO^- + 2\ ATP + 2\ NADH + 2\ H_2O + 2\ H^+$$

The chemical formula of pyruvate is CH_3COCOO^-. P_i stands for the inorganic phosphate.

As shown by the reaction equation, glycolysis causes the reduction of two molecules of NAD^+ to NADH. Two ADP molecules are also converted to two ATP and two water molecules via substrate-level phospho relation.

3 - Effect of oxygen

Fermentation does not require oxygen. If oxygen is present, some species of yeast (e.g., *Kluyveromyces lactis* or *Kluyveromyces lipolytica*) will oxidize pyruvate completely to carbon dioxide and water. This process is called cellular respiration. But these species of yeast will produce ethanol only in an anaerobic environment (not cellular respiration).

How ever, many yeasts such as the commonly used baker's yeast *Saccharomyces cerevisiae*, or fission yeast *Schizosaccharomyces pombe*, prefer fermentation to respiration. These yeasts will produce ethanol even under aerobic conditions, if they are provided with the right kind of nutrition . During batch fermentation, the rate of ethanol production per milligram of cell protein is maximal for a brief period early in this process and declines progressively as ethanol accumulates in the surrounding broth. Our studies demonstrate that the removal of this accumulated ethanol does not immediately restore fermentative activity, and they provide evidence that the decline in metabolic rate is due to physiological changes (including possible ethanol damage) rather than to the presence of ethanol. Several potential causes for the decline in fermentative activity have been investigated. Viability remained at or above 90%, internal pH remained near neutrality, and the specific activities of the glycolytic and alcohologenic enzymes (measured in vitro) remained high throughout batch fermentation. None of these factors appears to be causally related to the fall in fermentative activity during batch fermentation.

4 - Baking bread

The formation of carbon dioxide — a by product of ethanol fermentation — causes bread to rise.

Ethanol fermentation causes bread dough to rise. Yeast organisms consume sugars in the dough and produce ethanol and carbon dioxide as waste products. The carbon dioxide forms bubbles in the dough, expanding it into something of a foam. Nearly all the ethanol evaporates from the dough when the bread is baked.

5 - Alcoholic beverages

All ethanol contained in alcoholic beverages (including ethanol produced by carbonic maceration) is produced by means of fermentation induced by yeast.

Wine is produced by fermentation of the natural sugars present in grapes and other kinds of fruit.

Mead is produced by fermentation of the natural sugars present in honey.

Beer, whiskey, and vodka are produced by fermentation of grain starches that have been converted to sugar by the enzyme amylase, which is present in grain kernels that have been germinated.

Rum is produced by fermentation of sugar cane.

In all cases, fermentation must take place in a vessel that allows carbon dioxide to escape but prevents outside air from coming in. This is because exposure to oxygen would prevent the formation of ethanol.

6 - Feed stocks for fuel production

Yeast fermentation of various carbohydrate products is also used to produce the ethanol that is added to gasoline.

The dominant ethanol feedstock in warmer regions is sugarcane. In temperate regions, corn or sugar beets are used.

In the United States, the main feedstock for the production of ethanol is currently corn. Approximately 2.8 gallons of ethanol are produced from one bushel of corn (0.42 liter per kilogram). While much of the corn turns into ethanol, some of the corn also yields by-products such as DDGS (distillers dried grains with solubles) that can be used as feed for livestock. A bushel of corn produces about 18 pounds of DDGS (320 kilograms of DDGS per metric ton of maize). Although most of the fermentation plants have been built in corn-producing regions, sorghum is also an important feedstock for ethanol production in the Plains states. Pearl millet is showing promise as an ethanol feedstock for the southeastern U.S. and the potential of duckweed is being studied.

In some parts of Europe, particularly France and Italy, grapes have become a *de facto* feedstock for fuel ethanol by the distillation of surplus wine. In Japan, it has been proposed to use rice normally made into sake as an ethanol source.

6 – 1 - Cassava as ethanol feed stock

Ethanol can be made from mineral oil or from sugars or starches. Starches are cheapest. The starchy crop with highest energy content per acre is cassava, which grows in tropical countries.

Thailand already had a large cassava industry in the 1990s, for use as cattle feed and as a cheap admixture to wheat flour. Nigeria and Ghana are already establishing cassava - to - ethanol plants. Production of ethanol from cassava is currently economically feasible when crude oil prices are above US $ 120 per barrel.

New varieties of cassava are being developed, so the future situation remains uncertain. Currently, cassava can yield between 25 - 40 tones per hectare (with irrigation and fertilizer), and from a tone of cassava roots, circa 200 liters of ethanol can be produced (assuming cassava with 22 % starch content). A liter of ethanol contains circa 21.46 MJ of energy. The overall energy efficiency of cassava - root to ethanol conversion is circa 32 %.

The yeast used for processing cassava is *Endomycopsis fibuligera*, sometimes used together with bacterium *Zymomonas mobilis*.

7 – By products of fermentation

Ethanol fermentation produces un harvested byproducts such as heat, carbon dioxide, food for livestock, and water.

8 - Microbes used in ethanol fermentation

Yeast
Zymomonas mobilis

Cellulosic Ethanol

Contents

1 - Introduction

Cellulosic ethanol is a biofuel produced from wood, grasses, or the inedible parts of plants.

It is a type of biofuel produced from ligno cellulose, a structural material that comprises much of the mass of plants. Ligno cellulose is composed mainly of cellulose ,hemi cellulose and lignin. Corn stover, *Panicum virgatum*(switch grass), *Miscanthus* grass species, wood chips and the byproducts of lawn and tree maintenance are some of the more popular cellulosic materials for ethanol production. Production of ethanol from ligno cellulose has the advantage of abundant and diverse raw material compared to sources such as corn and cane sugars, but requires a greater amount of processing to make the sugar monomers available to the microorganisms typically used to produce ethanol by fermentation.

Switch grass and *Miscanthus* are the major biomass materials being studied today, due to their high productivity per acre. Cellulose, however, is contained in nearly every natural, free-growing plant, tree, and bush, in meadows, forests, and fields all over the world without agricultural effort or cost needed to make it grow.

According to Michael Wang of Argonne National Laboratory, one of the benefits of cellulosic ethanol is it reduces greenhouse gas emissions (GHG) by 85% over reformulated gasoline.[1] By contrast, starch ethanol (e.g., from corn), which most frequently uses natural gas to provide energy for the process, may not reduce GHG emissions at all depending on how the starch-based feedstock is produced. According to the National Academy of Sciences, there is no commercially viable bio - refinery in existence to convert lignocellulosic biomass to fuel. Absence of production of cellulosic ethanol in the quantities required by the regulation was the basis of aUnited States Court of Appeals for the District of Columbiadecision announced January 25, 2013 voiding a requirement imposed on car and truck fuel producers in the United States by the Environmental Protection Agency requiring addition of cellulosic biofuels to their products.[4]These issues, along with many other difficult production challenges, lead George Washington University policy researchers to state that "in the short term, [cellulosic] ethanol cannot meet the energy security and environmental goals of a gasoline alternative."

2 - History

The first attempt at commercializing a process for ethanol from wood was done in Germany in 1898. It involved the use of dilute acid to hydrolyze the cellulose to glucose, and was able to produce 7.6 liters of ethanol per 100 kg of wood waste (18 US gal (68 L) per ton). The Germans soon developed an industrial process optimized for yields of around 50 US gallons (190 L) per ton of biomass. This process soon found its way to the US, culminating in two commercial plants operating in the southeast during WWI. These plants used what was called "the American Process" — a one-stage dilute sulfuric acid hydrolysis. Though the yields were half that of the original German process (25 US gallons (95 L) of ethanol per ton versus 50), the throughput of the American process was much higher. A drop in lumber production forced the plants to close shortly after the end of WWI. In the meantime, a small but steady amount of research on dilute acid hydrolysis continued at the USFS's Forest Products

Laboratory. During World War II, the US again turned to cellulosic ethanol, this time for conversion to butadiene to produce synthetic rubber. The Vulcan Copper and Supply Company was contracted to construct and operate a plant to convert sawdust into ethanol. The plant was based on modifications to the original German Scholler process as developed by the Forest Products Laboratory. This plant achieved an ethanol yield of 50 US gal (190 L) per dry ton, but was still not profitable and was closed after the war.

With the rapid development of enzyme technologies in the last two decades, the acid hydrolysis process has gradually been replaced by enzymatic hydrolysis. Chemical pretreatment of the feedstock is required to prehydrolyze (separate) hemicellulose, so it can be more effectively converted into sugars. The dilute acid pretreatment is developed based on the early work on acid hydrolysis of wood at the USFS's Forest Products Laboratory. Recently, the Forest Products Laboratory together with the University of Wisconsin – Madison developed a sulfite pretreatment to overcome the recalcitrance of ligno cellulose for robust enzymatic hydrolysis of wood cellulose.

US President George W. Bush, in his State of the Union address delivered January 31, 2006, proposed to expand the use of cellulosic ethanol. In his State of the Union Address on January 23, 2007, President Bush announced a proposed mandate for 35 billion US gallons (130,000,000 m^3) of ethanol by 2017. It is widely recognized that the maximum production of ethanol from corn starch is 15 billion US gallons (57,000,000 m^3) per year, implying a proposed mandate for production of some 20 billion US gallons (76,000,000 m^3) per year of cellulosic ethanol by 2017. Bush's proposed plan includes $2 billion funding (from 2007-2017?) for cellulosic ethanol plants, with an additional $1.6 billion (from 2007-2017?) announced by the USDA on January 27, 2007.

In March 2007, the US government awarded $385 million in grants aimed at jump-starting ethanol production from nontraditional sources like wood chips, switch grass and citrus peels. Half of the six projects chosen will use thermo chemical methods and half will use cellulosic ethanol methods.

The American company Range Fuels announced in July 2007 that it was awarded a construction permit from the state of Georgia to build the first commercial - scale 100 - million - US - gallon (380,000 m^3) – per - year cellulosic ethanol plant in the US. Construction began in November, 2007 . The Range Fuels plant was built in Soperton, GA, but was shut down in January 2011 without ever having produced any ethanol. It had received a $76 million grant from the US Dept of Energy, plus $6 million from the State of Georgia, plus an $ 80 million loan guaranteed by the U.S. Biorefinery Assistance Program.

3 - Production methods

The two ways of producing ethanol from cellulose are :

Cellulolysis processes which consist of hydrolysis on pretreated ligno cellulosic materials, using enzymes to break complex cellulose into simple sugars such as glucose , followed by fermentation and distillation.

Gasification that transforms the lignocellulosic raw material into gaseous carbon monoxide and hydrogen. These gases can be converted to ethanol by fermentation or chemical catalysis.

As is normal for pure ethanol production, these methods include distillation.

3 – 1 - Cellulolysis (biological approach)

The stages to produce ethanol using a biological approach are :

A "pretreatment" phase, to make the ligno cellulosic material such as wood or straw amenable to hydrolysis

Cellulose hydrolysis (cellulolysis), to break down the molecules into sugars

Separation of the sugar solution from the residual materials, notably lignin

Microbial fermentation of the sugar solution

Distillation to produce roughly 95 % pure alcohol

Dehydration by molecular sieves to bring the ethanol concentration to over 99.5 %

In 2010, a genetically engineered yeast strain was developed to produce its own cellulose-digesting enzymes.[15] Assuming this technology can be scaled to industrial levels, it would eliminate one or more steps of cellulolysis , reducing both the time required and costs of production.

3 – 1 – 1 - Pretreatment

Although ligno cellulose is the most abundant plant material resource, its susceptibility has been curtailed by its rigid structure. As the result, an effective pretreatment is needed to liberate the cellulose from the lignin seal and its crystalline structure so as to render it accessible for a subsequent hydrolysis step.[16] By far, most pretreatments are done through physical or chemical means. To achieve higher efficiency, both physical and chemical pretreatments are required. Physical pretreatment is often called size reduction to reduce biomass physical size. Chemical pretreatment is to remove chemical barriers so the enzymes can have access to cellulose for microbial destruction.

To date, the available pretreatment techniques includeacid hydrolysis, steam explosion, ammonia fiber expansion, organo solve, sulfite pretreatment to overcome recalcitrance of ligno cellulose (SPORL) , alkaline wet oxidation and ozone pretreatment. Besides effective cellulose liberation, an ideal pretreatment has to minimize the formation of degradation products because of their inhibitory effects on subsequent hydrolysis and fermentation processes. The presence of inhibitors will not only further complicate the ethanol production but also increase the cost of production due to entailed detoxification steps. Even though pretreatment by acid hydrolysis is probably the oldest and most studied pretreatment technique, it produces several potent inhibitors including furfural and hydroxy methyl furfural (HMF) which are by far regarded as the most toxic inhibitors present in ligno cellulosic hydrolysate. Ammonia Fiber

Expansion (AFEX) is a promising pretreatment with no inhibitory effect in resulting hydrolysate .

Most pretreatment processes are not effective when applied to feed stocks with high lignin content, such as forest biomass. Organo solv and SPORL are the only two processes that can achieve over 90 % cellulose conversion for forest biomass, especially those of softwood species. SPORL is the most energy efficient (sugar production per unit energy consumption in pretreatment) and robust process for pretreatment of forest biomass with very low production of fermentation inhibitors. Organo solv pulping is particularly effective for hardwoods and offers easy recovery of a hydrophobic lignin product by dilution and precipitation.

3 – 1 – 2 - Cellulolytic processes

The cellulose molecules are composed of long chains of sugar molecules. In the hydrolysis process, these chains are broken down to free the sugar, before it is fermented for alcohol production.

There are two major cellulose hydrolysis (cellulolysis) processes: a chemical reaction using acids, or an enzymatic reaction.

3 – 1 – 2 - 1 - Chemical hydrolysis

In the traditional methods developed in the 19th century and at the beginning of the 20th century, hydrolysis is performed by attacking the cellulose with an acid. Dilute acid may be used under high heat and high pressure, or more concentrated acid can be used at lower temperatures and atmospheric pressure. A decrystallized cellulosic mixture of acid and sugars reacts in the presence of water to complete individual sugar molecules (hydrolysis). The product from this hydrolysis is then neutralized and yeast fermentation is used to produce ethanol. As mentioned, a significant obstacle to the dilute acid process is that the hydrolysis is so harsh that toxic degradation products are produced that can interfere with fermentation. Blue Fire Renew ables uses concentrated acid because it does not produce nearly as many fermentation inhibitors, but must be separated from the sugar stream for recycle [simulated moving bed (SMB) chromatographic separation, for example] to be commercially attractive.

Agricultural Research Service scientists found they can access and ferment almost all of the remaining sugars inwheat straw. The sugars are located in the plant’s cell walls, which are notoriously difficult to break down. To access these sugars, scientists pretreated the wheat straw with alkaline peroxide, and then used specialized enzymes to break down the cell walls. This method produced 93 US gallons (350 L) of ethanol per ton of wheat straw.

3 – 1 – 2 – 2 - Enzymatic hydrolysis

Cellulose chains can be broken into glucose molecules by cellulase enzymes.

This reaction occurs at body temperature in the stomachs of ruminants such as cattle and sheep, where the enzymes are produced by microbes. This process uses several enzymes at various stages of this conversion. Using a similar enzymatic system, ligno cellulosic materials can be enzymatic ally hydrolyzed at a relatively mild condition (50°C and pH 5), thus enabling effective cellulose breakdown without the formation of by products that would otherwise inhibit enzyme activity. All major pretreatment methods, including dilute acid, require an enzymatic hydrolysis step to achieve high sugar yield for ethanol fermentation. Currently, most pretreatment studies have been laboratory based, but companies are exploring means to transition from the laboratory to pilot, or production scale.

Various enzyme companies have also contributed significant technological breakthroughs in cellulosic ethanol through the mass production of enzymes for hydrolysis at competitive prices.

The fungus *Trichoderma reesei* is used by Iogen Corporation to secrete "specially engineered enzymes" for an enzymatic hydrolysis process . Their raw material (wood or straw) has to be pre-treated to make it amenable to hydrolysis.

Another Canadian company , Sun Opta, markets a patented technology known as "Steam Explosion" to pre treat cellulosic biomass, overcoming its "recalcitrance" to make cellulose and hemi cellulose accessible to enzymes for conversion into fermentable sugars. Sun Opta designs and engineers cellulosic ethanol bio refineries and its process technologies and equipment are in use in the first three commercial demonstration plants in the world: Verenium (formerly Celunol Corporation)'s facility in Jennings, Louisiana, Abengoa's facility in Salamanca, Spain, and a facility in China owned by China Resources Alcohol Corporation (CRAC). The CRAC facility is currently producing cellulosic ethanol from local corn stover on a 24-hour a day basis using Sun Opta's process and technology.

Genencor and Novozymes have received United States Department of Energy funding for research into reducing the cost of cellulases , key enzymes in the production of cellulosic ethanol by enzymatic hydrolysis.

Other enzyme companies, such as Dyadic International,] are developing genetically engineered fungi which would produce large volumes of cellulase , xylanase and hemi cellulase enzymes, which can be used to convert agricultural residues such as corn stover, distiller grains, wheat straw and sugarcane bagasse andenergy crops such as switch grass into fermentable sugars which may be used to produce cellulosic ethanol.

In 2010, BP Biofuels bought out the cellulosic ethanol venture share of Verenium, which had itself been formed by the merger of Diversa and Celunol, and with which it jointly owned and operated a 1.4- million-US-gallon (5,300 m^3) per year demonstration plant in Jennings, LA, and the laboratory facilities and staff in San Diego, CA. BP Biofuels continues to operate these facilities, and has begun first phases to construct commercial facilities. Ethanol produced in the Jennings facility was shipped to London and blended with gasoline to provide fuel for the Olympics.

KL Energy Corporation , formerly KL Process Design Group, began commercial operation of a 1.5-million-US-gallon (5,700 m^3) per year cellulosic ethanol facility in Upton, WY in the last quarter of 2007. The Western Biomass Energy facility is currently achieving yields of 40 – 45 US gallons (150–170 L) per dry ton. It is the first operating commercial cellulosic ethanol facility in the nation. The KL Energy process uses a thermo mechanical breakdown and enzymatic conversion process. The primary feedstock is soft wood, but lab tests have already proven the KL Energy process on wine pomace, sugarcane bagasse, municipal solid waste, and switch grass.

3 – 1 – 3 - Microbial fermentation

Traditionally, baker's yeast (*Saccharomyces cerevisiae*), has long been used in the brewery industry to produce ethanol from hexoses (six - carbon sugars). Due to the complex nature of the carbohydrates present in ligno cellulosic biomass, a significant amount of xylose and arabinose (five-carbon sugars derived from the hemi cellulose portion of the ligno cellulose) is also present in the hydrolysate. For example, in the hydrolysate of corn stover, approximately 30 % of the total fermentable sugars is xylose. As a result, the ability of the fermenting microorganisms to use the whole range of sugars available from the hydrolysate is vital to increase the economic competitiveness of cellulosic ethanol and potentially biobased proteins.

In recent years, metabolic engineering for microorganisms used in fuel ethanol production has shown significant progress. Besides *Saccharomyces cerevisiae*, microorganisms such as *Zymomonas mobilis* and*Escherichia coli* have been targeted through metabolic engineering for cellulosic ethanol production.

Recently, engineered yeasts have been described efficiently fermenting xylose, and arabinose , and even both together. Yeast cells are especially attractive for cellulosic ethanol processes because they have been used in biotechnology for hundreds of years, are tolerant to high ethanol and inhibitor concentrations and can grow at low pH values to reduce bacterial contamination.

3 – 1 – 4 - Combined hydrolysis and fermentation

Some species of bacteria have been found capable of direct conversion of a cellulose substrate into ethanol. One example is *Clostridium thermocellum*, which uses a complex cellulosome to break down cellulose and synthesize ethanol. However , *C. thermocellum* also produces other products during cellulose metabolism, including acetate and lactate, in addition to ethanol, lowering the efficiency of the process. Some research efforts are directed to optimizing ethanol production by genetically engineering bacteria that focus on the ethanol-producing pathway.

3 – 2 – Gasification process (thermo hemical approach)

Fluidized Bed Gasifier in Güssing Burgenland Austria

The gasification process does not rely on chemical decomposition of the cellulose chain (cellulolysis). Instead of breaking the cellulose into sugar molecules, the carbon in the raw material is converted into synthesis gas, using what amounts to partial combustion. The carbon monoxide, carbon dioxide and hydrogen may then be fed into a special kind of fermenter. Instead of sugar fermentation with yeast, this process uses *Clostridium ljungdahlii* bacteria . This microorganism will ingest carbon monoxide, carbon dioxide and hydrogen and produce ethanol and water. The process can thus be broken into three steps:

Gasification — Complex carbon - based molecules are broken apart to access the carbon as carbon monoxide, carbon dioxide and hydrogen

Fermentation — Convert the carbon monoxide, carbon dioxide and hydrogen into ethanol using the *Clostridium ljungdahlii* organism

Distillation — Ethanol is separated from water

A recent study has found another *Clostridium* bacterium that seems to be twice as efficient in making ethanol from carbon monoxide as the one mentioned above.

Alternatively, the synthesis gas from gasification may be fed to a catalytic reactor where it is used to produce ethanol and other higher alcohols through a thermo chemical process. This process can also generate other types of liquid fuels, an alternative concept successfully demonstrated by the Montreal-based company Enerkem at their facility in Westbury, Quebec.

4 - Economics

Start-up costs for pilot scale ligno cellulosic ethanol plants are high. On 28 February 2007, the U.S. Dept. of Energy announced $ 385 million in grant funding to six cellulosic ethanol plants. This grant funding accounts for 40 % of the investment costs. The remaining 60 % comes from the promoters of those facilities. Hence, a total of $ 1 billion will be invested for approximately 140-million-US-gallon (530,000 m^3) capacity. This translates into $7/annual gallon production capacity in capital investment costs for pilot plants; future capital costs are expected to be lower . Corn-to-ethanol plants cost roughly $1–3/annual gallon capacity, though the cost of the corn itself is considerably greater than for switch grass or waste biomass.

As of 2007, ethanol is produced mostly from sugars or starches, obtained from fruits and grains. In contrast, cellulosic ethanol is obtained from cellulose, the main component of wood, straw, and much of the structure of plants. Since cellulose cannot be digested by humans, the production of cellulose does not compete with the production of food, other than conversion of land from food production to cellulose production (which has recently started to become an issue, due to rising wheat prices.) The price per ton of the raw material is thus much cheaper than that of grains or fruits.

Moreover, since cellulose is the main component of plants, the whole plant can be harvested. This results in much better yields—up to 10 short tons per acre (22 t/ha), instead of 4-5 short tons/acre (9–11 t/ha) for the best crops of grain .

The raw material is plentiful. An estimated 323 million tons of cellulose-containing raw materials which could be used to create ethanol are thrown away each year in US alone. This includes 36.8 million dry tons of urban wood wastes, 90.5 million dry tons of primary mill residues, 45 million dry tons of forest residues, and 150.7 million dry tons of corn stover and wheat straw. Transforming them into ethanol using efficient and cost-effective hemi (cellulase) enzymes or other processes might provide as much as 30% of the current fuel consumption in the United States. Moreover, even land marginal for agriculture could be planted with cellulose-producing crops such as switch grass, resulting in enough production to substitute for all the current oil imports into the United States.

Paper, cardboard, and packaging comprise a substantial part of the solid waste sent to landfills in the United States each day, 41.26% of all organic municipal solid waste(MSW) according to California Integrated Waste Management Board's city profiles . These city profiles account for accumulation of 612.3 short tons (555.5 t) daily per landfill where an average population density of 2,413 per square mile persists. Organic waste consists of 0.4% manure, 1.6% gypsum board, 4.2 % glossy paper, 4.2 % paper ledger, 9.2 % wood, 10.5 % envelopes, 11.9 % newsprint, 12.3 % grass and leaves, 30.0% food scrap, 34.0% office paper, 35.2 % corrugated cardboard, and 46.4% agricultural composites, makes up 71.51 % of landfill. All these, except gypsum board, contain cellulose, which is transformable into cellulosic ethanol . This may have additional environmental benefits because decomposition of these products produces methane, a potent greenhouse gas.

Reduction of the disposal of solid waste through cellulosic ethanol conversion would reduce solid waste disposal costs by local and state governments. It is estimated that each person in the US throws away 4.4 lb (2.0 kg) of trash each day, of which 37% contains waste paper, which is largely cellulose. That computes to 244 thousand tons per day of discarded waste paper that contains cellulose. The raw material to produce cellulosic ethanol is not only free, it has a negative cost — i.e., ethanol producers can get paid to take it away.

In June 2006, a U.S. Senate hearing was told the current cost of producing cellulosic ethanol is US $2.25 per US gallon (US $ 0.59 / liter), primarily due to the current poor conversion efficiency. At that price, it would cost about $120 to substitute a barrel of oil (42 US gallons (160 L)), taking into account the lower energy content ofethanol. However, the Department of Energy is optimistic and has requested a doubling of research funding. The same Senate hearing was told the research target was to reduce the cost of production to US $1.07 per US gallon (US $0.28/litre) by 2012. "The production of cellulosic ethanol represents not only a step toward true energy diversity for the country, but a very cost-effective alternative to fossil fuels. It is advanced weaponry in the war on oil," said Vinod Khosla, managing partner of Khosla Ventures, who recently told a Reuters Global Biofuels Summit that he could see cellulosic fuel prices sinking to $1 per gallon within ten years.

In September 2010, a report by Bloom berg analyzed the European biomass infrastructure and future refinery development. Estimated prices for a liter of ethanol in August 2010 are EUR 0.51 for 1g and 0.71 for 2g. The report suggested Europe should copy the current US subsidies of up to $ 50 per dry tonne.

5 - Environmental effects: corn-based vs. grass-based

In 2008, there was only a small amount of switch grass dedicated for ethanol production. In order for it to be grown on a large-scale production it must compete with existing uses of agricultural land, mainly for the production of crop commodities. Of the United States' 2.26 billion acres (9.1 million km^2) of unsubmerged land, 33 % are forestland, 26 % pastureland and grassland, and 20% crop land. A study done by the U.S. Departments of Energy and Agriculture in 2005 determined whether there were enough available land resources to sustain production of over 1 billion dry tons of biomass annually to replace 30 % or more of the nation's current use of liquid transportation fuels. The study found that there could be 1.3 billion dry tons of biomass available for ethanol use, by making little changes in agricultural and forestry practices and meeting the demands for forestry products, food, and fiber . A recent study done by the University of Tennessee reported that as many as 100 million acres (400,000 km^2, or 154,000 sq mi) of cropland and pasture will need to be allocated to switch grass production in order to offset petroleum use by 25 percent.

Currently, corn is easier and less expensive to process into ethanol in comparison to cellulosic ethanol. The Department of Energy estimates that it costs about $2.20 per gallon to produce cellulosic ethanol, which is twice as much as ethanol from corn. Enzymes that destroy plant cell wall tissue cost 30 to 50 cents per gallon of ethanol compared to 3 cents per gallon for corn.[*citation needed*] The Department of Energy hopes to reduce production cost to $1.07 per gallon by 2012 to be effective. However, cellulosic biomass is cheaper to produce than corn, because it requires fewer inputs, such as energy, fertilizer, herbicide, and is accompanied by less soil erosion and improved soil fertility. Additionally, nonfermentable and unconverted solids left after making ethanol can be burned to provide the fuel needed to operate the conversion plant and produce electricity. Energy used to run corn-based ethanol plants is derived from coal and natural gas. The Institute for Local Self - Reliance estimates the cost of cellulosic ethanol from the first generation of commercial plants will be in the $ 1.90 – $ 2.25 per gallon range, excluding incentives. This compares to the current cost of $ 1.20 – $ 1.50 per gallon for ethanol from corn and the current retail price of over $ 4.00 per gallon for regular gasoline (which is subsidized and taxed).

One of the major reasons for increasing the use of biofuels is to reduce greenhouse gas emissions. In comparison to gasoline, ethanol burns cleaner, thus putting less carbon dioxide and overall pollution in the air . Additionally, only low levels of smog are produced from combustion . According to the U.S. Department of Energy, ethanol from cellulose reduces green house gas emission by 86 percent, when compared to gasoline and in comparison to corn-based ethanol which decreases emissions by 52 percent. Carbon dioxide gas emissions are shown to be 85% lower than those from gasoline. Cellulosic ethanol contributes little to the greenhouse effect and has a five times better net energy balance than corn-based ethanol.[52] When used as a fuel, cellulosic ethanol releases less sulfur, carbon monoxide, particulates, and greenhouse gases. Cellulosic ethanol should earn producers carbon reduction credits, higher than those given to producers who grow corn for ethanol, which is about 3 to 20 cents per gallon.

It takes 0.76 J of energy from fossil fuels to produce 1 J worth of ethanol from corn. This total includes the use of fossil fuels used for fertilizer, tractor fuel, ethanol plant operation, etc. Research has shown that fossil fuel can produce over five times the volume of ethanol from prairie grasses, according to Terry Riley, President of Policy at the Theodore Roosevelt Conservation Partnership. The United States Department of Energy concludes that corn-based ethanol provides 26 percent more energy than it requires for production, while cellulosic ethanol provides 80 percent more energy. Cellulosic ethanol yields 80 percent more energy than is required to grow and convert it. The process of turning corn into ethanol requires about 1700 times (by volume) as much water as ethanol produced. Additionally, it leaves 12 times its volume in waste. Grain ethanol uses only the edible portion of the plant. Expansion of corn acres for the production of ethanol poses threats to biodiversity. Corn lacks a large root system, which allows extreme soil erosion to take place. This has a direct effect on soil particles, along with excess fertilizers and other chemicals, washing into local waterways, damaging water quality and harming aquatic life. Planting riparian areas can serve as a buffer to waterways, and decrease runoff.

Cellulose is not used for food and can be grown in all parts of the world. The entire plant can be used when producing cellulosic ethanol. Switch grass yields twice as much ethanol per acre than corn. Therefore, less land is needed for production and thus less habitat fragmentation. Biomass materials require fewer inputs, such as fertilizer, herbicides, and other chemicals that can pose risks to wildlife. Their extensive roots improve soil quality, reduce erosion, and increase nutrient capture. Herbaceous energy crops reduce soil erosion by greater than 90 %, when compared to conventional commodity crop production. This can translate into improved water quality for rural communities. Additionally, herbaceous energy crops add organic material to depleted soils and can increase soil carbon, which can have a direct effect on climate change, as soil carbon can absorb carbon dioxide in the air. As compared to commodity crop production, biomass reduces surface runoff and nitrogen transport. Switchgrass provides an environment for diverse wildlife habitation, mainly insects and ground birds. Conservation Reserve Program (CRP) land is composed of perennial grasses, which are used for cellulosic ethanol, and may be available for use.

For years American farmers have practiced row cropping, with crops such as sorghum and corn. Because of this, much is known about the effect of these practices on wildlife. The most significant effect of increased corn ethanol would be the additional land that would have to be converted to agricultural use and the increased erosion and fertilizer use that goes along with agricultural production. Increasing our ethanol production through the use of corn could produce negative effects on wildlife, the magnitude of which will depend on the scale of production and whether the land used for this increased production was formerly idle, in a natural state, or planted with other row crops. Another consideration is whether to plant a switchgrass monoculture or use a variety of grasses and other vegetation. While a mixture of vegetation types likely would provide better wildlife habitat, the technology has not yet developed to allow the processing of a mixture of different grass species or vegetation types into bioethanol. Of course, cellulosic ethanol production is still in its infancy, and the possibility of using diverse vegetation stands instead of mono cultures deserves further exploration as research continues.

A study by Nobel Prize winner Paul Crutzen found ethanol produced from corn had a "net climate warming" effect when compared to oil when the full life cycle assessment properly considers the nitrous oxide (N20) emissions that occur during corn ethanol production. Crutzen found that crops with less nitrogen demand , such as grasses and woody coppice species, have more favour able climate impacts.

6 – Feed stocks

In general there are two types of feedstocks: **forest (woody) Biomass** and **agricultural biomass**. In the US, about 1.4 billion dry tons of biomass can be sustainably produced annually. About 370 million tons or 30 % are forest biomass . Forest biomass has higher cellulose and lignin content and lower hemi cellulose and ash content than agricultural biomass. Because of the difficulties and low ethanol yield in fermenting pretreatment hydrolysate, especially those with very high 5 carbon hemi cellulose sugars such as xylose, forest biomass has significant advantages over agricultural biomass. Forest biomass also has high density which significantly reduces transportation cost. It can be harvested year around which eliminates long term storage. The close to zero ash content of forest biomass significantly reduces dead load in transportation and processing. To meet the needs for biodiversity, forest biomass will be an important biomass feedstock supply mix in the future biobased economy. However, forest biomass is much more recalcitrant than agricultural biomass. Recently, the USDA Forest Products Laboratory together with the University of Wisconsin – Madison developed efficient technologies that can overcome the strong recalcitrance of forest (woody) biomass including those of softwood species that have low xylan content. Short-rotation intensive culture or tree farming can offer an almost unlimited opportunity for forest biomass production.

Wood chips from slashes and tree tops and saw dust from saw mills, and waste paper pulp are common forest biomass feedstocks for cellulosic ethanol production.

The following are a few examples of agricultural biomass:

Switch grass (*Panicum virgatum*) is a native tall grass prairie grass . Known for its hardiness and rapid growth, this perennial grows during the warm months to heights of 2–6 feet. Switchgrass can be grown in most parts of the United States, including swamplands, plains, streams, and along the shores & *interstate highways*. It is *self-seeding*(no tractor for sowing, only for mowing), resistant to many diseases and pests, & can produce high yields with low applications of fertilizer and other chemicals. It is also tolerant to poor soils, flooding, & drought; improves soil quality and prevents erosion due its type of root system.

Switch grass is an approved cover crop for land protected under the federal Conservation Reserve Program (CRP). CRP is a government program that pays producers a fee for not growing crops on land on which crops recently grew. This program reduces soil erosion, enhances water quality, and increases wildlife habitat. CRP land serves as a habitat for upland game, such as pheasants and ducks, and a number of insects. Switch grass for biofuel production has been considered for use on Conservation Reserve Program (CRP) land, which could increase ecological sustainability and lower the cost of the CRP program. However, CRP rules would have to be modified to allow this economic use of the CRP land.

Miscanthus x giganteus is another viable feed stock for cellulosic ethanol production. This species of grass is native to Asia and is the sterile triploid hybrid of *Miscanthus sinensis* and *Miscanthus sacchariflorus*. It can grow up to 12 feet (3.7 m) tall with little water or fertilizer input. Miscanthus is similar to switchgrass with respect to cold and drought tolerance and water use efficiency. Miscanthus is commercially grown in the European Union as a combustible energy source.

Corn cobs and **corn stover** are the most popular agricultural biomass.

It has been suggested that Kudzu may become a valuable source of biomass.

6 - Cellulosic ethanol commercialization

Cellulosic ethanol commercialization is the process of building an industry out of methods of turning cellulose-containing organic matter into fuel. Companies such as Iogen, POET, and Abengoa are building refineries that can process biomass and turn it into ethanol, while companies such as Genencor, Diversa, Novozymes, and Dyadic are producing enzymes which could enable a cellulosic ethanol future. The shift from food crop feedstocks to waste residues and native grasses offers significant opportunities for a range of players, from farmers to biotechnology firms, and from project developers to investors.

The cellulosic ethanol industry developed some new commercial-scale plants in 2008. In the United States, plants totaling 12 million liters (3.17 million gal) per year were operational, and an additional 80 million liters (21.1 million gal.) per year of capacity - in 26 new plants - was under construction. In Canada, capacity of 6 million liters per year was operational. In Europe, several plants were operational in Germany, Spain, and Sweden, and capacity of 10 million liters per year was under construction.

Italy - based Mossi & Ghisolfi Group broke ground for its 13 MMgy cellulosic ethanol facility in northwestern Italy on April 12, 2011. The project will be the largest cellulosic ethanol project in the world, 10 times larger than any of the currently operating demonstration-scale facilities.

Corn Ethanol

Corn is the main feedstock used for producing ethanol fuel in the United States.

Contents

Corn ethanol is ethanol produced from corn that is used as a biomass. Corn ethanol is produced by means of ethanol fermentation and distillation.

Corn ethanol is mainly used as an oxygenate in gasoline to produce a low-level blend. To a lesser extent, it is used as fuel for E85 flex - fuel vehicles.

Corn is the main feedstock used for producing ethanol fuel in the United States.

2 - Production process

There are two main types of corn ethanol production: dry milling and wet milling. The products of each type are utilized in different ways.

An ethanol fuel plant in West Burlington, Iowa.

In the dry milling process the entire corn kernel is ground into flour and referred to as "meal." The meal is then slurried by adding water . Enzymes are added to the mash that convert starch to dextrose, a simple sugar . Ammonias added to control the pH and as a nutrient for the yeast, which is added later. The mixture is processed at high-temperatures to reduce the bacteria levels and transferred and cooled in fermenters. This is where the yeast is added and conversion from sugar to ethanol and carbon dioxide begins.

The entire process takes between 40 to 50 hours, during which time the mash is kept cool and agitated in order to facilitate yeast activity. After the process is complete, everything is transferred to distillation columns where the ethanol is removed from the "stillage". The ethanol is dehydrated to about 200 proof using a molecular sieve system and a denaturant such as gasoline is added to render the product undrinkable. With this last addition, the process is complete and the product is ready to ship to gasoline retailers or terminals. The remaining stillage then undergoes a different process to produce a highly nutritious livestock feed. The carbon dioxide released from the process is also utilized to carbonate beverages and to aid in the manufacturing of dry ice.

The process of wet milling takes the corn grain and steeps it in a dilute combination of sulfuric acid and water for 24 to 48 hours in order to separate the grain into many components. The slurry mix then goes through a series of grinders to separate out the corn germ. Corn oil is a by-product of this process and is extracted and sold. The remaining components of fiber, gluten and starch are segregated out using screen, hydro clonic and centrifugal separators.

The gluten protein is dried and filtered to make a corn gluten-meals co - product and is highly sought after by poultry broiler operators as a feed ingredient. The steeping liquor produced is concentrated and dried with the fiber and sold as corn gluten feed to in the livestock industry. The heavy steep water is also sold as a feed ingredient and is used as an environmentally friendly alternative to salt in the winter months. The corn starch and remaining water can then be processed one of three ways: 1) fermented into ethanol, through a similar process as dry milling, 2) dried and sold as modified corn starch, or 3) made into corn syrup.

The production of corn ethanol uses water in two ways – irrigation and processing. There are two types of ethanol processing, wet milling and dry milling, and the central difference between the two processes is how they initially treat the grain. In wet milling, the corn grain is steeped in water, and then separated for processing in the first step. Dry milling, which is more common, requires a different process. According to a report by the National Renewable Energy Laboratory, "Over 80 % of U.S. ethanol is produced from corn by the dry grind process." The dry grind process proceeds as follows:

"Corn grain is milled, then slurried with water to create 'mash.' Enzymes are added to the mash and this mixture is then cooked to hydrolyze the starch into glucose sugars. Yeast ferment these sugars into ethanol and carbon dioxide and the ethanol is purified through a combination of distillation and molecular sieve dehydration to create fuel ethanol. The byproduct of this process is known as distiller's dried grains and solubles (DDGS) and is used wet or dry as animal feed."

3 - Environmental and social issues

Since most U.S. ethanol is produced from corn and the required electricity from many distilleries comes mainly from coal plants, there has been considerable debate on the sustainability of corn-based bio-ethanol in replacing fossil fuels. Controversy and concerns relate to the large amount of arable land required for crops and its impact on grain supply, direct and indirect land use change effects, as well as issues regarding its energy balance and carbon intensity considering the full life cycle of ethanol production, and also issues regarding water use and pollution due to the increase expansion of ethanol production.

The initial assumption that biofuels were good for the environment because they had a smaller carbon footprintis in debate over the contention that the production of grain alcohol, and therefore E85, may actually have a greater environmental impact than fossil fuel.

That view says that one must consider :

The impact of fertilizers and carbon requiring inputs vs carbon offsetting byproducts like distillers grains.

The carbon footprint of the agricultural machinery run to plant, harvest and apply chemicals.[*citation needed*]

The environmental impact of those chemicals themselves, including fertilizers and pesticides necessary for efficient mass-production of the grains used.

The larger amount of energy required to ship and process the grains and turn them into alcohol, versus the more efficient process of converting oil into gasoline or diesel.

Even resources such as water, needed in huge amounts for grain production, can have serious environmental impact, including ground water depletion, pollution runoff, and algae blooms from waste runoff.

The U.S. Department of Energy has published facts stating that current corn-based ethanol results in a 19% reduction in greenhouse gases, and is better for the environment than other gasoline additives such as MTBE.

Ethanol produced today results in fewer greenhouse gas (GHG) emissions than gasoline and is fully biodegradable, unlike some fuel additives.

Today, on a life cycle basis, ethanol produced from corn results in about a 20 percent reduction in GHG emissions relative to gasoline. With improved efficiency and use of renewable energy, this reduction could be as much as 52 percent.

In the future, ethanol produced from cellulose has the potential to cut life cycle GHG emissions by up to 86 percent relative to gasoline.

Ethanol blended fuels currently in the market – whether E10 or E85 – meet stringent tailpipe emission standards.

Ethanol readily biodegrades without harm to the environment, and is a safe, high - performance replacement for fuel additives such as MTBE.

Others say that ethanol from corn, as a fuel available now, and cellulosic ethanol in the future, are both much better fuels for the environment . Ethanol derived from sugar-beet as used in Europe or sugar-cane as grown in Brazil in industrial scale is generally seen as having a very positive CO_2 balance with up to 80% reduction in well-to-wheel CO_2.

A University of Nebraska study in 2009 showed corn ethanol directly emits 51% less greenhouse gas than gasoline. However this study does not take into account the greenhouse gasses involved in production and transportation

3 – 1 - Economic impact of corn ethanol

The use of ethanol for fuel has had a damaging impact on food markets, especially in poorer countries. In the United States, ethanol is mostly made from yellow corn, and as the market boomed for alternative fuel, yellow corn went up in price. Many farmers saw the potential to make more money, and switched from white corn to yellow corn. White corn is the main ingredient of tortillas in Mexico, and as the supply dropped, the price doubled, making the base of most Mexican foods unaffordable. Many people see this as un acceptable, and want no overlap between food crops and fuel crops. Others point out that the earth is thought to be able to support double the current human population, and press that the resources available, such as unused farmable land, should be better handled.

The Rene wable Fuels Association confirm ethanol production does in fact increase the price of corn by increasing demand. It is cited as a positive economic effect for US farmers and tax payers, but does not elaborate on the effect for other populations where field corn is part of the staple diet. "FACT: By increasing the demand for corn, and thus raising corn prices, ethanol helps to lower federal farm program costs. In a January 2007 statement, the USDA Chief Economist stated that farm program payments were expected to be reduced by some $ 6 billion due to the higher value of a bushel of corn."

Corn production in 2009 reached over 13.2 billion bushels, and a per acre yield jumped to over 165 bushels per acre.

4 - Alternatives to corn as a feed stock

Remnants from food production such as corn stover could be used to produce ethanol instead of food corn. The use of cellulosic biomass to produce ethanol is a new trend in biofuel production. Fuels from these products are considered second generation biofuels and are considered by some to be a solution to the food verses fuel debate. The possibility of using this material has been acknowledged by the scientific community and the political community as well.

Ethanol From Coal

Ethanol from coal is the ethanol produced using coal as its carbon source. The anaerobic bacterium *Clostridium ljungdahlii* produces ethanol and acetic acid from CO, CO_2, and H_2 in synthesis gas. Early studies with *C. ljungdahlii* showed that relatively high concentrations of ethanol were produced. This process involves three main steps:

1 - Gasification : Thermal gasification at temperatures of up to 2,200°F in a reducing, very low oxygen atmosphere transforms organic materials into simple CO, CO_2 and H_2 gases.

2 - Fermentation : The acetogenic *C. ljungdahlii* convert the carbon monoxide into ethanol.

3 - Distillation: Ethanol is separated from hydrogen and water.

Acetone – Butanol - Ethanol Fermentation

(*ABE Fermentation*)

Acetone-butanol-ethanol (ABE) fermentation is a process that uses bacterial Fermentation to produce acetone, n-Butanol, and ethanol from starch. It was developed by the chemist Chaim Weizmann and was the primary process used to make acetone during World War I, such as to produce cordite. The process is anaerobic (done in the absence of oxygen), similar to how yeast ferments sugars to produce ethanol for wine, beer, or fuel. The process produces these solvents in a ratio of 3-6-1, or 3 parts acetone, 6 parts butanol and 1 part ethanol. It usually uses a strain of bacteria from the Clostridia Class (Clostridium Family). Clostridium acetobutylicum is the most well-known strain, although Clostridium beijerinckii has also been used for this process with good results.

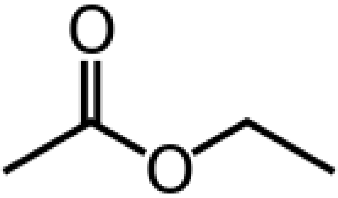
The production of butanol by biological means was first performed by Louis Pasteur in 1861. In 1905, Schardinger found that acetone could similarly be produced. Fernbach's work of 1911 involved the use of potato starch as a feedstock in the production of butanol. Industrial exploitation of ABE fermentation started in 1916 with Chaim Weizmann's isolation of Clostridium acetobutylicum, as described in U.S. patent 1315585.

In order to make ABE fermentation profitable, many in-situ product recovery systems have been developed. These include gas stripping, per evaporation, membrane extraction, adsorption, and reverse osmosis. However, at this time none of them have been implemented at an industrial scale.

For gas stripping, the most common gases used are the off-gases from the fermentation itself, a mixture of carbon dioxide and hydrogen gas.

ABE fermentation, however, is not profitable when compared to the production of these solvents from petroleum. As such there are no currently operating ABE plants. During the 1950s and 1960s, ABE fermentation was replaced by petroleum chemical plants. Due to different raw materials costs, ABE fermentation was viable in South Africa until the early 1980s, with the last plant closing in 1983.

Ethyl Acetate



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1 - Introduction

Ethyl acetate (systematically, ethyl ethanoate, commonly abbreviated EtOAc or EA) is the organic compound with the formula $CH_3COOCH_2CH_3$. This colorless liquid has a characteristic sweet smell (similar to pear drops) and is used in glues, nail polish removers, decaffeinating tea and coffee, and cigarettes (see list of additives in cigarettes). Ethyl acetate is the ester of ethanol and acetic acid; it is manufactured on a large scale for use as a solvent. The combined annual production in 1985 of Japan, North America, and Europe was about 400,000 tons. In 2004, an estimated 1.3M tons were produced worldwide.

IUPAC name ; Ethyl acetate	
Systematic name : Ethyl ethanoate	
Molecular formula	$C_4 H_8 O_2$
Molar mass	88 g mol^{-1}
Appearance	Colorless liquid
Density	0.897 g / cm^3

Melting point	−83.6 °C
Boiling point	77.1 °C
Solubility in water	8.3 g/100 mL (20 °C)
Solubility in ethanol, acetone, diethyl ether, benzene	Miscible
Refractive index (n_D)	1.3720
Viscosity	0.426 cP at 25 °C
Main hazards	Flammable (F), Irritant (Xi)
Flash point	− 4 °C
LD_{50}	11.3 g / kg, rat
Structure and properties	n, ε_r, etc.
Thermo dynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

2 - Production

Ethyl acetate is synthesized in industry mainly via the classic Fischer esterification reaction of ethanol and acetic acid. This mixture converts to the ester in about 65% yield at room temperature:

$$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

The reaction can be accelerated by acid catalysis and the equilibrium can be shifted to the right by removal of water. It is also prepared in industry using the Tishchenko reaction, by combining two equivalents of acetaldehyde in the presence of an alkoxide catalyst:

$$2\ CH_3CHO \rightarrow CH_3COOCH_2CH_3$$

2 – 1 - By dehydrogenation of ethanol

A specialized industrial route entails the catalytic dehydrogenation of ethanol. This method is less cost effective than the esterification but is applied with surplus ethanol in a chemical plant. Typically, dehydrogenation is conducted with copper at an elevated temperature but below 250 °C. The copper may have its surface area increased by depositing it on zinc, promoting the growth of snowflake, fractal like structures (dendrites). Surface area can be again increased by deposition onto a zeolite, typically ZSM-5. Traces of rare earth and alkali metals are beneficial to the process. Byproducts of the dehydrogenation include diethyl ether, which is thought to arise primarily due to aluminum sites in the catalyst, acetaldehyde and its aldol products, higher esters, and ketones. Separations of the byproducts are complicated by the fact that ethanol forms an azeotrope with water, as does ethyl acetate with ethanol and water, and methyl ethyl ketone (MEK, which forms from 2-butanol) with both ethanol and ethyl acetate. These azeotropes are "broken" by pressure swing distillation or membrane distillation.

3 - Uses

Ethyl acetate is used primarily as a solvent and diluent, being favored because of its low cost, low toxicity, and agreeable odor. For example, it is commonly used to clean circuit boards and in some nail varnish removers (acetone and acetonitrile are also used). Coffee beans and tea leaves are decaffeinated with this solvent. It is also used in paints as an activator or hardener. Ethyl acetate is present in confectionery, perfumes, and fruits. In perfumes, it evaporates quickly, leaving only the scent of the perfume on the skin.

3 – 1 - Laboratory uses

In the laboratory, mixtures containing ethyl acetate are commonly used in column chromatography and extractions. Ethyl acetate is rarely selected as a reaction solvent because it is prone to hydrolysis and trans esterification.

Ethyl acetate is very volatile and has a boiling point of 77 °C. Due to these properties, it can be removed from a sample by heating in a hot water bath and providing ventilation with compressed air.

3 – 2 - Occurrence in wines

Ethyl acetate is the most common ester in wine, being the product of the most common volatile organic acid — acetic acid, and the ethyl alcohol generated during the fermentation. The aroma of ethyl acetate is most vivid in younger wines and contributes towards the general perception of "fruitiness" in the wine. Sensitivity varies, with most people having a perception threshold around 120 mg/L. Excessive amounts of ethyl acetate are considered a wine fault. Exposure to oxygen can exacerbate the fault due to the oxidation of ethanol to acetaldehyde, which leaves the wine with a sharp vinegar-like taste.

3 – 3 - Entomological killing agent

In the field of entomology, ethyl acetate is an effective asphyxiant for use in insect collecting and study. In a killing jar charged with ethyl acetate, the vapors will kill the collected (usually adult) insect quickly without destroying it. Because it is not hygroscopic, ethyl acetate also keeps the insect soft enough to allow proper mounting suitable for a collection.

4 - Reactions

Ethyl acetate can be hydrolyzed in acidic or basic conditions to regain acetic acid and ethanol. The use of an acid catalyst accelerates the hydrolysis, which is subject to the Fischer equilibrium mentioned above. In the laboratory, and usually for illustrative purposes only, ethyl esters are typically hydrolyzed in a two step process starting with a stoichiometric amount of strong base, such as sodium hydroxide. This reaction gives ethanol and sodium acetate, which is unreactive toward ethanol:

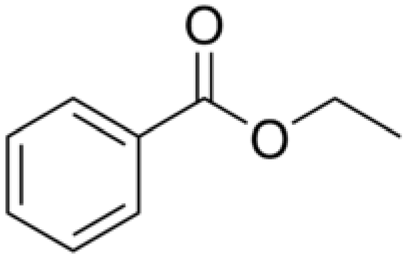
$$CH_3CO_2C_2H_5 + Na\,OH \rightarrow C_2H_5OH + CH_3CO_2Na$$

The rate constant is 0.111 $dm^3/mol.sec$ at 25 °C.

5 - Safety

The LD_{50} for rats is 11.3 g/kg, indicating low toxicity.[1]

Ethyl Benzoate

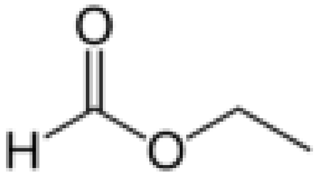


Ethyl benzoate, $C_9H_{10}O_2$, is the ester formed by the condensation of benzoic acid and ethanol. It is a colorless liquid that is almost insoluble in water, but miscible with most organic solvents.

As with many volatile esters, ethyl benzoate has a pleasant odor which could be described similar to wintergreen mint. It is a component of some artificial fruit flavors.

IUPAC name : Ethyl benzoate	
Molecular formula	$C_9 H_{10} O_2$
Molar mass	150 g / mol
Density	1.050 g / cm^3
Melting point	- 34 °C
Boiling point	211–213 °C

Ethyl Formate



Contents

1 – Introduction

Ethyl formate is an ester formed when ethanol (an alcohol) reacts with formic acid (a carboxylic acid). It is also known as **ethyl methanoate** because formic acid is also known as methanoic acid. Ethyl formate has the characteristic smell of rum and is also partially responsible for the flavor of raspberries.

IUPAC name : Ethyl formate	
Systematic name : Ethyl methanoate	
Molecular formula	$C_3 H_6 O_2$
Molar mass	74 g mol^{-1}
Density	0.917 g / cm^3
Melting point	- 80 °C
Boiling point	54.0 °C

2 - Exposure

Ethyl methanoate is generally recognized as safe by the U.S. Food and Drug Administration.

According to the U.S Occupational Safety and Health Administration (OSHA), ethyl formate can irritate eyes, skin, mucous membranes, and the respiratory system of humans and other animals; it is also a central nervous system depressant. In industry, it is used as a solvent for cellulose nitrate, cellulose acetate, oils, and greases. It can be used as a substitute for acetone; workers may also be exposed to it under the following circumstances :

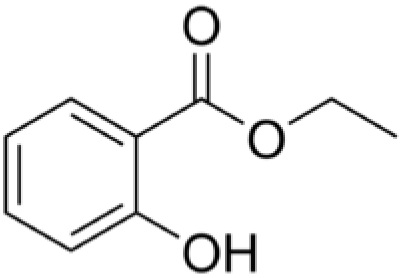
during spray, brush, or dip applications of lacquers
during the manufacture of safety glass
when fumigating tobacco, cereals, and dried fruits (as an alternative to methyl bromide under the U.S. Department of Agriculture quarantine system)

OSHA considers a time-weighted average of 100 parts per million (300 milligrams per cubic meter) over an eight-hour period as the permissible exposure limit.

3 - In space

Astronomers have identified ethyl formate in dust clouds in an area of the Milky Way galaxy called Sagittarius B2. The astronomers, from the Max Planck Institute for Radio Astronomy in Bonn, Germany, used the 30 metre IRAM radio telescope in Spain to analyse the spectra of radiation emitted from hot regions near a new star. It is among 50 molecules identified by the astronomers.

Ethyl Salicylate



Ethyl salicylate is the ester formed by the condensation of salicylic acid and ethanol. It is a clear liquid that is sparingly soluble in water, but soluble in alcohol and ether. It has a pleasant odor resembling wintergreen and is used in perfumery and artificial flavors.

IUPAC name : Ethyl 2-hydroxybenzoate	
Molecular formula	$C_9H_{10}O_3$
Molar mass	166 g / mol
Density	1.131 g / cm^3
Melting point	1 °C
Boiling point	231– 234 °C

List of Countries by Alcohol Consumption

This is a **list of countries** by alcohol consumption measured in equivalent liters of pure ethyl alcohol consumed per capita per year, according to the most recent data from the World Health Organization. The methodology used by the WHO calculated use by persons 15 years of age or older.

All columns refer to 2005 only, except the columns "recorded" and "total". The column "recorded" refers to the average recorded consumption for the period 2003–2005. Unrecorded consumption was calculated using empirical investigations and expert judgments. Total is the sum of the first two columns. The last four columns are a breakdown of the (2005) recorded alcohol consumption by type. Beer refers to malt beer, wine refers to grape wine, spirits refers to all distilled beverages, and the column "other" refers to all other alcoholic beverages. The values were corrected for tourism only in countries where the number of tourists per year was at least equal to the number of inhabitants.

Pure alcohol consumption among adults (age 15+) in liters per capita per year							
country	**recorded**	**unrecorded**	**total**	**beer**	**wine**	**spirits**	**other**
Czech	14.97	1.48	16.45	8.51	2.33	3.59	0.39
Hungary	12.27	4.00	16.27	4.42	4.94	3.02	0.14
Russia	11.03	4.73	15.76	3.65	0.10	6.88	0.34
Ukraine	8.10	7.50	15.60	2.69	0.58	5.21	0.02
Estonia	13.77	1.80	15.57	5.53	1.09	9.19	0.43
Andorra	14.08	1.40	15.48	3.93	5.69	3.14	0.00
Romania	11.30	4.00	15.30	4.07	2.33	4.14	0.00
Slovenia	12.19	3.00	15.19	4.10	5.10	1.33	0.00
Belarus	11.22	3.91	15.13	1.84	0.80	4.08	2.67
Croatia	12.61	2.50	15.11	4.66	5.80	1.91	0.14

Lithuania	12.03	3.00	15.03	5.60	1.80	4.50	0.60
South Korea	11.80	3.00	14.80	2.14	0.06	9.57	0.04
Portugal	12.45	2.10	14.55	3.75	6.65	1.27	0.51
Ireland	13.39	1.00	14.41	7.04	2.75	2.51	1.09
France	13.30	0.36	13.66	2.31	8.14	2.62	0.17
United Kingdom	11.67	1.70	13.37	4.93	3.53	2.41	0.67
Denmark	11.37	2.00	13.37	5.06	4.43	1.78	0.00
Slovakia	10.33	3.00	13.33	3.90	1.70	5.40	0.00
Poland	9.55	3.70	13.25	4.72	3.26	1.56	0.00
Austria	12.60	0.64	13.24	6.70	4.10	1.60	0.40
Luxembourg	13.01	1.00	13.01	1.59	8.16	2.00	0.00
Germany	11.81	1.00	12.81	6.22	3.15	2.30	0.00
Finland	9.72	2.80	12.52	4.59	2.24	2.82	0.31
Latvia	9.50	3.00	12.50	3.61	1.10	6.24	0.10
Bulgaria	11.24	1.20	12.44	3.53	2.44	4.88	0.10
Nigeria	9.78	2.50	12.28	0.54	0.01	0.02	9.17
Uganda	10.93	1.00	11.93	0.51	0.00	0.18	14.52
Saint Lucia	11.35	0.50	11.85	3.49	0.71	8.21	0.31
Spain	10.22	1.40	11.62	4.52	3.59	1.31	0.61
Armenia	10.05	1.30	11.35	1.05	0.39	0.65	9.36
Serbia	9.97	1.12	11.09	4.40	2.21	3.42	0.04
Switzerland	10.56	0.50	11.06	3.10	5.10	1.80	0.10
Kazakhstan	6.06	4.90	10.96	1.69	0.30	4.19	0.01
Belgium	9.77	1.00	10.77	5.49	3.55	0.62	0.03
Greece	8.95	1.80	10.75	2.20	4.51	2.38	0.13
Italy	8.33	2.35	10.68	1.73	6.38	0.42	0.00
Azerbaijan	7.30	3.30	10.60	7.00	0.03	0.97	0.00
Seychelles	9.59	1.00	10.59	7.15	3.15	1.59	0.00
Grenada	9.85	0.50	10.35	3.16	0.42	7.15	0.04

Sweden	6.70	3.60	10.30	2.60	2.90	1.10	0.00
Palau	9.10	1.00	10.10	8.68	0.52	2.10	0.00
Netherlands	9.55	0.50	10.05	4.72	3.26	1.56	0.00
Australia	9.89	0.13	10.02	4.56	3.12	1.16	1.02
Argentina	8.00	2.00	10.00	2.49	4.62	0.52	0.20
Niue	8.85	1.00	9.85	4.63	0.11	2.95	0.00
Rwanda	6.80	3.00	9.80	0.54	0.00	0.01	6.44
Canada	7.77	2.00	9.77	4.10	1.50	2.10	0.00
Sierra Leone	6.72	3.00	9.72	0.46	0.01	0.02	6.06
Bosnia and Herzegovina	9.63	0.00	9.63	2.22	0.34	7.08	0.00
New Zealand	9.12	0.50	9.62	4.09	3.04	1.37	0.81
Namibia	5.87	3.75	9.62	4.35	0.48	1.30	0.35
Guyana	7.50	2.00	9.50	1.14	0.31	5.70	0.01
Nepal	7.20	2.20	9.48	1.15	0.00	0.07	0.00
Burundi	6.47	3.00	9.47	1.16	0.01	0.00	5.07
South Africa	6.96	2.50	9.46	3.93	1.17	1.15	0.75
United States	8.44	1.00	9.44	4.47	1.36	2.65	0.00
Saint Kitts and Nevis	8.93	0.50	9.43	3.98	0.18	6.00	0.10
Ecuador	4.01	5.37	9.38	2.30	0.07	1.69	0.00
Gabon	7.32	2.00	9.32	5.38	0.80	1.69	0.00
Cyprus	8.26	1.00	9.26	3.25	2.97	2.95	0.12
Moldova	8.22	1.00	9.22	4.57	4.67	4.42	0.00
Brazil	6.16	3.00	9.16	3.36	0.33	2.49	0.03
Bahamas	8.16	0.60	8.76	3.99	1.55	5.27	0.23
São Tomé and Príncipe	5.82	2.92	8.74	1.12	3.40	0.83	0.00
Chile	6.55	2.00	8.55	2.03	2.59	2.16	0.04
Macedonia	5.61	2.90	8.51	2.11	1.62	2.08	0.00
Mexico	5.02	3.40	8.42	3.96	0.02	1.09	0.03

Venezuela	6.83	1.40	8.23	5.19	0.07	1.65	0.00
Uruguay	6.14	2.00	8.14	1.33	3.95	1.21	0.06
Japan	7.83	0.20	8.03	1.72	0.29	3.37	2.61
Botswana	4.96	3.00	7.96	2.56	0.04	0.00	1.88
Paraguay	6.38	1.50	7.88	3.48	0.97	1.77	0.19
Dominica	7.34	0.50	7.84	0.50	0.80	6.69	0.07
Norway	6.21	1.60	7.81	2.98	2.00	1.28	0.11
Cameroon	4.97	2.60	7.57	2.05	0.05	0.00	2.60
Antigua and Barbuda	6.76	0.46	7.22	2.67	1.70	5.04	0.09
Thailand	6.37	0.71	7.08	1.75	0.02	4.69	0.00
Burkina Faso	4.48	2.50	6.98	0.41	0.09	0.42	3.77
Barbados	6.41	0.50	6.91	2.90	0.73	3.78	0.17
Peru	2.90	4.00	6.90	2.16	0.32	0.61	0.00
Panama	5.85	1.00	6.85	3.71	0.22	1.91	0.01
Tanzania	4.75	2.00	6.75	0.57	0.02	0.15	4.51
Laos	5.73	1.00	6.73	1.42	0.03	4.35	0.00
Albania	4.58	2.10	6.68	1.61	0.94	2.30	0.02
Haiti	5.99	0.62	6.61	0.01	0.01	5.20	0.00
Ivory Coast	4.48	2.00	6.48	0.61	0.33	0.05	3.55
Dominican	5.76	0.65	6.41	2.69	0.14	2.92	0.01
Georgia	3.90	2.50	6.40	0.76	0.83	2.56	0.02
Philippines	4.38	2.00	6.38	1.29	0.02	2.91	0.00
Iceland	5.91	0.40	6.31	3.67	1.95	1.33	0.10
Trinidad and Tobago	5.78	0.50	6.28	3.10	0.11	2.78	0.04
Colombia	4.17	2.00	6.17	2.71	0.08	1.44	0.02
Suriname	5.19	0.90	6.09	2.00	0.13	3.26	0.05
Equatorial Guinea	5.31	0.77	6.08	0.45	4.18	0.00	0.00
Belize	5.07	1.00	6.07	3.89	0.13	1.78	0.01

China	4.21	1.70	5.91	1.50	0.15	2.51	0.23
Puerto Rico	5.47	0.28	5.75	3.68	0.34	1.35	0.05
Swaziland	5.70	0.00	5.70	1.64	0.21	0.15	3.05
Costa Rica	4.15	1.40	5.55	2.29	0.18	1.71	0.02
Lesotho	1.90	3.65	5.55	1.24	0.00	0.01	0.69
Cuba	4.41	1.10	5.51	1.48	0.05	2.94	0.01
Federated States of Micronesia	4.50	1.00	5.50	1.43	1.31	0.60	0.00
Saint Vincent and the Grenadines	4.94	0.50	5.44	2.55	0.12	3.16	0.05
Angola	3.80	1.60	5.40	1.81	1.37	1.12	0.41
Nicaragua	3.77	1.60	5.37	1.13	0.03	2.55	0.00
Bolivia	2.62	2.50	5.12	2.17	0.06	0.61	0.00
Kyrgyzstan	3.19	1.90	5.09	0.45	0.10	2.26	0.01
Zimbabwe	4.08	1.00	5.08	0.96	0.19	0.06	2.61
Liberia	3.47	1.59	5.06	0.30	0.01	3.16	0.01
Jamaica	3.50	1.50	5.00	1.49	0.11	1.80	0.10
Cape Verde	2.06	2.90	4.96	0.36	1.99	0.14	0.00
Nauru	2.33	2.50	4.83	2.24	0.08	0.00	0.00
Samoa	3.80	1.00	4.80	3.31	0.08	0.24	0.00
Cambodia	1.77	3.00	4.77	0.74	0.02	1.21	0.00
Turkmenistan	2.33	2.30	4.63	0.21	0.90	1.22	0.00
Honduras	3.08	1.40	4.48	1.29	0.04	1.87	0.00
Chad	0.38	4.00	4.38	0.23	0.01	0.02	0.15
Malta	3.85	0.42	4.27	1.79	1.45	1.86	0.15
Republic congo	2.04	2.23	4.20	1.76	0.00	0.11	0.12
Kenya	1.64	2.50	4.14	0.84	0.02	0.51	0.55
Guatemala	2.43	1.60	4.03	1.12	3.92	1.20	0.05
Ethiopia	0.52	3.50	4.02	0.19	0.01	0.13	0.25

Zambia	2.35	1.50	3.85	0.42	0.01	0.27	1.62
Tonga	3.28	0.50	3.78	0.89	2.29	0.64	0.18
Vietnam	1.07	2.70	3.77	1.13	0.01	0.02	0.00
Mauritius	2.72	1.00	3.72	1.92	0.32	0.39	0.00
Kiribati	1.71	2.00	3.71	1.56	0.02	0.02	0.00
Cook Islands	3.20	0.50	3.70	0.54	1.39	3.45	0.00
Guinea-Bissau	2.58	1.10	3.68	0.24	0.66	0.53	1.75
Bahrain	3.56	0.10	3.66	1.91	0.52	1.24	0.00
El Salvador	2.61	1.00	3.61	0.88	0.04	1.57	0.00
Uzbekistan	1.64	1.90	3.54	0.28	0.19	1.30	0.00
Papua New Guinea	1.49	2.00	3.49	0.57	0.02	0.90	0.00
Gambia	2.40	0.99	3.39	0.19	0.06	0.04	2.07
Tajikistan	0.39	3.00	3.39	0.08	0.02	0.29	0.00
Central African Republic	1.65	1.70	3.35	0.21	0.02	0.03	1.37
Democratic Republic of the Congo	1.97	1.26	3.30	0.32	0.01	0.02	1.67
Mongolia	1.24	2.00	3.24	0.39	0.11	0.67	0.21
Ghana	1.47	1.50	2.97	0.40	0.07	0.03	0.97
Israel	2.39	0.50	2.89	0.97	0.18	1.30	0.04
Djibouti	1.37	1.50	2.87	0.78	0.07	0.46	0.00
Mozambique	1.56	1.00	2.56	0.00	0.00	0.27	1.08
Tuvalu	1.94	0.50	2.44	0.71	0.02	0.58	0.00
Fiji	1.43	1.00	2.43	1.46	0.02	0.58	0.00
Iraq	0.20	2.21	2.41	0.07	0.00	0.13	0.00
Sudan	1.56	0.82	2.38	0.52	0.09	0.79	0.05
Lebanon	1.73	0.50	2.23	0.36	0.56	0.78	0.01
Benin	1.15	1.00	2.15	0.49	0.14	0.15	0.30
Brunei	1.76	0.25	2.01	1.67	0.02	0.05	0.00

Togo	0.99	1.00	1.99	0.43	0.32	0.06	0.22
Turkey	1.37	0.50	1.87	0.24	0.08	1.35	0.00
Malawi	1.24	0.50	1.74	0.14	0.00	0.22	0.74
Solomon Islands	1.16	0.50	1.66	0.66	0.03	0.40	0.00
Singapore	0.55	1.00	1.55	1.45	0.25	0.40	0.00
Eritrea	0.94	0.60	1.54	0.56	0.00	0.25	0.00
Morocco	0.46	1.00	1.46	0.23	0.17	0.06	0.00
Syria	1.13	0.30	1.43	0.04	0.32	0.69	0.00
Madagascar	0.78	0.55	1.33	0.34	0.11	0.32	0.00
Tunisia	1.09	0.20	1.29	0.67	0.34	0.04	0.00
Qatar	0.85	0.40	1.25	0.04	0.11	0.73	0.01
Mali	0.54	0.50	1.04	0.07	0.00	0.01	0.46
Iran	0.02	1.00	1.02	0.02	0.00	0.00	0.00
Algeria	0.66	0.30	0.96	0.09	0.07	0.00	0.50
Oman	0.64	0.30	0.94	0.27	0.00	0.39	0.00
Vanuatu	0.43	0.50	0.93	0.46	0.19	0.19	0.00
Timor-Leste	0.36	0.50	0.86	0.30	0.01	0.00	0.00
Malaysia	0.50	0.32	0.82	0.38	0.02	0.08	0.00
Sri Lanka	0.35	0.44	0.79	0.02	0.00	0.33	0.00
Comoros	0.26	0.50	0.76	0.17	0.02	0.03	0.00
India	0.55	0.20	0.75	0.06	0.02	0.05	0.00
Jordan	0.41	0.30	0.71	0.04	0.01	0.34	0.01
Senegal	0.30	0.30	0.60	0.15	0.12	0.01	0.00
Indonesia	0.06	0.50	0.59	0.06	0.00	0.00	0.00
Myanmar	0.11	0.46	0.57	0.10	0.00	0.01	0.01
Bhutan	0.22	0.33	0.55	0.21	0.00	0.00	0.00
United Arab Emirates	0.34	0.20	0.54	0.30	0.01	0.00	0.02
Egypt	0.27	0.10	0.37	0.10	0.02	0.06	0.00

Guinea	0.26	0.10	0.36	0.14	0.02	0.06	0.00
Niger	0.09	0.25	0.34	0.05	0.01	0.03	0.00
Saudi Arabia	0.05	0.20	0.25	0.00	0.00	0.05	0.00
Bangladesh	0.00	0.20	0.20	0.00	0.00	0.00	0.00
Kuwait	0.00	0.17	0.17	0.00	0.00	0.00	0.00
Libya	0.01	0.10	0.11	0.00	0.00	0.00	0.00
Mauritania	0.01	0.10	0.11	0.00	0.00	0.01	0.00
Somalia	0.00	0.10	0.10	0.00	0.00	0.00	0.00
Pakistan	0.01	0.05	0.06	0.00	0.00	0.00	0.01
Afghanistan	0.00	0.02	0.02	0.00	0.00	0.01	0.00
Yemen	0.00	0.02	0.02	0.00	0.00	0.00	0.00

Molasses

Blackstrap molasses

Contents

1 - Introduction

Molasses is a viscous by-product of the refining of sugar cane, grapes, or sugar beets into sugar. The word comes from the Portuguese *melaço,* ultimately derived from *mel,* the Latin word for "honey". The quality of molasses depends on the maturity of the source plant, the amount of sugar extracted, and the method employed.

Sweet sorghum is known in some parts of the United States as molasses, though it is not a true molasses.

2 - Cane molasses

To make molasses, the cane of a sugar plant is harvested and stripped of its leaves. Its juice is extracted usually by crushing or mashing, but also by cutting. The juice is boiled to concentrate it, which promotes the crystallisation of the sugar. The result of this first boiling and of the sugar crystals is first syrup, usually referred to in the Southern states of the USA as "cane syrup" as opposed to molasses, which has the highest sugar content because comparatively little sugar has been extracted from the source. Second molasses is created from a second boiling and sugar extraction, and has a slight bitter tinge to its taste.

The third boiling of the sugar syrup yields blackstrap molasses, known for its robust flavour. The term blackstrap molasses is an Americanism dating from around 1875. The majority of sucrose from the original juice has been crystallised and removed. The food energy content of blackstrap molasses is still mostly from the small remaining sugar content. However, unlike refined sugars, it contains trace amounts of vitamins and significant amounts of several minerals. Blackstrap molasses is a source of calcium, magnesium, potassium, and iron; one tablespoon provides up to 20 % of the daily value of each of those nutrients. Blackstrap has long been sold as a health supplement. It is also used in the manufacture of ethyl alcohol for industry and as an ingredient in cattle feed.

3 - Sugar beet molasses

Molasses made from sugar beet is different from sugar cane molasses. Only the syrup left from the final crystal ligation stage is called molasses; intermediate syrups are referred to as high green and low green, and these are recycled within the crystallization plant to maximize extraction. Beet molasses is about 50% sugar by dry weight, predominantly sucrose, but also contains significant amounts of glucose and fructose. Beet molasses is limited in biotin (vitamin H or B_7) for cell growth; hence, it may need to be supplemented with a biotin source. The non-sugar content includes many salts, such as calcium, potassium, oxalate, and chloride. It also contains the compounds betaine and the trisaccharide raffinose. These are either as a result of concentration from the original plant material or as a result of chemicals used in the processing, and make it unpalatable to humans. Hence it is mainly used as an additive to animal feed (called "molassed sugar beet feed") or as a fermentation feedstock .

It is possible to extract additional sugar from beet molasses through a process known as molasses desugarisation. This technique exploits industrial - scale chromatography to separate sucrose from non-sugar components. The technique is economically viable in trade-protected areas, where the price of sugar is supported above the world market price. As such, it is practiced in the U.S. and parts of Europe. Molasses is also used for yeast production.

4 - Substitutes

Cane molasses is a common ingredient in baking and cooking. One of the following may be substituted (in varying proportions) depending on whether the dish is sweet or savory:

Black treacle
Honey
Sweet sorghum syrup
Barley malt syrup
Maple syrup
Brown sugar
Dark corn syrup
Kecap manis, a thick Indonesian soy sauce sweetened with palm sugar

5 - Other forms

In Middle Eastern cuisine, molasses is produced variously from carob, grapes, dates, pomegranates, and mulberries. In Nepal it is called *chaku* (Nepal Bhasa) and used in the preparation of various Newari condiments such as *yomari*. It is also a popular ingredient in *ghya-chaku*.

6 - Other uses

6 – 1 - Food products and additives

Molasses can be used as:

The principal ingredient in the distillation of rum

In stouts or Porters

An additive in tobacco smoked in a *hookah*, *shisha*, or *narghile* (found in the brands Mazaya, Al-Fakher, Nakhla, Tangiers and Salloum)

An additive in livestock feeds

An ingredient in fishing groundbait

A source for yeast production.

An iron supplement

The main ingredient in the production of Citric acid

6 – 2 - Chemical

The carbon source for *in situ* remediation of chlorinated hydrocarbons.

Blended with magnesium chloride and used for de-icing.

A stock for ethanol fermentation to produce an alternative fuel for motor vehicles

6 – 3 - Industrial

As a chelating agent to remove rust

As a minor component of mortar for brick work

Mixed with glue to case ink rollers on early printing presses

6 – 4 - Horticultural

As a soil additive to promote microbial activity

As a source for sugar in hydroponic gardening .

7 - Nutritional information

Molasses contains no protein or dietary fiber and close to no fat. Each tablespoon (20 g) contains 58 kcal (240 kJ), 14.95 g of carbohydrates, and 11.1 g of sugar divided amongst:

Sucrose: 5.88 g
Glucose: 2.38 g
Fructose: 2.56 g

Anaerobic Digestion

Anaerobic digestion and regenerative thermal oxidizer component of Lübeck mechanical biological treatment plant in Germany, 2007

Contents

1 - Introduction

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen. It is used for industrial or domestic purposes to manage waste and/or to release energy. Much of the fermentation used industrially to produce food and drink products, as well as home fermentation, uses anaerobic digestion. Silage is produced by anaerobic digestion.

The digestion process begins with bacterial hydrolysis of the input materials to break down insoluble organic polymers, such as carbohydrates, and make them available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenic bacteria then convert these resulting organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Finally, methanogens convert these products to methane and carbon dioxide . The methanogenic archaea populations play an indispensable role in anaerobic wastewater treatments.

It is used as part of the process to treat biodegradable waste and sewage sludge. As part of an integrated waste management system, anaerobic digestion reduces the emission of landfill gas into the atmosphere. Anaerobic digesters can also be fed with purpose-grown energy crops, such as maize.

Anaerobic digestion is widely used as a source of renewable energy. The process produces a biogas, consisting of methane, carbon dioxide and traces of other ‘contaminant’ gases.[1] This biogas can be used directly as cooking fuel, in combined heat and power gas engines or upgraded to natural gas-quality biomethane. The use of biogas as a fuel helps to replace fossil fuels. The nutrient-rich digestate also produced can be used as fertilizer.

Anaerobic digestion facilities have been recognized by the United Nations Development Program as one of the most useful decentralized sources of energy supply, as they are less capital-intensive than large power plants . With increased focus on climate change mitigation, the re-use of waste as a resource and new technological approaches which have lowered capital costs, anaerobic digestion has in recent years received increased attention among governments in a number of countries, among these the United Kingdom (2011) , Germany and Denmark (2011).

2 - History

Gas street lamp

Scientific interest in the manufacturing of gas produced by the natural decomposition of organic matter was first reported in the 17th century by Robert Boyle and Stephen Hale, who noted that flammable gas was released by disturbing the sediment of streams and lakes.[10] In 1808, Sir Humphry Davy determined that methane was present in the gases produced by cattle manure. The first anaerobic digester was built by a leper colony in Bombay, India, in 1859. In 1895, the technology was developed in Exeter, England, where a septic tank was used to generate gas for the sewer gas destructor lamp, a type of gas lighting. Also in England, in 1904, the first dual-purpose tank for both sedimentation and sludge treatment was installed in Hampton. In 1907, in Germany, a patent was issued for the Imhoff tank, an early form of digester.

Through scientific research, anaerobic digestion gained academic recognition in the 1930s. This research led to the discovery of anaerobic bacteria, the microorganisms that facilitate the process. Further research was carried out to investigate the conditions under which methanogenic bacteria were able to grow and reproduce.[14] This work was developed during World War II, during which in both Germany and France, there was an increase in the application of anaerobic digestion for the treatment of manure.

3 - Process

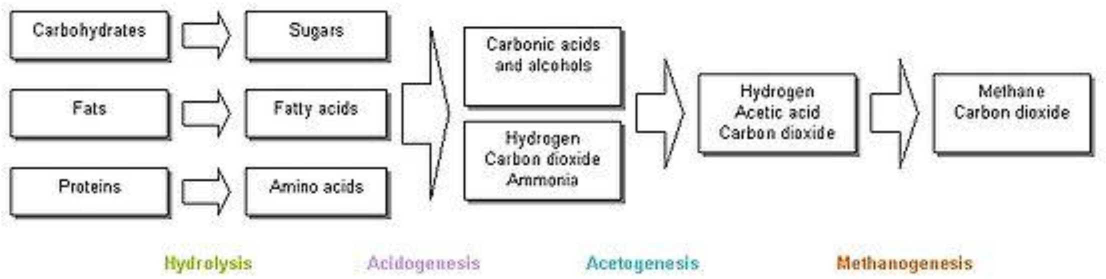
Many microorganisms are involved in the process of anaerobic digestion, including acetic acid-forming bacteria (acetogens) and methane-forming archaea (methanogens). These organisms feed upon the initial feedstock, which undergoes a number of different processes, converting it to intermediate molecules, including sugars, hydrogen, and acetic acid, before finally being converted to biogas.

Different species of bacteria are able to survive at different temperature ranges. Ones living optimally at temperatures between 35 and 40 °C are called mesophiles or mesophilic bacteria. Some of the bacteria can survive at the hotter and more hostile conditions of 55 to 60 °C; these are called thermophiles or thermophilic bacteria. Methanogens come from the domain of archaea. This family includes species that can grow in the hostile conditions of hydrothermal vents, so are more resistant to heat, and can, therefore, operate at high temperatures, a property unique to thermophiles.

As with aerobic systems, the bacteria, the growing and reproducing microorganisms within anaerobic systems, require a source of elemental oxygen to survive, but in anaerobic systems, there is an absence of gaseous oxygen. Gaseous oxygen is prevented from entering the system through physical containment in sealed tanks. Anaerobes access oxygen from sources other than the surrounding air, which can be the organic material itself or may be supplied by inorganic oxides from within the input material. When the oxygen source in an anaerobic system is derived from the organic material itself, the 'intermediate' end products are primarily alcohols, aldehydes, and organic acids, plus carbon dioxide. In the presence of specialized methanogens, the intermediates are converted to the 'final' end products of methane, carbon dioxide, and trace levels of hydrogen sulfide . In an anaerobic system, the majority of the chemical energy contained within the starting material is released by methanogenic bacteria as methane.

Populations of anaerobic microorganisms typically take a significant period of time to establish themselves to be fully effective. Therefore, common practice is to introduce anaerobic microorganisms from materials with existing populations, a process known as "seeding" the digesters, typically accomplished with the addition of sewage sludge or cattle slurry.

3 – 1 - Process stages



The key process stages of anaerobic digestion

There are four key biological and chemical stages of anaerobic digestion :

Hydrolysis
Acidogenesis
Acetogenesis
Methanogenesis

In most cases, biomass is made up of large organic polymers. For the bacteria in anaerobic digesters to access the energy potential of the material, these chains must first be broken down into their smaller constituent parts. These constituent parts, or monomers, such as sugars, are readily available to other bacteria. The process of breaking these chains and dissolving the smaller molecules into solution is called hydrolysis. Therefore, hydrolysis of these high-molecular-weight polymeric components is the necessary first step in anaerobic digestion . Through hydrolysis the complex organic molecules are broken down into simple sugars, amino acids, and fatty acids.

Acetate and hydrogen produced in the first stages can be used directly by methanogens. Other molecules, such as volatile fatty acids (VFAs) with a chain length greater than that of acetate must first be catabolised into compounds that can be directly used by methanogens.

The biological process of acidogenesis results in further breakdown of the remaining components by acidogenic (fermentative) bacteria. Here, VFAs are created, along with ammonia, carbon dioxide, and hydrogen sulfide, as well as other byproducts. The process of acidogenesis is similar to the way milk sours.

The third stage of anaerobic digestion is acetogenesis. Here, simple molecules created through the acidogenesis phase are further digested by acetogens to produce largely acetic acid, as well as carbon dioxide and hydrogen.

The terminal stage of anaerobic digestion is the biological process of methanogenesis. Here, methanogens use the intermediate products of the preceding stages and convert them into methane, carbon dioxide, and water. These components make up the majority of the biogas emitted from the system. Methanogenesis is sensitive to both high and low pHs and occurs between pH 6.5 and pH 8 . The remaining, indigestible material the microbes cannot use and any dead bacterial remains constitute the digestate.

A simplified generic chemical equation for the overall processes outlined above is as follows:

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$$

3 – 2 - Configuration

Anaerobic digesters can be designed and engineered to operate using a number of different process configurations :

Batch or continuous
Temperature: Mesophilic or thermophilic
Solids content: High solids or low solids
Complexity: Single stage or multistage

3 – 2 – 1 - Batch or continuous

Anaerobic digestion can be performed as a batch process or a continuous process.

In a batch system biomass is added to the reactor at the start of the process. The reactor is then sealed for the duration of the process.

In its simplest form batch processing needs inoculation with already processed material to start the anaerobic digestion. In a typical scenario, biogas production will be formed with a normal distribution pattern over time. Operator can use this fact to determine when they believe the process of digestion of the organic matter has completed. There can be severe odour issues if a batch reactor is opened and emptied before the process is well completed.

A more advanced type of batch approach has limited the odour issues by integrating anaerobic digestion with in-vessel composting. In this approach inoculation takes place through the use of recirculated degasified percolate. After anaerobic digestion has completed, the biomass is kept in the reactor which is then used for in-vessel composting before it is opened

As the batch digestion is simple and requires less equipment and lower levels of design work, it is typically a cheaper form of digestion.

Using more than one batch reactor at a plant can ensure constant production of biogas.

In continuous digestion processes, organic matter is constantly added (continuous complete mixed) or added in stages to the reactor (continuous plug flow; first in – first out). Here, the end products are constantly or periodically removed, resulting in constant production of biogas. A single or multiple digesters in sequence may be used. Examples of this form of anaerobic digestion include continuous stirred-tank reactors, upflow anaerobic sludge blankets, expanded granular sludge beds and internal circulation reactors.

3 – 2 – 2 - Temperature

The two conventional operational temperature levels for anaerobic digesters are determined by the species of methanogens in the digesters :

Mesophilic digestion takes place optimally around 30 to 38 °C, or at ambient temperatures between 20 and 45 °C, where mesophiles are the primary microorganism present.

Thermophilic digestion takes place optimally around 49 to 57 °C, or at elevated temperatures up to 70 °C, where thermophiles are the primary microorganisms present.

A limit case has been reached in Bolivia, with anaerobic digestion in temperature working conditions of less than 10 °C. The anaerobic process is very slow, taking more than three times the normal mesophilic time process.[31] In experimental work at University of Alaska Fairbanks, a 1000 litre digester using psychrophiles harvested from "mud from a frozen lake in

Alaska" has produced 200 –300 liters of methane per day, about 20 to 30% of the output from digesters in warmer climates.[32]

Mesophilic species outnumber thermophiles, and they are also more tolerant to changes in environmental conditions than thermophiles. Mesophilic systems are, therefore, considered to be more stable than thermophilic digestion systems.

Though thermophilic digestion systems are considered to be less stable and the energy input is higher, more energy is removed from the organic matter. The increased temperatures facilitate faster reaction rates and, hence, faster gas yields. Operation at higher temperatures facilitates greater sterilization of the end digestate. In countries where legislation, such as the Animal By-Products Regulations in the European Union, requires end products to meet certain levels of reduction in the amount of bacteria in the output material, this may be a benefit.

Certain processes shred the waste finely and use a thermal pretreatment stage (hygienisation) to significantly enhance the gas output of the following standard mesophilic stage. The hygienisation process is also applied to reduce the pathogenic micro-organisms in the feedstock. Hygienisation may be achieved by using a Landia Bio Chop hygienisation unit or similar method of combined heat treatment and solids maceration.

A drawback of operating at thermophilic temperatures is that more heat energy input is required to achieve the correct operational temperatures, which may not be outweighed by the increase in the outputs of biogas from the systems. Therefore, it is important to consider an energy balance for these systems.

3 – 2 – 3 - Solids content

In a typical scenario, three different operational parameters are associated with the solids content of the feedstock to the digesters:

High solids (dry — stack able substrate)
High solids (wet — pump able substrate)
Low solids (wet — pump able substrate)

High solids (dry) digesters are designed to process materials with a solids content between 25 and 40%. Unlike wet digesters that process pump able slurries, high solids (dry – stackable substrate) digesters are designed to process solid substrates without the addition of water. The primary styles of dry digesters are continuous vertical plug flow and batch tunnel horizontal digesters. Continuous vertical plug flow digesters are upright, cylindrical tanks where feedstock is continuously fed into the top of the digester, and flows downward by gravity during digestion. In batch tunnel digesters, the feedstock is deposited in tunnel-like chambers with a gas-tight door. Neither approach has mixing inside the digester. The amount of pretreatment, such as contaminant removal, depends both upon the nature of the waste streams being processed and the desired quality of the digestate. Size reduction (gringing) is beneficial in continuous vertical systems, as it accelerates digestion, while batch systems avoid grinding and instead require structure (e.g. yard waste) to reduce compaction of the stacked pile. Continuous vertical dry digesters have a smaller footprint due to the shorter effective retention time and vertical design.

Wet digesters can be designed to operate in either a high-solids content, with a total suspended solids (TSS) concentration greater than ~ 20 %, or a low - solids concentration less than ~15 % .

High solids (wet) digesters process a thick slurry that requires more energy input to move and process the feedstock. The thickness of the material may also lead to associated problems with abrasion. High solids digesters will typically have a lower land requirement due to the lower volumes associated with the moisture. High solids digesters also require correction of conventional performance calculations (e.g. gas production, retention time, kinetics, etc.) originally based on very dilute sewage digestion concepts, since larger fractions of the feedstock mass are potentially convertible to biogas.

Low solids (wet) digesters can transport material through the system using standard pumps that require significantly lower energy input. Low solids digesters require a larger amount of land than high solids due to the increased volumes associated with the increased liquid-to-feedstock ratio of the digesters. There are benefits associated with operation in a liquid environment, as it enables more thorough circulation of materials and contact between the bacteria and their food. This enables the bacteria to more readily access the substances on which they are feeding, and increases the rate of gas production .

3 – 2 – 4 – Complexity

Two-stage, low solids, UASB digestion component of a mechanical biological treatment system

Digestion systems can be configured with different levels of complexity :

In a **single-stage digestion system** (one-stage), all of the biological reactions occur within a single, sealed reactor or holding tank. Using a single stage reduces construction costs, but results in less control of the reactions occurring within the system. Acidogenic bacteria, through the production of acids, reduce the pH of the tank. Methanogenic bacteria, as outlined earlier, operate in a strictly defined pH range. There fore, the biological reactions of the different species in a single-stage reactor can be in direct competition with each other. Another one-stage reaction system is an anaerobic lagoon. These lagoons are pond-like, earthen basins used for the treatment and long-term storage of manures. Here the anaerobic reactions are contained within the natural anaerobic sludge contained in the pool.

In a **two-stage digestion system** (multistage), different digestion vessels are optimized to bring maximum control over the bacterial communities living within the digesters. Acidogenic bacteria produce organic acids and more quickly grow and reproduce than methanogenic bacteria. Methanogenic bacteria require stable pH and temperature to optimise their performance.

Under typical circumstances, hydrolysis, acetogenesis, and acidogenesis occur within the first reaction vessel. The organic material is then heated to the required operational temperature (either mesophilic or thermophilic) prior to being pumped into a methanogenic reactor. The initial hydrolysis or acidogenesis tanks prior to the methanogenic reactor can provide a buffer to the rate at which feedstock is added. Some European countries require a degree of elevated heat treatment to kill harmful bacteria in the input waste.[41] In this instance, there may be a pasteurization or sterilization stage prior to digestion or between the two digestion tanks. Notably, it is not possible to completely isolate the different reaction phases, and often some biogas is produced in the hydrolysis or acidogenesis tanks.

3 – 3 – Residence time

The residence time in a digester varies with the amount and type of feed material, the configuration of the digestion system, and whether it be one-stage or two - stage.

In the case of single-stage thermophilic digestion, residence times may be in the region of 14 days, which, compared to mesophilic digestion, is relatively fast. The plug-flow nature of some of these systems will mean the full degradation of the material may not have been realised in this timescale. In this event, digestate exiting the system will be darker in colour and will typically have more odour.

In two-stage mesophilic digestion, residence time may vary between 15 and 40 days.

In the case of mesophilic UASB digestion, hydraulic residence times can be 1 hour to 1 day, and solid retention times can be up to 90 days. In this manner, the UASB system is able to separate solids and hydraulic retention times with the use of a sludge blanket.

Continuous digesters have mechanical or hydraulic devices, depending on the level of solids in the material, to mix the contents, enabling the bacteria and the food to be in contact. They also allow excess material to be continuously extracted to maintain a reasonably constant volume within the digestion tanks .

4 - Feed stocks

Anaerobic lagoon and generators at the Cal Poly Dairy, United States 2003

The most important initial issue when considering the application of anaerobic digestion systems is the feedstock to the process. Almost any organic material can be processed with anaerobic digestion ; however, if biogas production is the aim, the level of putrescibility is the key factor in its successful application. The more putrescible (digestible) the material, the higher the gas yields possible from the system.

Feed stocks can include biodegradable waste materials, such as waste paper, grass clippings, leftover food, sewage, and animal waste. Woody wastes are the exception, because they are largely unaffected by digestion, as most anaerobes are unable to degrade lignin. Xylophalgeous anaerobes (lignin consumers) or using high temperature pretreatment, such as pyrolysis, can be used to break down the lignin. Anaerobic digesters can also be fed with specially grown energy crops, such as silage, for dedicated biogas production. In Germany and continental Europe, these facilities are referred to as "biogas" plants. A codigestion or cofermentation plant is typically an agricultural anaerobic digester that accepts two or more input materials for simultaneous digestion.

Anaerobes can break down material with varying degrees of success from readily, in the case of short-chain hydrocarbons such as sugars, to over longer periods of time, in the case of cellulose and hemi cellulose. Anaerobic microorganisms are unable to break down long-chain woody molecules, such as lignin.

Anaerobic digesters were originally designed for operation using sewage sludge and manures. Sewage and manure are not, however, the material with the most potential for anaerobic digestion, as the biodegradable material has already had much of the energy content taken out by the animals that produced it. Therefore, many digesters operate with codigestion of two or more types of feedstock. For example, in a farm-based digester that uses dairy manure as the primary feedstock, the gas production may be significantly increased by adding a second feedstock, e.g., grass and corn (typical on-farm feedstock), or various organic byproducts, such as slaughterhouse waste, fats, oils and grease from restaurants, organic household waste, etc. (typical off-site feedstock).

Digesters processing dedicated energy crops can achieve high levels of degradation and biogas production . Slurry-only systems are generally cheaper, but generate far less energy than those using crops, such as maize and grass silage; by using a modest amount of crop material (30 %), an anaerobic digestion plant can increase energy output tenfold for only three times the capital cost, relative to a slurry-only system.

4 - 1 - Moisture content

A second consideration related to the feedstock is moisture content. Dryer, stackable substrates, such as food and yard waste, are suitable for digestion in tunnel-like chambers. Tunnel-style systems typically have near-zero wastewater discharge, as well, so this style of system has advantages where the discharge of digester liquids are a liability. The wetter the material, the more suitable it will be to handling with standard pumps instead of energy-intensive concrete pumps and physical means of movement. Also, the wetter the material, the more volume and area it takes up relative to the levels of gas produced. The moisture content of the target feedstock will also affect what type of system is applied to its treatment. To use a high-solids anaerobic digester for dilute feedstocks, bulking agents, such as compost, should be applied to increase the solids content of the input material.[53] Another key consideration is the carbon:nitrogen ratio of the input material. This ratio is the balance of food a microbe requires to grow; the optimal C:N ratio is 20–30:1. Excess N can lead to ammonia inhibition of digestion.

4 - 2 - Contamination

The level of contamination of the feedstock material is a key consideration. If the feedstock to the digesters has significant levels of physical contaminants, such as plastic, glass, or metals, then processing to remove the contaminants will be required for the material to be used . If it is not removed, then the digesters can be blocked and will not function efficiently. It is with this understanding that mechanical biological treatment plants are designed. The higher the level of pretreatment a feedstock requires, the more processing machinery will be required, and, hence, the project will have higher capital costs.

After sorting or screening to remove any physical contaminants from the feedstock, the material is often shredded, minced, and mechanically or hydraulically pulped to increase the surface area available to microbes in the digesters and, hence, increase the speed of digestion. The maceration of solids can be achieved by using a chopper pump to transfer the feedstock material into the airtight digester, where anaerobic treatment takes place.

4 - 3 - Substrate composition

Substrate composition is a major factor in determining the methane yield and methane production rates from the digestion of biomass. Techniques to determine the compositional characteristics of the feedstock are available, while parameters such as solids, elemental, and organic analyses are important for digester design and operation.

5 - Applications

Using anaerobic digestion technologies can help to reduce the emission of greenhouse gases in a number of key ways:

Replacement of fossil fuels

Reducing or eliminating the energy footprint of waste treatment plants

Reducing methane emission from landfills

Displacing industrially produced chemical fertilizers

Reducing vehicle movements

Reducing electrical grid transportation losses

Reducing usage of LP Gas for cooking

5 - 1 - Waste treatment

Anaerobic digestion is particularly suited to organic material, and is commonly used for effluent and sewage treatment.[58] Anaerobic digestion, a simple process, can greatly reduce the amount of organic matter which might otherwise be destined to be dumped at sea, dumped in landfills, or burnt in incinerators.

Pressure from environmentally related legislation on solid waste disposal methods in developed countries has increased the application of anaerobic digestion as a process for reducing waste volumes and generating useful byproducts. It may either be used to process the source-separated fraction of municipal waste or alternatively combined with mechanical sorting systems, to process residual mixed municipal waste. These facilities are called mechanical biological treatment plants.

If the putrescible waste processed in anaerobic digesters were disposed of in a landfill, it would break down naturally and often an aerobically. In this case, the gas will eventually escape into the atmosphere. As methane is about 20 times more potent as a greenhouse gas than carbon dioxide, this has significant negative environmental effects.

In countries that collect household waste, the use of local anaerobic digestion facilities can help to reduce the amount of waste that requires transportation to centralized landfill sites or incineration facilities. This reduced burden on transportation reduces carbon emissions from the collection vehicles. If localized anaerobic digestion facilities are embedded within an electrical distribution network, they can help reduce the electrical losses associated with transporting electricity over a national grid.

5 - 2 - Power generation

See also: Electrical energy efficiency on United States farms

In developing countries, simple home and farm-based anaerobic digestion systems offer the potential for low-cost energy for cooking and lighting . Anaerobic digestion facilities have been recognized by the United Nations Development Programme as one of the most useful decentralized sources of energy supply . From 1975, China and India have both had large, government - backed schemes for adaptation of small biogas plants for use in the household for cooking and lighting. At present, projects for anaerobic digestion in the developing world can gain financial support through the United Nations Clean Development Mechanism if they are able to show they provide reduced carbon emissions.

Methane and power produced in anaerobic digestion facilities can be used to replace energy derived from fossil fuels, and hence reduce emissions of greenhouse gases, because the carbon in biodegradable material is part of a carbon cycle. The carbon released into the atmosphere from the combustion of biogas has been removed by plants for them to grow in the recent past, usually within the last decade, but more typically within the last growing season. If the plants are regrown, taking the carbon out of the atmosphere once more, the system will be carbon neutral . In contrast, carbon in fossil fuels has been sequestered in the earth for many millions of years, the combustion of which increases the overall levels of carbon dioxide in the atmosphere.

Biogas from sewage works is sometimes used to run a gas engine to produce electrical power, some or all of which can be used to run the sewage works. Some waste heat from the engine is then used to heat the digester. The waste heat is, in general, enough to heat the digester to the required temperatures. The power potential from sewage works is limited – in the UK, there are about 80 MW total of such generation, with the potential to increase to 150 MW, which is insignificant compared to the average power demand in the UK of about 35,000 MW. The scope for biogas generation from nonsewage waste biological matter – energy crops, food waste, abattoir waste, etc. - is much higher, estimated to be capable of about 3,000 MW Farm biogas plants using animal waste and energy crops are expected to contribute to reducing CO_2 emissions and strengthen the grid, while providing UK farmers with additional revenues.

Some countries offer incentives in the form of, for example, feed-in tariffs for feeding electricity onto the power grid to subsidize green energy production.

In Oakland, California at the East Bay Municipal Utility District's main wastewater treatment plant (EBMUD), food waste is currently codigested with primary and secondary municipal waste water solids and other high-strength wastes. Compared to municipal wastewater solids digestion alone, food waste codigestion has many benefits. Anaerobic digestion of food waste pulp from the EBMUD food waste process provides a higher normalized energy benefit, compared to municipal wastewater solids: 730 to 1,300 kWh per dry ton of food waste applied compared to 560 to 940 kWh per dry ton of municipal wastewater solids applied.

5 - 3 - Grid injection

Biogas grid - injection is the injection of biogas into the natural gas grid. As an alternative, the electricity and the heat can be used for on-site generation , resulting in a reduction of losses in the transportation of energy. Typical energy losses in natural gas transmission systems range from 1 – 2 % , whereas the current energy losses on a large electrical system range from 5 – 8 %.

In October 2010, Didcot Sewage Works became the first in the UK to produce biomethane gas supplied to the national grid, for use in up to 200 homes in Oxfordshire.

5 - 4 - Fertilizer and soil conditioner

The solid, fibrous component of the digested material can be used as a soil conditioner to increase the organic content of soils. Digester liquor can be used as a fertilizer to supply vital nutrients to soils instead of chemical fertilizers that require large amounts of energy to produce and transport. The use of manufactured fertilizers is, therefore, more carbon-intensive than the use of anaerobic digester liquor fertilizer. In countries such as Spain, where many soils are organically depleted, the markets for the digested solids can be equally as important as the biogas.

5 - 5 - Cooking gas

By using a bio - digester, which produces the bacteria required for decomposing, cooking gas is generated. The organic garbage like fallen leaves, kitchen waste, food waste etc. are fed into a crusher unit, where the mixture is conflated with a small amount of water. The mixture is then fed into the bio-digester, where the bacteria decomposes it to produce cooking gas. This gas is piped to kitchen stove. A 2 cubic meter bio - digester can produce 2 cubic meter of cooking gas. This is equivalent to 1 kg of LPG. The notable advantage of using a bio-digester is the sludge which is a rich organic manure.[83]

6 - Products

The three principal products of anaerobic digestion are biogas, digestate, and water.

6 - 1 - Biogas

Typical composition of biogas

Matter	%
Methane, CH_4	50 – 75
Carbon dioxide, CO_2	25 – 50
Nitrogen, N_2	0 – 10
Hydrogen, H_2	0 – 1
Hydrogen sulfide, H_2S	0 – 3
Oxygen, O_2	0 – 2

Biogas is the ultimate waste product of the bacteria feeding off the input biodegradable feedstock (the methanogenesis stage of anaerobic digestion is performed by archaea - a micro-organism on a distinctly different branch of the phylogenetic tree of life to bacteria), and is mostly methane and carbon dioxide,[87][88] with a small amount hydrogen and trace hydrogen sulfide. (As-produced, biogas also contains water vapor, with the fractional water vapor volume a function of biogas temperature). Most of the biogas is produced during the middle of the digestion, after the bacterial population has grown, and tapers off as the putrescible material is exhausted . The gas is normally stored on top of the digester in an inflatable gas bubble or extracted and stored next to the facility in a gas holder.

Biogas holder with lightning protection rods and backup gas flare

Biogas carrying pipes

The methane in biogas can be burned to produce both heat and electricity, usually with a reciprocating engine or micro turbine often in a cogeneration arrangement where the electricity and waste heat generated are used to warm the digesters or to heat buildings. Excess electricity can be sold to suppliers or put into the local grid. Electricity produced by anaerobic digesters is considered to be renewable energy and may attract subsidies . Biogas does not contribute to increasing atmospheric carbon dioxide concentrations because the gas is not released directly into the atmosphere and the carbon dioxide comes from an organic source with a short carbon cycle.

Biogas may require treatment or 'scrubbing' to refine it for use as a fuel. Hydrogen sulfide, a toxic product formed from sulfates in the feedstock, is released as a trace component of the biogas. National environmental enforcement agencies, such as the U.S. Environmental Protection Agency or the English and Welsh Environment Agency, put strict limits on the levels of gases containing hydrogen sulfide, and, if the levels of hydrogen sulfide in the gas are high, gas scrubbing and cleaning equipment (such as amine gas treating) will be needed to process the biogas to within regionally accepted levels. Alternatively, the addition of ferrous chloride $FeCl_2$ to the digestion tanks inhibits hydrogen sulfide production.

Volatile siloxanes can also contaminate the biogas; such compounds are frequently found in household waste and wastewater. In digestion facilities accepting these materials as a component of the feedstock, low-molecular-weight siloxanes volatilize into biogas. When this gas is combusted in a gas engine, turbine, or boiler, siloxanes are converted into silicon dioxide (SiO_2), which deposits internally in the machine, increasing wear and tear. Practical and cost - effective technologies to remove siloxanes and other biogas contaminants are available at the present time. In certain applications, *in situ* treatment can be used to increase the methane purity by reducing the offgas carbon dioxide content, purging the majority of it in a secondary reactor.

In countries such as Switzerland, Germany, and Sweden, the methane in the biogas may be compressed for it to be used as a vehicle transportation fuel or input directly into the gas mains. In countries where the driver for the use of anaerobic digestion are renewable electricity subsidies, this route of treatment is less likely, as energy is required in this processing stage and reduces the overall levels available to sell.

6 - 2 - Digestate

Digestate is the solid remnants of the original input material to the digesters that the microbes cannot use. It also consists of the mineralized remains of the dead bacteria from within the digesters. Digestate can come in three forms: fibrous, liquor, or a sludge - based combination of the two fractions. In two-stage systems, different forms of digestate come from different digestion tanks. In single-stage digestion systems, the two fractions will be combined and, if desired, separated by further processing.

The second byproduct (acidogenic digestate) is a stable, organic material consisting largely of lignin and cellulose, but also of a variety of mineral components in a matrix of dead bacterial cells; some plastic may be present. The material resembles domestic compost and can be used as such or to make low-grade building products, such as fiber board . The solid digestate can also be used as feedstock for ethanol production .

The third byproduct is a liquid (methanogenic digestate) rich in nutrients, which can be used as a fertiliser, depending on the quality of the material being digested. Levels of potentially toxic elements (PTEs) should be chemically assessed. This will depend upon the quality of the original feedstock. In the case of most clean and source-separated biodegradable waste streams, the levels of PTEs will be low. In the case of wastes originating from industry, the levels of PTEs may be higher and will need to be taken into consideration when determining a suitable end use for the material.

Digestate typically contains elements, such as lignin, that cannot be broken down by the anaerobic microorganisms. Also, the digestate may contain ammonia that is phytotoxic, and may hamper the growth of plants if it is used as a soil-improving material. For these two reasons, a maturation or composting stage may be employed after digestion. Lignin and other materials are available for degradation by aerobic micro organisms, such as fungi, helping reduce the overall volume of the material for transport. During this maturation, the ammonia will be oxidized into nitrates, improving the fertility of the material and making it more suitable as a soil improver. Large composting stages are typically used by dry anaerobic digestion technologies.

6 - 3 – Waste water

The final output from anaerobic digestion systems is water, which originates both from the moisture content of the original waste that was treated and water produced during the microbial reactions in the digestion systems. This water may be released from the dewatering of the digestate or may be implicitly separate from the digestate.

The wastewater exiting the anaerobic digestion facility will typically have elevated levels of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). These measures of the reactivity of the effluent indicate an ability to pollute. Some of this material is termed 'hard COD', meaning it cannot be accessed by the anaerobic bacteria for conversion into biogas. If this effluent were put directly into watercourses, it would negatively affect them by causing eutrophication. As such, further treatment of the wastewater is often required. This treatment will typically be an oxidation stage wherein air is passed through the water in a sequencing batch reactors or reverse osmosis unit.

Alcoholic Beverage

Contents

1 - Introduction

An alcoholic beverage is a drink containing the psychoactive drug ethyl alcohol (ethanol) and small quantities of other alcohols. Alcoholic beverages are divided into three general classes for taxation and regulation of production: beers, wines, and spirits (or distilled beverage). They are legally consumed in most countries with over 100 countries having laws regulating their production, sale, and consumption . In particular, such laws specify the minimum age at which a person may legally buy or drink them. This minimum age varies between 16 and 25 years, depending upon the country and the type of drink. Most nations set the age at 18 years.

The production and consumption of alcohol occurs in most cultures of the world, from hunter-gatherer peoples to nation-states. Alcoholic beverages are often an important part of social events in these cultures.

2 - Alcoholic beverages

2 - 1- Distilled beverage

An old distilled beverage

A distilled beverage, spirit, or liquor is an alcoholic beverage produced by distilling (i.e., concentrating by distillation) ethanol produced by means of fermenting grain, fruit, or vegetables . The term hard liquor is used in North America to distinguish distilled beverages from undistilled ones (implicitly weaker). Vodka, gin, baijiu, tequila, whisky, brandy, and soju are examples of distilled beverages. Undistilled fermented beverages include beer, wine, and cider. Freeze distillation concentrates ethanol along with methanol and fusel alcohols (fermentation by-products partially removed by distillation) in applejack.

2 - 1 – 1 - Rectified spirit

A rectified spirit, rectified alcohol, or neutral spirit is highly concentrated ethanol which has been purified by means of repeated distillation, a process that is called rectification. It typically contains 95 % alcohol by volume. Rectified spirits are used in mixed drinks, in the production of liqueurs, for medicinal purposes, and as a household solvent. In chemistry, a tincture is a solution that has alcohol as its solvent.

2 – 1 – 2 - Neutral grain spirit

Neutral grain spirit (also called pure grain alcohol (PGA) or grain neutral spirit (GNS) is a clear, colorless, flammable liquid that has been distilled from a grain-based mash to a very high level of ethanol content. The term neutral refers to the spirit's lacking the flavor that would have been present if the mash ingredients were distilled to a lower level of alcoholic purity, and also lacking any flavoring added to it after distillation (as is done, for example, with gin). Other kinds of spirits, such as whisky, are distilled to a lower alcohol percentage in order to preserve the flavor of the mash.

2 – 2 - Fermented beverages

Beer and wine are produced by fermentation of sugar- or starch-containing plant material. Beverages produced by fermentation followed by distillation have a higher alcohol content and are known as liquor or spirits.

2 - 2 – 1 - Chemical composition

2 - 2 – 1 – 1 - Alcohols

Alcohol is a general term for any organic compound in which a hydroxyl group (- O H) is bound to a carbon atom, which in turn may be bound to other carbon atoms. Alcohols other than ethanol are found in trace quantities in alcoholic beverages. Ethanol is the active ingredient in alcoholic beverages and is produced by fermentation.

2 - 2 – 1 – 1 - Congeners

Congeners are biologically active chemicals (chemicals which exert an effect on the body or brain) found in fermenation ethanol in trace quantities. Bourbon has a higher congener concentration than vodka. It has been suggested that some of these substances contribute to the symptoms of a hangover . Congeners include:

2 – 2 – 1 – 2 – 1 - Furfural

Furfural is a congener that inhibits yeast metabolism. It may be added to alcoholic beverages during the fermentation stage. Although it occurs in many foods and flavorants, furfural is toxic with an LD_{50} of 65 mg / kg (oral, rat).

2 – 2 – 1 – 2 – 2 - Tannins

Tannins are congeners found in wine. Tannins contain powerful antioxidants such as poly phenols.

2 – 2 – 1 – 2 – 3 - alcohol

Fusel alcohols, also sometimes called fusel oils, or potato oil in Europe, are a mixture of several alcohols (chiefly 2 - methyl - 1 - butanol) produced as a by - product of ethanol fermentation.

The term *fusel* is German for "bad liquor".

Fusel alcohols may contain up to 50 different components, where the chief constituents are iso butanol (2-methyl-1-propanol), propanol, and above all, the pair of iso amyl alkohols: 2-methyl-1-butanol and 3 - methyl -1- butanol . Occurrence of flavor compounds and some other compounds in alcoholic beverages for beer, wine, and spirits, are listed in hundreds in a document. Methanol is a toxic alcohol also found in trace quantities.

Excessive concentrations of these fractions may cause off-flavors, sometimes described as "spicy", "hot", or "solvent-like". Some beverages, such as rum, whisky (especially Bourbon), incompletely rectified vodka (e.g. Siwucha), and traditional ales and ciders, are expected to have relatively high concentrations of fusel alcohols as part of their flavor profile. In other beverages, such as Korn, vodka, and lagers, the presence of fusel alcohols is considered a fault.

2 – 2 – 2 - Beverages by fermentation ingredients

The names of some alcoholic beverages are determined by their base material.

Beer: In general, a beverage fermented from a grain mash will be called a beer. Beer is made from barley or a blend of several grains. If the fermented mash is distilled, then the beverage is a spirit.

Wine and brandy are usually made from grapes but when they are made from another kind of fruit, they are distinguished as fruit wine or fruit brandy. The kind of fruit must be specified, such as "cherry brandy" or "plum wine."

Whiskey (or whisky) is made from grain or a blend of several grains. The type of whiskey (scotch, rye, bourbon, or corn) is determined by the primary grain.

Vodka: Vodka is distilled from fermented grain. It is highly distilled so that it will contain less of the flavor of its base material. Gin is a similar distillate but it is flavored by juniper berries and sometimes by other herbs as well. Applejack is sometimes made by means of freeze distillation.

Cider: In the United States and Canada, *cider* often means unfermented apple juice (sometimes called *sweet cider*), and fermented apple juice is called *hard cider*. In the United Kingdom and Australia, *cider* refers to the alcoholic beverage.

Grains	**Name of fermented beverage**	**Name of distilled beverage**
barley	beer, ale, barley wine	Scotch whisky, Irish whiskey, shōchū (mugijōchū) (Japan)
rye	rye beer, kvass	rye whiskey, vodka (Poland), Korn (Germany)
corn	chicha, corn beer, tesguino	Bourbon whiskey; and vodka (rarely)
sorghum	burukutu (Nigeria), pito (Ghana), merisa (southern Sudan), bilibili (Chad, Central African Republic, Cameroon)	maotai, gaoliang, certain other types of baijiu (China).
wheat	wheat beer	horilka (Ukraine), vodka, wheat whisky, weizenkorn (Germany)
rice	beer, brem (Bali), huangjiu and choujiu (China), Ruou gao (Vietnam), sake (Japan), sonti (India), makgeolli (Korea), tuak (Borneo Island), thwon (Nepal)	aila (Nepal), rice baijiu (China), shōchū (komejōchū) and awamori (Japan), soju (Korea)
millet	millet beer (Sub-Saharan Africa), tongba (Nepal, Tibet), boza (the Balkans, Turkey)	
buck wheat	shōchū (sobajōchū) (Japan)	
Fruit juice	Name of fermented beverage	Name of distilled beverage
grapes juice	wine	brandy, Cognac (France), Vermouth, Armagnac (France), Branntwein (Germany), pisco (Peru,

		Chile), (Grozdova) Rakia (The Balkans, Turkey), singani (Bolivia), Arak (Syria, Lebanon, Jordan), törkölypálinka (Hungary)
apples juice	cider (U.S.: "hard cider"), Apfelwein	applejack (or apple brandy), calvados, cider
pears juice	perry, or pear cider; poiré (France)	Poire Williams, pear brandy, Eau-de-vie (France), pálinka (Hungary), Krushova rakia / Krushevitsa (Bulgaria)
plums juice	plum wine	slivovitz, țuică, umeshu, pálinka, Slivova rakia / Slivovitsa (Bulgaria)
apricots juice		Kaisieva rakia (Bulgaria)
pineapples juice	tepache (Mexico), Pineapple Wine (Hawaii)	
junipers		borovička (Slovakia)
bananas or plantains	Chuoi hot (Vietnam), urgwagwa (Uganda, Rwanda), mbege (with millet malt; Tanzania), kasikisi (with sorghum malt; Democratic Republic of the Congo)	
gouqi	gouqi jiu (China)	gouqi jiu (China)
coconut	Toddy (Sri Lanka, India)	arrack, lambanog (Sri Lanka, India, Philippines)
ginger with sugar, ginger with raisins	ginger ale, ginger beer, ginger wine	
Myrica rubra	yangmei jiu (China)	yangmei jiu (China)
pomace	pomace wine	Raki/Ouzo/Pastis/Sambuca (Turkey/Greece/France/Italy), tsipouro/tsikoudia (Greece),

		grappa (Italy), Trester (Germany), marc (France), orujo (Spain), zivania (Cyprus), aguardente (Portugal), tescovină (Romania), Arak (Iraq)
Vegetables	Name of fermented beverage	Name of distilled beverage
cassava	Cauim and tiquira (Brazil), kasiri (Sub-Saharan Africa), masato (Peruvian Amazonia chicha), parakari (Guyana), nihamanchi (South America) aka nijimanche (Ecuador and Peru), sakurá (Brazil, Surinam)	
juice of ginger root	ginger beer (Botswana)	
potato	potato beer	horilka (Ukraine), vodka (Poland and Germany), akvavit (Scandinavia), poitín (poteen) (Ireland)
sweet potato	shōchū (imojōchū) (Japan), soju (Korea)	
juice of sugarcane, or molasses	basi, betsa-betsa (regional)	rum (Caribbean), pinga or cachaça (Brasil), aguardiente, guaro
juice of agave	pulque	tequila, mezcal, raicilla
Other ingredients	Name of fermented beverage	Name of distilled beverage
sap of palm	coyol wine (Central America), tembo (Sub-Saharan Africa), toddy	

	(Indian subcontinent)	
sap of Arenga pinnata, Coconut, Borassus flabellifer	Tuak (Indonesia)	Arrack
honey	mead, horilka (Ukraine), tej (Ethiopia)	distilled mead (mead brandy or honey brandy)
milk	kumis, kefir, blaand	arkhi (Mongolia)
sugar	kilju and mead or *sima* (Finland)	shōchū (kokutō shōchū): made from brown sugar (Japan)

2 – 2 – 2 - 1- Flavoring

Alcohol is a moderately good solvent for many fatty substances and essential oils. This attribute facilitates the use of flavoring and coloring compounds in alcoholic beverages, especially distilled beverages. Flavors may be naturally present in the beverage's base material. Beer and wine may be flavored before fermentation. Spirits may be flavored before, during, or after distillation.

Sometimes flavor is obtained by allowing the beverage to stand for months or years in oak barrels, usually American or French oak.

A few brands of spirits have fruit or herbs inserted into the bottle at the time of bottling.

2 – 2 – 3 - Tax regulated classes

2 – 2 – 3 - 1 - Beer

Beer is one of the world's oldest and most widely consumed alcoholic beverages, and the third most popular drink overall after water and tea . It is produced by the brewing and fermentation of starches which are mainly derived from cereal grains — most commonly malted barley although wheat , maize (corn), and rice are also used.

Alcoholic beverages that are distilled after fermentation, or are fermented from non-cereal sources (such as grapes or honey), or are fermented from un malted cereal grain are not classified as beer.

The two main types of beer are lager and ale. Ale is further classified into varieties such as pale ale, stout, and brown ale, whereas different types of lager include black lager, pilsener, and bock.

Most beer is flavored with s, which add bitterness and act as a natural preservative. Other flavorings, such as fruits or herbs, may also be used.

The alcoholic strength of beer is usually 4 – 6 % alcohol by volume (ABV), but it may be less than 2 % or greater than 25%. Beers having an ABV of 60 % (120 proof) have been produced by freezing brewed beer and removing water in the form of ice, a process referred to as "ice distilling".

Beer is part of the drinking culture of various nations and has acquired social traditions such as beer festivals, pub games, and pub crawling (sometimes known as bar ping).

The basics of brewing beer are shared across national and cultural boundaries. The beer - brewing industry is global in scope, consisting of several dominant multinational companies and thousands of smaller producers, which range from regional breweries to microbreweries.

2 – 2 – 3 - 2 - Wine

Wine is produced from grapes, and from fruits such as plums, cherries, or apples. Wine involves a longer fermentation process than beer and also a long aging process (months or years), resulting in an alcohol content of 9 – 16 % ABV. Sparkling wine can be made by means of a secondary fermentation.

Fortified wine is wine (such as port or sherry), to which a distilled beverage (usually brandy) has been added.

2 – 2 – 3 - 3 – Spirits (*Distilled beverage)*

Unsweetened, distilled, alcoholic beverages that have an alcohol content of at least 20 % ABV are called *spirits* . Spirits are produced by the distillation of a fermented base product. Distilling concentrates the alcohol and eliminates some of the congeners. For the most common distilled beverages, such as whiskey and vodka, the alcohol content is around 40 %.

Spirits can be added to wines to create *fortified wines*, such as port and sherry.

Distilled alcoholic beverages were first recorded in Europe in the mid -12 th century. By the early 14th century, they had spread throughout the European continent . They also spread eastward from Europe, mainly due to the Mongols, and began to be seen in China no later than the 14th century .

Paracelsus gave alcohol its modern name, which is derived from an Arabic word that means "finely divided" (a reference to distillation).

2 – 3 - Fortified beverages

2 – 3 – 1 - Fortified wine

Fortified wine is wine with an added distilled beverage (usually brandy) . Fortified wine is distinguished from spirits made from wine in that spirits are produced by means of distillation, while fortified wine is simply wine that has had a spirit added to it. Many different styles of fortified wine have been developed, including Port, Sherry, Madeira, Marsala, Commandaria wine and the aromatized wine Vermouth.

2 – 3 – 2 - Mixed drinks

Mixed drinks include alcoholic mixed drinks (cocktails, beer cocktails, flaming beverages, fortified wines, mixed drink shooters and drink shots, wine cocktails) and non-alcoholic mixed drinks (including punches).

Blending and caffeinated alcoholic drinks may also be called mixed drinks.

2 – 3 – 3 - Ready to drink

Alcopops

3 - Standards

3 - 1 Alcohol concentration

The concentration of alcohol in a beverage is usually stated as the percentage of alcohol by volume (ABV) or as *proof*. In the United States, *proof* is twice the percentage of alcohol by volume at 60 degrees Fahrenheit (e.g. 80 proof = 40 % ABV). *Degrees proof* were formerly used in the United Kingdom, where 100 degrees proof was equivalent to 57.1 % ABV. Historically, this was the most dilute spirit that would sustain the combustion of gunpowder.

Ordinary distillation cannot produce alcohol of more than 95.6% ABV (191.2 proof) because at that point alcohol is an azeotrope with water. A spirit which contains a very high level of alcohol and *does not contain any added flavoring* is commonly called a neutral spirit. Generally, any distilled alcoholic beverage of 170 proof or higher is considered to be a neutral spirit.

Most yeasts cannot reproduce when the concentration of alcohol is higher than about 18%, so that is the practical limit for the strength of fermented beverages such as wine, beer, and sake. However, some strains of yeast have been developed that can reproduce in solutions of up to 25% ABV .

3 - 1 – 1 - Alcohol - free beverage definition controversy

The term alcohol - free (e.g. alcohol-free beer) is often used to describe a product that contains 0 % ABV ; As such, it is permitted by Islam, and they are also popular in countries that enforce alcohol prohibition, such as Saudi Arabia, Kuwait and Iran.

However, alcohol is legal in most countries of the world where alcohol culture also is prevalent. Laws vary in countries when beverages must indicate the strength but also what they define as alcohol - free; Experts calling the label “misleading” and a threat to recovering alcoholics.

In the EU the labeling of beverages containing more than 1.2% by volume of alcohol must indicate the actual alcoholic strength by volume, i.e. showing the word "alcohol" or the abbreviation "alc." followed by the symbol " % vol."

Most of the alcohol-free drinks sold in Sweden’s state-run liquor store monopoly System bola get actually contain alcohol, with experts calling the label “misleading” and a threat to recovering alcoholics. System bola get define alcohol - free as a drink that contains a maximum of 0.5 percent alcohol by volume . Interestingly, the drug policy of Sweden is based on zero tolerance.

3 – 2 - Standard drinks *# Pure alcohol measure, Alcohol equivalence, and Unit of alcohol*

A standard drink is a notional drink that contains a specified amount of pure alcohol. The standard drink is used in many countries to quantify alcohol intake. It is usually expressed as a measure of beer, wine, or spirits. One standard drink always contains the same amount of alcohol regardless of serving size or the type of alcoholic beverage.

The standard drink varies significantly from country to country. For example, it is 7.62 ml (6 grams) of alcohol in Austria, but in Japan it is 25 ml (19.75 grams).

In the United Kingdom, there is a system of units of alcohol which serves as a guideline for alcohol consumption. A single unit of alcohol is defined as 10 ml. The number of units present in a typical drink is printed on bottles. The system is intended as an aid to people who are regulating the amount of alcohol they drink; it is not used to determine serving sizes.

In the United States, the standard drink contains 0.6 US fluid ounces (18 ml) of alcohol. This is approximately the amount of alcohol in a 12-US-fluid-ounce (350 ml) glass of beer, a 5-US-fluid-ounce (150 ml) glass of wine, or a 1.5- US – fluid - ounce (44 ml) glass of a 40 % ABV (80 proof) spirit.

3 - 3 - Serving sizes

In the United Kingdom, serving size in licensed premises is regulated under the Weights and Measures Act (1985). Spirits (gin, whisky, rum, and vodka) are sold in 25 ml or 35 ml quantities or multiples thereof . Beer is typically served in pints (568 ml), but is also served in half-pints or third - pints.

In Ireland, the serving size of spirits is 35.5 ml or 71 ml. Beer is usually served in pints or half-pints ("glasses"). In the Netherlands and Belgium, standard servings are 250 and 500 ml for pilsner; 300 and 330 ml for ales.

The shape of a glass can have a significant effect on how much one pours. A Cornell University study of students and bartenders' pouring showed both groups pour more into short, wide glasses than into tall, slender glasses . Aiming to pour one shot of alcohol (1.5 ounces or 44.3 ml), students on average poured 45.5 ml & 59.6 ml (30% more) respectively into the tall and short glasses. The bartenders scored similarly, on average pouring 20.5 % more into the short glasses. More experienced bartenders were more accurate, pouring 10.3% less alcohol than less experienced bartenders. Practice reduced the tendency of both groups to over pour for tall, slender glasses but not for short, wide glasses. These misperceptions are attributed to two perceptual biases: (1) Estimating that tall, slender glasses have more volume than shorter, wider glasses; and (2) Over focusing on the height of the liquid and disregarding the width.

4 - Alcohol consumption

4 – 1 - History

Alcoholic beverages have been drunk by people around the world since ancient times.

Reasons that have been proposed for drinking them include :

They are part of a people's standard diet
They are drunk for medical reasons
For their relaxant effects
For their euphoric effects
For recreational purposes
For artistic inspiration
For their putative aphrodisiac effects

4 – 1 – 1 - Archaeological record

Chemical analysis of traces absorbed and preserved in pottery jars from the neolithic village of Jiahu in Henan province in northern China has revealed that a mixed fermented beverage made from rice, honey, and fruit was being produced as early as 9,000 years ago. This is approximately the time when barley beer and grape wine were beginning to be made in the Middle East.

Recipes have been found on clay tablets and art in Mesopotamia that show people using straws to drink beer from large vats and pots.

The Hindu ayurvedic texts describe both the beneficial effects of alcoholic beverages and the consequences of intoxication and alcoholic diseases.

The medicinal use of alcohol was mentioned in Sumerian and Egyptian texts dating from about 2100 BC. The Hebrew Bible recommends giving alcoholic drinks to those who are dying or depressed, so that they can forget their misery (Proverbs 31:6-7).

Wine was consumed in Classical Greece at breakfast or at symposia, and in the 1st century BC it was part of the diet of most Roman citizens. Both the Greeks and the Romans generally drank diluted wine (the strength varying from 1 part wine and 1 part water, to 1 part wine and 4 parts water).

In Europe during the Middle Ages, beer, often of very low strength, was an everyday drink for all classes and ages of people. A document from that time mentions nuns having an allowance of six pints of ale each day. Cider and pomace wine were also widely available; grape wine was the prerogative of the higher classes.

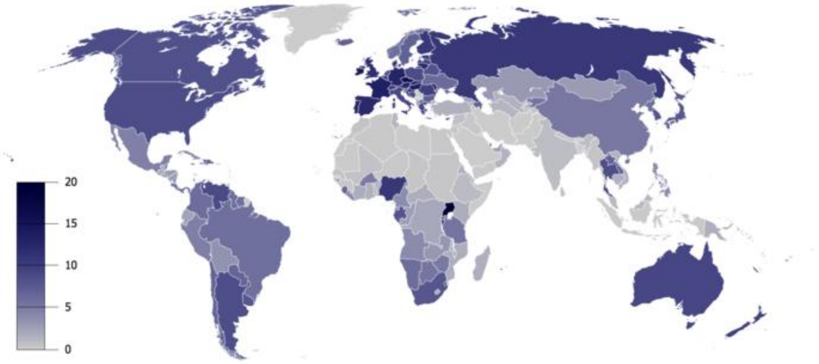
By the time the Europeans reached the Americas in the 15th century, several native civilizations had developed alcoholic beverages. According to a post - conquest Aztec document, consumption of the local "wine" (*pulque*) was generally restricted to religious ceremonies but was freely allowed to those who were older than 70 years.

The natives of South America produced a beer-like beverage from cassava or maize, which had to be chewed before fermentation in order to turn the starch into sugar. (Beverages of this kind are known today as *cauim* or *chicha*.) This chewing technique was also used in ancient Japan to make sake from rice and other starchy crops.

4 – 2 - Applications

In many countries, people drink alcoholic beverages at lunch and dinner. Studies have found that when food is eaten before drinking alcohol, alcohol absorption is reduced[27] and the rate at which alcohol is eliminated from the blood is increased. The mechanism for the faster alcohol elimination appears to be unrelated to the type of food. The likely mechanism is food-induced increases in alcohol-metabolizing enzymes and liver blood flow.

At times and places of poor public sanitation (such as Medieval Europe), the consumption of alcoholic drinks was a way of avoiding water-borne diseases such as cholera. Small beer and faux wine, in particular, were used for this purpose. Although alcohol kills bacteria, its low concentration in these beverages would have had only a limited effect. More important was that the boiling of water (required for the brewing of beer) and the growth of yeast (required for fermentation of beer and wine) would tend to kill dangerous microorganisms. The alcohol content of these beverages allowed them to be stored for months or years in simple wood or clay containers without spoiling. For this reason, they were commonly kept aboard sailing vessels as an important (or even the sole) source of hydration for the crew, especially during the long voyages of the early modern period.



2004 data of alcohol consumption per capita (age 15 or older), per year, by country, in liters of pure alcohol.

In cold climates, potent alcoholic beverages such as vodka are popularly seen as a way to "warm up" the body, possibly because alcohol is a quickly absorbed source of food energy and because it dilates peripheral blood vessels (peripherovascular dilation). This is a misconception because the "warmth" is actually caused by a transfer of heat from the body's core to its extremities, where it is quickly lost to the environment.

However, the perception alone may be welcomed when only comfort, rather than hypothermia, is a concern.

4 – 3 - Alcohol consumption by country

5 - Alcohol and health

Short - term effects of alcohol consumption include intoxication and dehydration. Long-term effects of alcohol include changes in the metabolism of the liver and brain and alcoholism (addiction to alcohol).

6 - Alcohol laws

Alcohol laws are laws in relation to the manufacture, use, influence and sale of ethanol or alcoholic beverages that contains ethanol. Alcohol laws often seek to reduce the availability of alcoholic beverages, often with the stated purpose of reducing the health and social side effect of their consumption. This can take the form of age limits for alcohol consumption, and distribution only in licensed stores or in monopoly stores. Often, this is combined with some form of alcohol taxation.

Industrial Fermentation

Contents

1 - Introduction

Industrial fermentation is the intentional use of fermentation by microorganisms such as bacteria and fungi to make products useful to humans. Fermented products have applications as food as well as in general industry.

2 - Food fermentation

Ancient fermented food processes, such as making bread, wine, cheese, curds, idli, dosa, etc., can be dated to more than seven thousand years ago. They were developed long before man had any knowledge of the existence of the microorganisms involved. Fermentation is also a powerful economic incentive for semi-industrialized countries, in their willingness to produce bio - ethanol.

3 - Pharmaceuticals and the biotechnology industry

There are 5 major groups of commercially important fermentation :

Microbial cells or biomass as the product, e.g. single cell protein , bakers yeast, lactobacillus, E. coli, etc.

* Microbial enzymes: catalase, amylase, protease, pectinase , glucose iso merase , cellulase, hemi cellulase, lipase, lactase, streptokinase, etc.

* Microbial metabolites :

Primary metabolites – ethanol, citric acid, glutamic acid, lysine, vitamins, polysaccharides etc.

Secondary metabolites: all antibiotic fermentation

Recombinant products: insulin, hepatitis B vaccine, interferon, granulocyte colony - stimulating factor, streptokinase

Bio trans formations: phenyl acetyl carbinol, steroid bio trans formation, etc.

3 - 1 - Nutrient sources for industrial fermentation

Growth media are required for industrial fermentation, since any microbe requires water, (oxygen), an energy source, a carbon source, a nitrogen source and micronutrients for growth.

Carbon & energy source + nitrogen source + O_2 + other requirements

→ Biomass + Product + byproducts + CO_2 + H_2O + heat

Nutrient	Raw material
Carbon	
Glucose	corn sugar , starch , cellulose
Sucrose	sugarcane , sugar beet molasses
glycerol	
Starch	
Malto dextrine	
Lactose	milk whey
fats	vegetable oils
Nitrogen	
Protein	soybean meal, corn steep liquor, distillers' solubles
Ammonia	pure ammonia or ammonium salts urea
Nitrate	nitrate salts
Phosphorus source	**phosphate salts**
Vitamins and growth factors	
	Yeast, Yeast extract
	Wheat germ meal, cotton seed meal
	Beef extract
	Corn steep liquor

Trace elements: Fe, Zn, Cu, Mn, Mo, Co

Antifoaming agents : Esters, fatty acids, fats, silicones, sulfonates, polypropylene glycol

Buffers: Calcium carbonate, phosphates

Growth factors: Some microorganisms cannot synthesize the required cell components themselves and need to be supplemented, e.g. with thiamine, biotin, calcium pentothenate

Precursors: Directly incorporated into the desired product: phenethylamine into benzyl penicillin, phenyl acetic acid into penicillin G

Inhibitors: To get the specific products: e.g. sodium barbital for rifamycin

Inducers: The majority of the enzymes used in industrial fermentation are inducible and are synthesized in response of inducers: e.g. starch for amylases, maltose for pollulanase, pectin for pectinase.

Chelators: Chelators are the chemicals used to avoid the precipitation of metal ions. Chelators like EDTA, citric acid, polyphosphates are used in low concentrations.

4 - Sewage disposal

In the process of sewage disposal, sewage is digested by enzymes secreted by bacteria. Solid organic matters are broken down into harmless, soluble substances and carbon dioxide. Liquids that result are disinfected to remove pathogens before being discharged into rivers or the sea or can be used as liquid fertilizers. Digested solids, known also as sludge, is dried and used as fertilizer. Gaseous byproducts such as methane can be utilized as biogas to fuel generators. One advantage of bacterial digestion is that it reduces the bulk and odour of sewage, thus reducing space needed for dumping, on the other hand, a major disadvantage of bacterial digestion in sewage disposal is that it is a very slow process.

4 – 1 - Phases of microbial growth

When a particular organism is introduced into a selected growth medium, the medium is inoculated with the particular organism. Growth of the inoculum does not occur immediately, but takes a little while. This is the period of adaptation, called the lag phase. Following the lag phase, the rate of growth of the organism steadily increases, for a certain period -- this period is the log or exponential phase. After a certain time of exponential phase, the rate of growth slows down, due to the continuously falling concentrations of nutrients and/or a continuously increasing (accumulating) concentrations of toxic substances. This phase, where the increase of the rate of growth is checked, is the deceleration phase. After the deceleration phase, growth ceases and the culture enters a stationary phase or a steady state. The biomass remains constant, except when certain accumulated chemicals in the culture lyse the cells (chemolysis). Unless other micro-organisms contaminate the culture, the chemical constitution remains unchanged. Mutation of the organism in the culture can also be a source of contamination, called internal contamination.

Distillation

Contents

1 - Introduction

Distillation is a method of separating mixtures based on differences in volatility of components in a boiling liquid mixture. Distillation is a unit operation, or a physical separation process, and not a chemical reaction.

Commercially, distillation has a number of applications. It is used to separate crude oil into more fractions for specific uses such as transport, power generation and heating. Water is distilled to remove impurities, such as salt from seawater. Air is distilled to separate its components—notably oxygen, nitrogen, and argon — for industrial use. Distillation of fermented solutions has been used since ancient times to produce distilled beverages with a higher alcohol content. The premises where distillation is carried out, especially distillation of alcohol, are known as a distillery. A still is the apparatus used for distillation.

2 - History *(Distilled beverage)*

The first clear evidence of distillation comes from Greek alchemists working in Alexandria in the 1st century AD. Distilled water has been known since at least c. 200, when Alexander of Aphrodisias described the process . Distillation in China could have begun during the Eastern Han Dynasty (1st – 2nd centuries), but archaeological evidence indicates that actual distillation of beverages began in the Jin and Southern Song dynasties. A still was found in an archaeological site in Qinglong, Hebei province dating to the 12th century. Distilled beverages were more common during the Yuan dynasty. Arabs learned the process from the Egyptians and used it extensively in their chemical experiments

Clear evidence of the distillation of alcohol comes from the School of Salerno in the 12th century. Fractional distillation was developed by Tadeo Alderotti in the 13th century.

In 1500, German alchemist Hieronymus Braunschweig published *Liber de arte destillandi* (The Book of the Art of Distillation) the first book solely dedicated to the subject of distillation, followed in 1512 by a much expanded version. In 1651, John French published The Art of Distillation the first major English compendium of practice, though it has been claimed that much of it derives from Braunschweig's work. This includes diagrams with people in them showing the industrial rather than bench scale of the operation.

Distillation

Simple liqueur distillation in East Timor

As alchemy evolved into the science of chemistry, vessels called retorts became used for distillations. Both alembics and retorts are forms of glassware with long necks pointing to the side at a downward angle which acted as air-cooled condensers to condense the distillate and let it drip downward for collection. Later, copper alembics were invented. Riveted joints were often kept tight by using various mixtures, for instance a dough made of rye flour . These alembics often featured a cooling system around the beak, using cold water for instance, which made the condensation of alcohol more efficient. These were called pot stills. Today, the retorts and pot stills have been largely supplanted by more efficient distillation methods in most industrial processes. However, the pot still is still widely used for the elaboration of some fine alcohols such as cognac, Scotch whisky, tequila and some vodkas. Pot stills made of various materials (wood, clay, stainless steel) are also used by bootleggers in various countries. Small pot stills are also sold for the domestic production of flower water or essential oils.

Early forms of distillation were batch processes using one vaporization and one condensation. Purity was improved by further distillation of the condensate. Greater volumes were processed by simply repeating the distillation. Chemists were reported to carry out as many as 500 to 600 distillations in order to obtain a pure compound.

In the early 19th century the basics of modern techniques including pre-heating and reflux were developed, particularly by the French, then in 1830 a British Patent was issued to Aeneas Coffey for a whiskey distillation column,[12] which worked continuously and may be regarded as the archetype of modern petrochemical units. In 1877, Ernest Solvay was granted a U.S. Patent for a tray column for ammonia distillation and the same and subsequent years saw developments of this theme for oil and spirits.

With the emergence of chemical engineering as a discipline at the end of the 19th century, scientific rather than empirical methods could be applied. The developing petroleum industry in the early 20 th century provided the impetus for the development of accurate design methods such as the McCabe-Thiele method and the Fenske equation. The availability of powerful computers has also allowed direct computer simulation of distillation columns.

3 - Applications of distillation

The application of distillation can roughly be divided in four groups: laboratory scale, industrial distillation, distillation of herbs for perfumery and medicinals (herbal distillate), and food processing. The latter two are distinctively different from the former two in that in the processing of beverages, the distillation is not used as a true purification method but more to transfer all volatiles from the source materials to the distillate.

The main difference between laboratory scale distillation and industrial distillation is that laboratory scale distillation is often performed batch-wise, whereas industrial distillation often occurs continuously. In batch distillation, the composition of the source material, the vapors of the distilling compounds and the distillate change during the distillation. In batch distillation, a still is charged (supplied) with a batch of feed mixture, which is then separated into its component fractions which are collected sequentially from most volatile to less volatile, with the bottoms (remaining least or non-volatile fraction) removed at the end. The still can then be recharged and the process repeated.

In continuous distillation, the source materials, vapors, and distillate are kept at a constant composition by carefully replenishing the source material and removing fractions from both vapor and liquid in the system. This results in a better control of the separation process.

4 - Idealized distillation model

The boiling point of a liquid is the temperature at which the vapor pressure of the liquid equals the pressure in the liquid, enabling bubbles to form without being crushed. A special case is the normal boiling point, where the vapor pressure of the liquid equals the ambient atmospheric pressure.

It is a common misconception that in a liquid mixture at a given pressure, each component boils at the boiling point corresponding to the given pressure and the vapors of each component will collect separately and purely. This, however, does not occur even in an idealized system. Idealized models of distillation are essentially governed by Raoult's law and Dalton's law, and assume that vapor-liquid equilibria are attained.

Raoult's law assumes that a component contributes to the total vapor pressure of the mixture in proportion to its percentage of the mixture and its vapor pressure when pure, or succinctly: partial pressure equals mole fraction multiplied by vapor pressure when pure. If one component changes another component's vapor pressure, or if the volatility of a component is dependent on its percentage in the mixture, the law will fail.

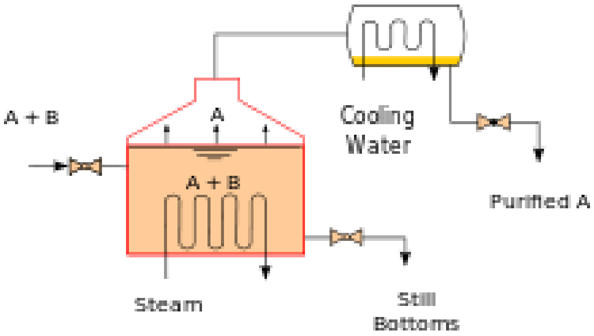
Dalton's law states that the total vapor pressure is the sum of the vapor pressures of each individual component in the mixture. When a multi-component liquid is heated, the vapor pressure of each component will rise, thus causing the total vapor pressure to rise. When the total vapor pressure reaches the pressure surrounding the liquid, boiling occurs and liquid turns to gas throughout the bulk of the liquid. Note that a mixture with a given composition has one boiling point at a given pressure, when the components are mutually soluble.

An implication of one boiling point is that lighter components never cleanly "boil first". At boiling point, all volatile components boil, but for a component, its percentage in the vapor is the same as its percentage of the total vapor pressure. Lighter components have a higher partial pressure and thus are concentrated in the vapor, but heavier volatile components also have a (smaller) partial pressure and necessarily evaporate also, albeit being less concentrated in the vapor. Indeed, batch distillation and fractionation succeed by varying the composition of the mixture. In batch distillation, the batch evaporates, which changes its composition; in fractionation, liquid higher in the fractionation column contains more lights and boils at lower temperatures.

The idealized model is accurate in the case of chemically similar liquids, such as benzene and toluene. In other cases, severe deviations from Raoult's law and Dalton's law are observed, most famously in the mixture of ethanol and water. These compounds, when heated together, form an azeotrope, which is a composition with a boiling point higher or lower than the boiling point of each separate liquid. Virtually all liquids, when mixed and heated, will display azeotropic behaviour. Although there are computational methods that can be used to estimate the behavior of a mixture of arbitrary components, the only way to obtain accurate vapor-liquid equilibrium data is by measurement.

It is not possible to *completely* purify a mixture of components by distillation, as this would require each component in the mixture to have a zero partial pressure. If ultra-pure products are the goal, then further chemical separation must be applied. When a binary mixture is evaporated and the other component, e.g. a salt, has zero partial pressure for practical purposes, the process is simpler and is called evaporation in engineering.

4 – 1 - Batch distillation



A batch still showing the separation of A and B.

Heating an ideal mixture of two volatile substances A and B (with A having the higher volatility, or lower boiling point) in a batch distillation setup (such as in an apparatus depicted in the opening figure) until the mixture is boiling results in a vapor above the liquid which contains a mixture of A and B. The ratio between A and B in the vapor will be different from the ratio in the liquid: the ratio in the liquid will be determined by how the original mixture was prepared, while the ratio in the vapor will be enriched in the more volatile compound, A (due to Raoult's Law, see above). The vapor goes through the condenser and is removed from the system. This in turn means that the ratio of compounds in the remaining liquid is now different from the initial ratio (i.e. more enriched in B than the starting liquid).

The result is that the ratio in the liquid mixture is changing, becoming richer in component B. This causes the boiling point of the mixture to rise, which in turn results in a rise in the temperature in the vapor, which results in a changing ratio of A : B in the gas phase (as distillation continues, there is an increasing proportion of B in the gas phase). This results in a slowly changing ratio A : B in the distillate.

If the difference in vapor pressure between the two components A and B is large (generally expressed as the difference in boiling points), the mixture in the beginning of the distillation is highly enriched in component A, and when component A has distilled off, the boiling liquid is enriched in component B.

4 – 2 - Continuous distillation

Continuous distillation is an ongoing distillation in which a liquid mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams as time passes during the operation. Continuous distillation produces at least two output fractions, including at least one volatile distillate fraction, which has boiled and been separately captured as a vapor condensed to a liquid. There is always a bottoms (or residue) fraction, which is the least volatile residue that has not been separately captured as a condensed vapor.

Continuous distillation differs from batch distillation in the respect that concentrations should not change over time. Continuous distillation can be run at a steady state for an arbitrary amount of time. For any source material of specific composition, the main variables that affect the purity of products in continuous distillation are the reflux ratio and the number of theoretical equilibrium stages (practically, the number of trays or the height of packing). Reflux is a flow from the condenser back to the column, which generates a recycle that allows a better separation with a given number of trays. Equilibrium stages are ideal steps where compositions achieve vapor-liquid equilibrium, repeating the separation process and allowing better separation given a reflux ratio. A column with a high reflux ratio may have fewer stages, but it refluxes a large amount of liquid, giving a wide column with a large holdup. Conversely, a column with a low reflux ratio must have a large number of stages, thus requiring a taller column

4 – 3 - General improvements

Both batch and continuous distillations can be improved by making use of a fractionating column on top of the distillation flask. The column improves separation by providing a larger surface area for the vapor and condensate to come into contact. This helps it remain at equilibrium for as long as possible. The column can even consist of small subsystems ('trays' or 'dishes') which all contain an enriched, boiling liquid mixture, all with their own vapor-liquid equilibrium.

There are differences between laboratory-scale and industrial-scale fractionating columns, but the principles are the same. Examples of laboratory - scale fractionating columns (in increasing efficiency) include :

Air condenser
Vigreux column (usually laboratory scale only)
Packed column (packed with glass beads, metal pieces, or other chemically inert material)
Spinning band distillation system.

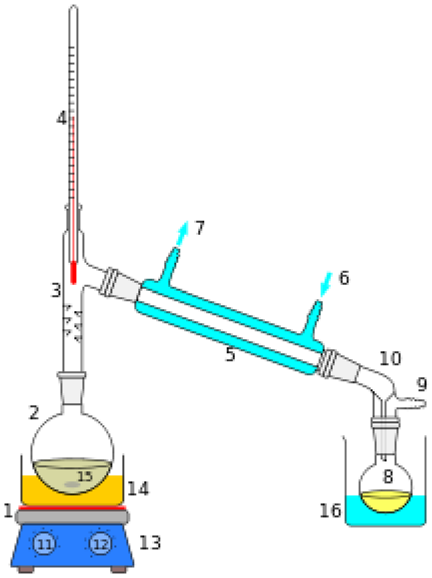
5 - Laboratory scale distillation

Laboratory scale distillations are almost exclusively run as batch distillations. The device used in distillation, sometimes referred to as a *still*, consists at a minimum of a reboiler or *pot* in which the source material is heated, a condenser in which the heated vapour is cooled back to the liquid state, and a receiver in which the concentrated or purified liquid, called the distillate, is collected. Several laboratory scale techniques for distillation exist (see also distillation types).

5 – 1 - Simple distillation

In simple distillation, all the hot vapors produced are immediately channeled into a condenser that cools and condenses the vapors. Therefore, the distillate will not be pure – its composition will be identical to the composition of the vapors at the given temperature and pressure, and can be computed from Raoult 's law.

As a result, simple distillation is usually used only to separate liquids whose boiling points differ greatly (rule of thumb is 25 °C) , or to separate liquids from non-volatile solids or oils. For these cases, the vapor pressures of the components are usually sufficiently different that Raoult's law may be neglected due to the insignificant contribution of the less volatile component. In this case, the distillate may be sufficiently pure for its intended purpose.



Laboratory display of distillation:

1 : A heating device 2 : Still pot 3 : Still head
4 : Thermometer/Boiling point temperature 5 : Condenser
6 : Cooling water in 7 : Cooling water out
8 : Distillate/receiving flask 9: Vacuum/gas inlet
10 : Still receiver 11 : Heat control
12 : Stirrer speed control 13 : Stirrer/heat plate
14 : Heating (Oil/sand) bath 15 : mechanical stirrer
16 : Cooling bath.

5 – 2 - Fractional distillation

For many cases, the boiling points of the components in the mixture will be sufficiently close that Raoult's law must be taken into consideration. Therefore, fractional distillation must be used in order to separate the components by repeated vaporization-condensation cycles within a packed fractionating column. This separation, by successive distillations, is also referred to as rectification.

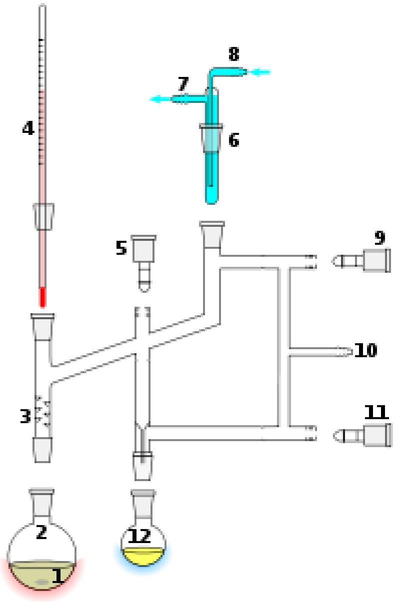
As the solution to be purified is heated, its vapors rise to the fractionating column. As it rises, it cools, condensing on the condenser walls and the surfaces of the packing material. Here, the condensate continues to be heated by the rising hot vapors; it vaporizes once more. However, the composition of the fresh vapors are determined once again by Raoult's law. Each vaporization-condensation cycle (called a *theoretical plate*) will yield a purer solution of the more volatile component.[16] In reality, each cycle at a given temperature does not occur at exactly the same position in the fractionating column; *theoretical plate* is thus a concept rather than an accurate description.

More theoretical plates lead to better separations. A spinning band distillation system uses a spinning band of Teflon or metal to force the rising vapors into close contact with the descending condensate, increasing the number of theoretical plates.

5 – 3 - Steam distillation

Like vacuum distillation, steam distillation is a method for distilling compounds which are heat-sensitive. The temperature of the steam is easier to control than the surface of a heating element, and allows a high rate of heat transfer without heating at a very high temperature. This process involves bubbling steam through a heated mixture of the raw material. By Raoult's law, some of the target compound will vaporize (in accordance with its partial pressure). The vapor mixture is cooled and condensed, usually yielding a layer of oil and a layer of water.

Steam distillation of various aromatic herbs and flowers can result in two products; an essential oil as well as a watery herbal distillate. The essential oils are often used in perfumery and aromatherapy while the watery distillates have many applications in aromatherapy, food processing and skin care.



Perkin triangle distillation setup

*1: Stirrer bar/anti-bumping granules 2 : Still pot
3 : Fractionating column 4 : Thermometer/Boiling point temperature 5 : Teflon tap 1 6 : Cold finger 7 : Cooling water out 8: Cooling water in 9 : Teflon tap 2 10 : Vacuum/gas inlet
11: Teflon tap 3 12 : Still receiver*

5 – 4 - Vacuum distillation

Some compounds have very high boiling points. To boil such compounds, it is often better to lower the pressure at which such compounds are boiled instead of increasing the temperature. Once the pressure is lowered to the vapor pressure of the compound (at the given temperature), boiling and the rest of the distillation process can commence. This technique is referred to as vacuum distillation and it is commonly found in the laboratory in the form of the rotary evaporator.

Dimethyl sulfoxide usually boils at 189 °C. Under a vacuum, it distills off into the receiver at only 70 °C.

This technique is also very useful for compounds which boil beyond their decomposition temperature at atmospheric pressure and which would therefore be decomposed by any attempt to boil them under atmospheric pressure.

Molecular distillation is vacuum distillation below the pressure of 0.01 torr. 0.01 torr is one order of magnitude above high vacuum, where fluids are in the free molecular flow regime, i.e. the mean free path of molecules is comparable to the size of the equipment. The gaseous phase no longer exerts significant pressure on the substance to be evaporated, and consequently, rate of evaporation no longer depends on pressure. That is, because the continuum assumptions of fluid dynamics no longer apply, mass transport is governed by molecular dynamics rather than fluid dynamics. Thus, a short path between the hot surface and the cold surface is necessary, typically by suspending a hot plate covered with a film of feed next to a cold plate with a line of sight in between. Molecular distillation is used industrially for purification of oils.

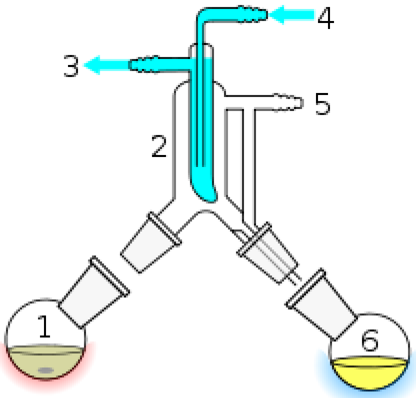
5 – 5 - Air - sensitive vacuum distillation

Some compounds have high boiling points as well as being air sensitive. A simple vacuum distillation system as exemplified above can be used, whereby the vacuum is replaced with an inert gas after the distillation is complete. However, this is a less satisfactory system if one desires to collect fractions under a reduced pressure. To do this a "cow" or "pig" adaptor can be added to the end of the condenser, or for better results or for very air sensitive compounds a Perkin triangle apparatus can be used.

The Perkin triangle, has means via a series of glass or Teflon taps to allows fractions to be isolated from the rest of the still, without the main body of the distillation being removed from either the vacuum or heat source, and thus can remain in a state of reflux. To do this, the sample is first isolated from the vacuum by means of the taps, the vacuum over the sample is then replaced with an inert gas (such as nitrogen or argon) and can then be stoppered and removed. A fresh collection vessel can then be added to the system, evacuated and linked back into the distillation system via the taps to collect a second fraction, and so on, until all fractions have been collected.

5 – 7 - Short path distillation

Short path distillation is a distillation technique that involves the distillate travelling a short distance, often only a few centimeters, and is normally done at reduced pressure . A classic example would be a distillation involving the distillate travelling from one glass bulb to another, without the need for a condenser separating the two chambers. This technique is often used for compounds which are unstable at high temperatures or to purify small amounts of compound. The advantage is that the heating temperature can be considerably lower (at reduced pressure) than the boiling point of the liquid at standard pressure, and the distillate only has to travel a short distance before condensing. A short path ensures that little compound is lost on the sides of the apparatus. The Kugelrohr is a kind of a short path distillation apparatus which often contain multiple chambers to collect distillate fractions.



Short path vacuum distillation apparatus with vertical condenser (cold finger), to minimize the distillation path ;
1: Still pot with stirrer bar/anti-bumping granules
2: Cold finger – bent to direct condensate
3: Cooling water out
4: cooling water in
5: Vacuum/gas inlet 6: Distillate flask/distillate.

5 – 7 - Zone distillation

Zone distillation is a distillation process in long container with partial melting of refined matter in moving liquid zone and condensation of vapor in the solid phase at condensate pulling in cold area. The process is worked in theory. When zone heater is moving from the top to the bottom of the container then solid condensate with irregular impurity distribution is forming. Then most pure part of the condensate may be extracted as product. The process may be iterated many times by moving (without turnover) the received condensate to the bottom part of the container on the place of refined matter. The irregular impurity distribution in the condensate (that is efficiency of purification) increases with number of repetitions of the process. Zone distillation is a distillation analog of zone recrystallization. Impurity distribution in the condensate is described by known equations of zone recrystallization with various numbers of iteration of process – with replacement distribution efficient k of crystallization on separation factor α of distillation.

5 – 8 - Other types

The process of reactive distillation involves using the reaction vessel as the still. In this process, the product is usually significantly lower-boiling than its reactants. As the product is formed from the reactants, it is vaporized and removed from the reaction mixture. This technique is an example of a continuous vs. a batch process; advantages include less downtime to charge the reaction vessel with starting material, and less work up.

Catalytic distillation is the process by which the reactants are catalyzed while being distilled to continuously separate the products from the reactants. This method is used to assist equilibrium reactions reach completion.

Perevaporation is a method for the separation of mixtures of liquids by partial vaporization through a non-porous membrane.

Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, that forms no azeotrope with the other components in the mixture.

Flash evaporation (or partial evaporation) is the partial vaporization that occurs when a saturated liquid stream undergoes a reduction in pressure by passing through a throttling valve or other throttling device. This process is one of the simplest unit operations, being equivalent to a distillation with only one equilibrium stage.

Co distillation is distillation which is performed on mixtures in which the two compounds are not miscible.

The unit process of evaporation may also be called "distillation":

In rotary evaporation a vacuum distillation apparatus is used to remove bulk solvents from a sample. Typically the vacuum is generated by a water aspirator or a membrane pump.

In a kugelrohr a short path distillation apparatus is typically used (generally in combination with a (high) vacuum) to distill high boiling (> 300 °C) compounds. The apparatus consists of an oven in which the compound to be distilled is placed, a receiving portion which is outside of the oven, and a means of rotating the sample. The vacuum is normally generated by using a high vacuum pump.

Other uses :

Dry distillation or destructive distillation, despite the name, is not truly distillation, but rather a chemical reaction known as pyrolysis in which solid substances are heated in an inert or reducing atmosphere and any volatile fractions, containing high-boiling liquids and products of pyrolysis, are collected. The destructive distillation of wood to give methanol is the root of its common name – *wood alcohol*.

Freeze distillation is an analogous method of purification using freezing instead of evaporation. It is not truly distillation, but a recrystallization where the product is the mother liquor, and does not produce products equivalent to distillation. This process is used in the production of ice beer and ice wine to increase ethanol and sugar content, respectively. It is also used to produce applejack. Unlike distillation, freeze distillation concentrates poisonous congeners rather than removing them; As a result, many countries prohibit such applejack as a health measure. However, reducing methanol with the absorption of 4A molecular sieve is a practical method for production. Also, distillation by evaporation can separate these since they have different boiling points.

6 - Azeotropic distillation

Interactions between the components of the solution create properties unique to the solution, as most processes entail nonideal mixtures, where Raoult's law does not hold. Such interactions can result in a constant-boiling azeotrope which behaves as if it were a pure compound (i.e., boils at a single temperature instead of a range). At an azeotrope, the solution contains the given component in the same proportion as the vapor, so that evaporation does not change the purity, and distillation does not effect separation. For example, ethyl alcohol and water form an azeotrope of 95.6 % at 78.1 °C.

If the azeotrope is not considered sufficiently pure for use, there exist some techniques to break the azeotrope to give a pure distillate. This set of techniques are known as azeotropic distillation. Some techniques achieve this by "jumping" over the azeotropic composition (by adding an additional component to create a new azeotrope, or by varying the pressure). Others work by chemically or physically removing or sequestering the impurity. For example, to purify ethanol beyond 95 %, a drying agent or a (desiccant such as potassium carbonate) can be added to convert the soluble water into insoluble water of crystallization. Molecular sieves are often used for this purpose as well.

Immiscible liquids, such as water and toluene, easily form azeotropes. Commonly, these azeotropes are referred to as a low boiling azeotrope because the boiling point of the azeotrope is lower than the boiling point of either pure component. The temperature and composition of the azeotrope is easily predicted from the vapor pressure of the pure components, without use of Raoult's law. The azeotrope is easily broken in a distillation set-up by using a liquid-liquid separator (a decanter) to separate the two liquid layers that are condensed overhead. Only one of the two liquid layers is refluxed to the distillation set-up.

High boiling azeotropes, such as a 20 weight percent mixture of hydrochloric acid in water, also exist. As implied by the name, the boiling point of the azeotrope is greater than the boiling point of either pure component.

To break azeotropic distillations and cross distillation boundaries, such as in the De Rosier Problem, it is necessary to increase the composition of the light key in the distillate.

6 – 1 - Breaking an azeotrope with unidirectional pressure manipulation

The boiling points of components in an azeotrope overlap to form a band. By exposing an azeotrope to a vacuum or positive pressure, it's possible to bias the boiling point of one component away from the other by exploiting the differing vapour pressure curves of each; the curves may overlap at the azeotropic point, but are unlikely to be remain identical further along the pressure axis either side of the azeotropic point. When the bias is great enough, the two boiling points no longer overlap and so the azeotropic band disappears.

This method can remove the need to add other chemicals to a distillation, but it has two potential drawbacks.

Under negative pressure, power for a vacuum source is needed and the reduced boiling points of the distillates requires that the condenser be run cooler to prevent distillate vapours being lost to the vacuum source. Increased cooling demands will often require additional energy and possibly new equipment or a change of coolant.

Alternatively, if positive pressures are required, standard glassware can not be used, energy must be used for pressurization and there is a higher chance of side reactions occurring in the distillation, such as decomposition, due to the higher temperatures required to effect boiling.

A unidirectional distillation will rely on a pressure change in one direction, either positive or negative.

6 – 2 - Pressure - swing distillation

Pressure - swing distillation is essentially the same as the unidirectional distillation used to break azeotropic mixtures, but here both positive and negative pressures may be employed.

This has an important impact on the selectivity of the distillation and allows a chemist to optimize a process such that fewer extremes of pressure and temperature are required and less energy is consumed. This is particularly important in commercial applications.

Pressure - swing distillation is employed during the industrial purification of ethyl acetate after its catalytic synthesis from ethanol.

7 - Industrial distillation

Typical industrial distillation towers

Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The most widely used industrial applications of continuous, steady-state fractional distillation are in petroleum refineries, petrochemical and chemical plants and natural gas processing plants.

Industrial distillation is typically performed in large, vertical cylindrical columns known as distillation towers or distillation columns with diameters ranging from about 65 centimeters to 16 meters and heights ranging from about 6 meters to 90 meters or more. When the process feed has a diverse composition, as in distilling crude oil, liquid outlets at intervals up the column allow for the withdrawal of different *fractions* or products having different boiling points or boiling ranges. The "lightest" products (those with the lowest boiling point) exit from the top of the columns and the "heaviest" products (those with the highest boiling point) exit from the bottom of the column and are often called the bottoms.

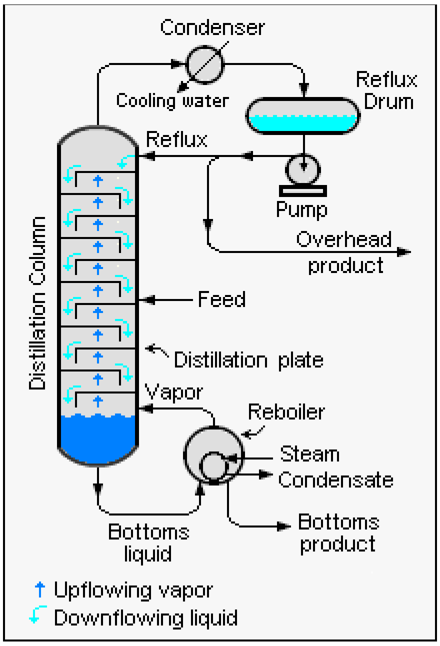
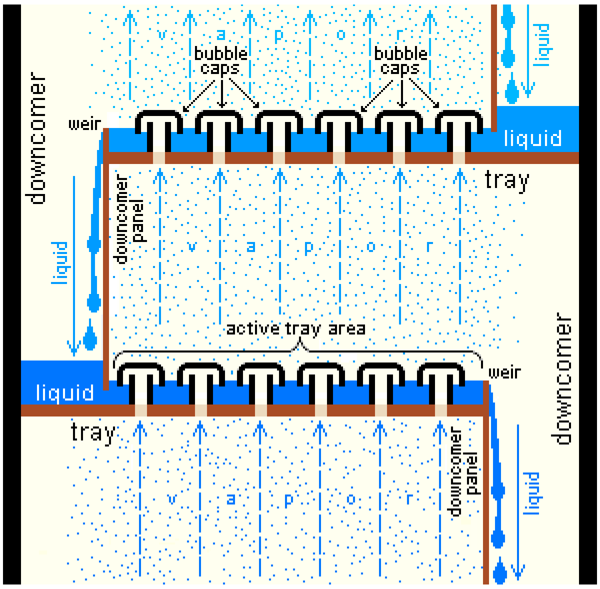


Diagram of a typical industrial distillation tower

Industrial towers use reflux to achieve a more complete separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower as shown in the schematic diagram of a typical, large-scale industrial distillation tower. Inside the tower, the down flowing reflux liquid provides cooling and condensation of the up flowing vapors thereby increasing the efficiency of the distillation tower. The more reflux that is provided for a given number of theoretical plates, the better the tower's separation of lower boiling materials from higher boiling materials. Alternatively, the more reflux that is provided for a given desired separation, the fewer the number of theoretical plates required.

Such industrial fractionating towers are also used in air separation, producing liquid oxygen, liquid nitrogen, and high purity argon. Distillation of chlorosilanes also enables the production of high-purity silicon for use as a semiconductor.



Section of an industrial distillation tower showing detail of trays with bubble caps

Design and operation of a distillation tower depends on the feed and desired products. Given a simple, binary component feed, analytical methods such as the McCabe - Thiele method or the Fenske equation can be used. For a multi-component feed, simulation models are used both for design and operation. Moreover, the efficiencies of the vapor-liquid contact devices (referred to as "plates" or "trays") used in distillation towers are typically lower than that of a theoretical 100% efficient equilibrium stage. Hence, a distillation tower needs more trays than the number of theoretical vapor-liquid equilibrium stages.

In modern industrial uses, a packing material is used in the column instead of trays when low pressure drops across the column are required. Other factors that favor packing are: vacuum systems, smaller diameter columns, corrosive systems, systems prone to foaming, systems requiring low liquid holdup and batch distillation. Conversely, factors that favor plate columns are: presence of solids in feed, high liquid rates, large column diameters, complex columns, columns with wide feed composition variation, columns with a chemical reaction, absorption columns, columns limited by foundation weight tolerance, low liquid rate, large turn-down ratio and those processes subject to process surges.

Large - scale, industrial vacuum distillation column

This packing material can either be random dumped packing (1–3" wide) such as Raschig rings or structured sheet metal. Liquids tend to wet the surface of the packing and the vapors pass across this wetted surface, where mass transfer takes place. Unlike conventional tray distillation in which every tray represents a separate point of vapor-liquid equilibrium, the vapor-liquid equilibrium curve in a packed column is continuous. However, when modeling packed columns, it is useful to compute a number of "theoretical stages" to denote the separation efficiency of the packed column with respect to more traditional trays. Differently shaped packings have different surface areas and void space between packings. Both of these factors affect packing performance.

Another factor in addition to the packing shape and surface area that affects the performance of random or structured packing is the liquid and vapor distribution entering the packed bed. The number of theoretical stages required to make a given separation is calculated using a specific vapor to liquid ratio. If the liquid and vapor are not evenly distributed across the superficial tower area as it enters the packed bed, the liquid to vapor ratio will not be correct in the packed bed and the required separation will not be achieved. The packing will appear to not be working properly. The height equivalent of a theoretical plate (HETP) will be greater than expected. The problem is not the packing itself but the mal - distribution of the fluids entering the packed bed. Liquid mal - distribution is more frequently the problem than vapor. The design of the liquid distributors used to introduce the feed and reflux to a packed bed is critical to making the packing perform to it maximum efficiency. Methods of evaluating the effectiveness of a liquid distributor to evenly distribute the liquid entering a packed bed can be found in references. Considerable work as been done on this topic by Fractionation Research, Inc. (commonly known as FRI).

7 – 1 - Multi - effect distillation

The goal of multi - effect distillation is to increase the energy efficiency of the process, for use in desalination, or in some cases one stage in the production of ultrapure water. The number of effects is proportional to the kW·h/m^3 of water recovered figure, and refers to the volume of water recovered per unit of energy compared with single-effect distillation. One effect is roughly 636 kW·h / m^3.

Multi-stage flash distillation Can achieve more than 20 effects with thermal energy input, as mentioned in the article.

Vapor compression evaporation Commercial large-scale units can achieve around 72 effects with electrical energy input, according to manufacturers.

There are many other types of multi-effect distillation processes, including one referred to as simply multi-effect distillation (MED), in which multiple chambers, with intervening heat exchangers, are employed.

8 - Distillation in food processing

8 – 1 - Distilled beverages

Carbohydrate - containing plant materials are allowed to ferment, producing a dilute solution of ethanol in the process. Spirits such as whiskey and rum are prepared by distilling these dilute solutions of ethanol. Components other than ethanol, including water, esters, and other alcohols, are collected in the condensate, which account for the flavor of the beverage.

9 - Gallery

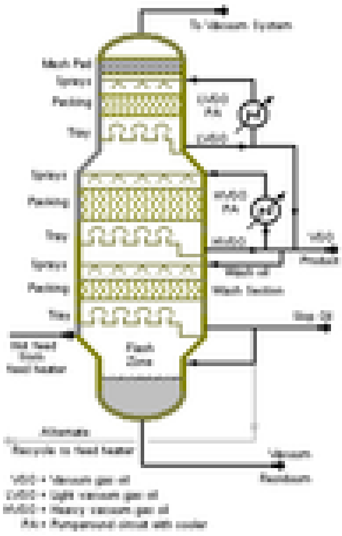


Diagram of an industrial-scale vacuum distillation column as commonly used in oil refineries

Distilled Beverage

Contents

1 - Introduction

A **distilled beverage**, **spirit**, or **liquor** is an alcoholic beverage containing ethanol that is produced by distilling (i.e., concentrating by distillation) ethanol produced by means of fermenting grain, fruit, or vegetables. This excludes undistilled fermented beverages such as beer, wine, and cider. Vodka, gin, baijiu, tequila, rum, whisky, brandy, and soju are examples of distilled beverages.

The term **hard liquor** is used in North America and India to distinguish distilled beverages from undistilled ones (implicitly weaker).

2 - Nomenclature

The term **spirit** refers to a distilled beverage that contains no added sugar and has at least 20 % alcohol by volume (ABV). Popular spirits include brandy, fruit brandy (also known as *eau-de-vie* or *Schnapps*), gin, rum, tequila, vodka, and whisky.

Distilled beverages bottled with added sugar and added flavorings, such as Grand Marnier, Frangelico, and American schnapps, are liqueurs. In common usage, the distinction between spirits and liqueurs is widely unknown or ignored; consequently, all alcoholic beverages other than beer and wine are generally referred to as spirits.

Beer and wine, which are not distilled beverages, are limited to a maximum alcohol content of about 20 % ABV, as most yeasts cannot reproduce when the concentration of alcohol is above this level; consequently, fermentation ceases at that point.

3 - Etymology

The origin of "liquor" and its close relative "liquid" was the Latin verb *liquere*, meaning "to be fluid". According to the *Oxford English Dictionary*, an early use of the word in the English language, meaning simply "a liquid", can be dated to 1225. The first use the *OED* mentions of its meaning "a liquid for drinking" occurred in the 14th century. Its use as a term for “an intoxicating alcoholic drink” appeared in the 16th century.

The term "spirit" in reference to alcohol stems from Middle Eastern alchemy. These alchemists were more concerned with medical elixirs than with transmuting lead into gold. The vapor given off and collected during an alchemical process (as with distillation of alcohol) was called a spirit of the original material.

4 - History of distillation

4 - 1 - Ancient history

The first clear evidence of distillation comes from Greek alchemists working in Alexandria in the first century AD. Distilled water was described in the second century AD by Alexander of Aphrodisias . The Alexandrians were using a distillation alembic or still device in the third century AD. Distillation in China could have begun during the Eastern Han Dynasty (1st – 2nd centuries), but archaeological evidence indicates that actual distillation of beverages began in the Jin and Southern Song dynasties. A still was found in an archaeological site in Qinglong, Hebei province dating to the 12th century. Distilled beverages were more common during the Yuan dynasty. The medieval Arabs learned the distillation process from the Alexandrians and used it extensively, but there is no evidence that they distilled alcohol.

4 - 2 - Central Asia

Freeze distillation, the "Mongolian still", is known to have been in use in Central Asia sometime in the early Middle Ages. This technique involves freezing the alcoholic beverage and then removing the ice. The freezing technique had limitations in geography and implementation, so was not widely used.

Many believe there is a notable drawback of this technique because it concentrates toxins such as methanol and fusel oil, rather than reducing their concentration. Yet this is untrue. Freezing distillation merely extracts the water out of the substance, leaving less liquid with more abv (alcohol by volume). Natural juices contain methanol (wood alcohol) and at low doses methanol is untoxic. A person may consume a bottle of wine (750mls at 12 percent abv), or rather use freezing distillation to remove two-thirds the excess water, leaving them with 250mls at 36 percent alcohol. Therefore the substance has not chemically changed, but rather been condensed by the withdraw of water. Fusel oils are not toxic either. Many whisky manufactures will add a hint of fusel oils to the main batch in order to give the whisky a rustic taste. Fusel oils are generally not used but rather disgarded because of their unpleasent taste.

4 - 3 - Medieval Europe

The earliest evidence of the distillation of alcohol comes from the School of Salerno in southern Italy in the 12th century.

Fractional distillation was developed by Tadeo Alderotti in the 13th century. The production method was written in code, suggesting it was being kept secret.

In 1437, "burned water" (brandy) was mentioned in the records of the County of Katzenelnbogen in Germany. It was served in a tall, narrow glass called a *Goderulffe*.

Paracelsus experimented with distillation. His test was to burn a spoonful without leaving any residue. Other ways of testing were to burn a cloth soaked in it without actually harming the cloth. In both cases, to achieve this effect, the alcohol had to have been at least 95 percent, close to the maximum concentration attainable through distillation (see purification of ethanol).

Claims upon the origin of specific beverages are controversial, often invoking national pride, but they are plausible after the 12th century AD, when Irish whiskey and German brandy became available. These spirits would have had a much lower alcohol content (about 40% ABV) than the alchemists' pure distillations, and they were likely first thought of as medicinal elixirs. Consumption of distilled beverages rose dramatically in Europe in and after the mid-14th century, when distilled liquors were commonly used as remedies for the Black Death. Around 1400, methods to distill spirits from wheat, barley, and rye beers, a cheaper option than grapes, were discovered. Thus began the "national" drinks of Europe: *jenever* (Belgium and the Netherlands), gin (England), *Schnaps* (Germany), *grappa* (Italy), *horilka* (Ukraine), *akvavit*/*snaps* (Scandinavia), *vodka* (Russia and Poland), *ouzo* (Greece), *rakia* (the Balkans), and *poitín* (Ireland). The actual names only emerged in the 16th century, but the drinks were well known prior to then.

4 - 4 - Modern distillation

Except for the invention of the continuous still in the 19th century, the basic process of distillation has not changed since the eighth century. Many changes in the methods used to prepare organic material for the still have occurred, and the ways the distilled beverage is finished and marketed have changed. Knowledge of the principles of sanitation and access to standardized yeast strains have improved the quality of the base ingredients. Larger, more efficient stills reduce waste and produce more beverage in smaller areas.

Chemists have discovered the scientific principles behind aging, and have devised ways to accelerate aging without introducing harsh flavors . Modern filters have allowed distillers to remove unwanted residues and produce smoother finished products . Most of all, marketing has developed a worldwide market for distilled beverages among populations that previously did not drink spirits.

4 – 4 - 1 - Government regulation

In some jurisdictions in the United States, it is legal for unlicensed individuals to make their own beer and wine. However, it is illegal to distill beverage alcohol without a license anywhere in the US. In some jurisdictions, it is also illegal to sell a still without a license.

It is legal to distill beverage alcohol as a hobby for personal use in some countries, including Italy, New Zealand, Netherlands, and (to a limited degree) the United Kingdom. In those jurisdictions where it is illegal to distill beverage alcohol, some people circumvent those laws by purporting to distill alcohol for fuel but consuming the product. It is important not to confuse ethanol, which is a type of alcohol used for both beverages and fuel, with methanol, which is a different alcohol fuel that is *much more* poisonous. Methanol is produced as a by - product of beverage distillation, but only in small amounts which are ordinarily separated out during the beverage production process. Methanol can cause blindness or death if ingested.

4 – 4 - 2 – Micro distilling

Micro distilling as a trend began to develop in the United States following the emergence and immense popularity of micro brewing and craft beer in the last decades of the 20th century. It is different from mega distilling in the quantity and quality of output.

5 - Flammability

Liquor that contains 40 % ABV (80 US proof) will catch fire if heated to about 26 °C and if an ignition source is applied to it. (This is called its flash point. The flash point of pure alcohol is 16.60 °C , less than average room temperature.)

The flash points of alcohol concentrations from 10 % ABV to 96 % ABV are :

Concentrations %	**°C**	
10	49	Ethanol-based water solution
12.5	52	Wine
20	36	Fortified wine
30	29	
40	26	Typical whisky or brandy
50	24	Strong whisky
60	22	
70	21	Absinthe
80	20	
90 % or more	17	Neutral grain spirit

Beverages with low concentrations of alcohol will burn if sufficiently heated and an ignition source (such as an electric spark or a match) is applied to them. For example, the flash point of ordinary wine containing 12.5 % alcohol is about 52 °C .

6 - Serving

Distilled beverages can be served:

Neat or straight — at room temperature without any additional ingredient(s)

Straight up — shaken or stirred with ice, strained, and served in a stemmed glass

On the rocks — over ice cubes

Blended or frozen — blended with ice

With a simple mixer, such as club soda, tonic water, juice, or cola

As an ingredient of a cocktail

Fractional Freezing

Contents

1 - Introduction

Fractional freezing is a process used in process engineering and chemistry to separate two liquids with different melting points. It can be done by partial melting of a solid, for example in zone refining of silicon or metals, or by partial crystallization of a liquid, for example "**freeze distillation**", also called "**normal freezing**" or "**progressive freezing**".

Partial crystallization can also be achieved by adding a dilute solvent to the mixture, and cooling and concentrating the mixture by evaporating the solvent, a process called "solution crystallization". Fractional freezing is generally used to produce ultra-pure solids, or to concentrate heat-sensitive liquids.

2 - Freeze distillation

Freeze distillation is a term for a process of enriching a solution by partially freezing it and removing frozen material that is poorer in the dissolved material than is the liquid portion left behind. Such enrichment parallels enrichment by true distillation, where the evaporated and re condensed portion is richer than the liquid portion left behind.

Such enrichment by freezing of a solution in water is sometimes oversimplified by saying that, for instance, because of the difference in freezing points of water (0 °C/32 °F), and ethyl alcohol (-114 °C), "the water freezes into ice...while the ethyl alcohol remains liquid."

This is false, and although some of the implications of that description are true and useful, other conclusions drawn from it would be false.

The detailed situation is the subject of thermodynamics, a subdivision of physics of importance to chemistry. Without resorting to mathematics, the following can be said for a mixture of water and alcohol:

Freezing in this scenario begins at a temperature significantly below 0 °C.

The first material to freeze is not the water, but a dilute solution of alcohol in water.

The liquid left behind is richer in alcohol, and as a consequence, further freezing would take place at progressively lower temperatures. The frozen material, while always poorer in alcohol than the (increasingly rich) liquid, becomes progressively richer in alcohol.

Further stages of removing frozen material and waiting for more freezing will come to naught once the liquid uniformly cools to the temperature of whatever is cooling it.

If progressively colder temperatures are available, the frozen material will contain progressively larger concentrations of alcohol, and the fraction of the original alcohol removed with the solid material will increase.

In practice, unless the removal of solid material carries away liquid, the degree of concentration will depend on the final temperature rather than on the number of cycles of removing solid material and chilling.

Thermo dynamics gives fair assurance , even without more information about alcohol and water than that they freely dissolve in each other, that even if temperatures *some what below* the freezing point of ethyl alcohol are achieved, there will still be alcohol and water mixed as a liquid , and at some still lower temperature, the remaining alcohol – and - water solution will freeze without an alcohol-poor solid being separable.

Fractional freezing of grapes to concentrate grape sugar for making ice wine.

The best-known freeze-distilled beverages areapplejack and ice beer.Ice wine is the result of a similar process, but in this case, the freezing happens*before* the fermentation, and thus it is sugar, not alcohol, that gets concentrated. For an in depth discussion of the physics and chemistry, see eutectic point.

3 - Purification of solids

When a pure solid is desired, two possible situations can occur. If the contaminant is soluble in the desired solid, a multiple stage fractional freezing is required, analogous to multistage distillation. If, however, a eutectic system forms (analogous to an azeotrope in distillation), a very pure solid can be recovered, as long as the liquid is not at its eutectic composition (in which case a mixed solid forms, which can be hard to separate) or above its eutectic composition (in which case the undesired solid forms).

4 - Concentration of Liquids

When the requirement is to concentrate a liquid phase, fractional freezing can be useful due to its simplicity. Fractional freezing is also used in the production of fruit juice concentrates and other heat-sensitive liquids, as it does not involve heating the liquid (as happens during evaporation).

4 – 1 - Desalination

Fractional freezing can be used to desalinate sea water. In a process that naturally occurs with sea ice, frozen salt water, when partially melted, leaves behind ice that is of a much lower salt content. Because sodium chloride lowers the melting point of water, the salt in sea water tends to be forced out of pure water while freezing. Likewise, the frozen water with the highest concentration of salt melts first. Either method decreases the salinity of the frozen water left over, and with multiple runs can be drinkable.

4 – 2 - Alcoholic beverages

Fractional freezing can be used as a simple method to increase the alcohol concentration in fermented alcoholic beverages, a process sometimes called freeze distillation. Examples are applejack, made from hard cider, and ice beer. In practice, while not able to produce an alcohol concentration comparable to distillation, this technique can achieve some concentration with far less effort than any practical distillation apparatus would require. Freeze distillation of alcoholic beverages is illegal in many countries.

Freeze distillation can concentrate methanol and fusel alcohols (by-products of fermentation which true distillation separates out) in applejack to unhealthy levels . As a result, many countries prohibit such applejack as a health measure. However, reducing methanol with the absorption of 4 A molecular sieve is a practical method for production . Also, distillation by evaporation can separate these since they have different boiling points.

4 – 3 - Alternative Fuels

Fractional freezing is commonly used as a simple method to reduce the gel point of Biodiesel and other alternative diesel fuels, whereby esters of higher gel point are removed from esters of lower gel point through cold filtering, or other methods to reduce the subsequent alternative fuel gel point of the fuel blend. This process employs fuel stratification whereby components in the fuel blend develop a higher specific gravity as they approach their respective gel points and thus sink to the bottom of the container, where they can be

Wine

16th - century wine press

Wine glasses of white wine and red wine

Contents

1 - Introduction

Wine is an alcoholic beverage made from fermented grapes or other fruits. The natural chemical balance of grapes lets them ferment without the addition of sugars , acids , enzymes , water, or other nutrients . Yeast consumes the sugars in the grapes and converts them into alcohol. Different varieties of grapes and strains of yeasts produce different types of wine. The well-known variations result from the very complex interactions between the biochemical development of the fruit, reactions involved in fermentation, and human intervention in the overall process. The final product may contain tens of thousands of chemical compounds in amounts varying from a few percent to a few parts per billion.

Wines made from fruits besides grapes are usually named after the fruit from which they are produced (for example , pomegranate wine , apple wine and elder berry wine) and are generically called fruit wine. The term "wine" can also refer to starch-fermented or fortified beverages having higher alcohol content, such as barley wine or sake.

Wine has a rich history dating back thousands of years, with the earliest known production occurring around 6000 BC in Georgia. It first appeared in the Balkans about 4500 BC and was very common in ancient Greece , Thrace and Rome. Wine has also played an important role in religion throughout history. The Greek god Dionysus and the Roman equivalent, Bacchus, represented wine . The drink is also used in Christian Eucharist ceremonies and the Jewish Kiddush.

2 - Etymology

The English word "wine" comes from the Proto - Germanic * *winam*, an early borrowing from the Latin *vinum*, "wine" or "(grape) vine" , itself derived from the Proto-Indo- Europeanstem * *win-o-* (cf. Hittite : *wiyana* ; Lycian : *oino*; Ancient Greek: *oinos* ; Aeolic Greek: *woinos*).

The earliest attested terms referring to wine are the Mycenaean Greek *me-tu-wo ne-wo* , meaning "the month of new wine" or "festival of the new wine", and *wo-no-wa-ti-si*, meaning "wine garden", written in Linear B inscriptions.

Wines from other fruits, such as apples and berries, are usually named after the fruit from which they are produced combined with the word "wine" (for example, apple wine and elder berry wine) and are generically called fruit wine or country wine (not to be confused with the French term *vin de pays*). Besides the grape varieties traditionally used for winemaking, most fruits naturally lack either a high amount of fermentable sugars, relatively low acidity, yeast nutrients needed to promote or maintain fermentation or a combination of these three characteristics. This is probably one of the main reasons why wine derived from grapes has historically been more prevalent by far than other types and why specific types of fruit wine have generally been confined to regions in which the fruits were native or introduced for other reasons.

Other wines, such as barley wine and rice wine (e.g. sake), are made from starch-based materials and resemble beermore than wine, while ginger wine is fortified with brandy. In these latter cases, the term "wine" refers to the similarity in alcohol content rather than to the production process . The commercial use of the English word "wine" (and its equivalent in other languages) is protected by law in many jurisdictions.

3 - History

Archaeological evidence suggests that the earliest known production of wine, made by fermenting grapes, took place from the late Neolithic or early Chalcolithic , possibly as early as the sixth millennium BC, between the Caucasus and the Middle East, with evidence of winemaking at different sites dated from 6000 BC in Georgia , 5000 BC in Iran, and 4100 BC in Armenia . During an extensive gene-mapping project in 2006, archaeologists analyzed the heritage of more than 110 modern grape cultivars, narrowing their origin to a region in Georgia, where wine residues were also discovered on the inner surfaces of 8,000-year-old ceramic storage jars. Chemical analysis of 7,000-year-old pottery shards indicated early winemaking in the Neolithic village of Hajji Firuz Tepe in Iran's Zagros Mountains. Other notable areas of wine production have been discovered in Greece and date back to 4500 BC. The same sites also contain the world's earliest evidence of crushed grapes. A wine making press found in 2011 in the Areni-1 site of Armenia has been dated to around 4100 BC.

However, the spread of wine culture westwards was most probably due to the Phoenicians who were centered on the coastal strip of today’s Lebanon – itself one of the world’s oldest sites of wine production. The wines of Byblos were exported to Egypt during the Old Kingdom (2686 BC–2134 BC) and throughout the Mediterranean. Evidences include two Phoenician shipwrecks from 750 BC discovered by Robert Ballard, whose cargo of wine was still intact.[23] As the first great traders of wine ('Cherem'), the Phoenicians seem to have protected it from oxidation with a layer of olive oil, followed by a seal of pinewood and resin - this may well be the origin of the Greek retsina.

Literary references to wine are abundant in Homer (8th century BC, but possibly composed even earlier), Alkman (7th century BC), and others. In ancient Egypt, six of 36 wine amphoras were found in the tomb of King Tutankhamun bearing the name "Kha'y", a royal chief vintner. Five of these amphoras were designated as originating from the king's personal estate, with the sixth from the estate of the royal house of Aten. Traces of wine have also been found in central Asian Xinjiang in modern-day China, dating from the second and first millennia BC.

The first known mention of grape -based wines in Indiais from the late 4th-century BC writings of Chanakya, the chief minister of Emperor Chandragupta Maurya. In his writings, Chanakya condemns the use of alcohol while chronicling the emperor and his court's frequent indulgence of a style of wine known as *madhu*.

Pressing wine after the harvest ; Tacuinum Sanitatis, 14th century

A 2003 report by archaeologists indicates a possibility that grapes were mixed with rice to produce mixed fermented beverages in China in the early years of the seventh millennium BC. Pottery jars from the Neolithic site of Jiahu, Henan, contained traces of tartaric acid and other organic compounds commonly found in wine. However, other fruits indigenous to the region, such as hawthorn, cannot be ruled out . If these beverages, which seem to be the precursors of rice wine, included grapes rather than other fruits, they would have been any of the several dozen indigenous wild species in China, rather than *Vitis vinifera*, which was introduced there some 6,000 years later.

One of the lasting legacies of the ancient Roman Empirewas the viticultural foundation laid by the Romans in the areas that today are world - renowned wine regions. In places with garrison towns (e.g. Bordeaux, Trier, and Colchester), the Romans planted vineyards to supply local needs and limit the cost of long-distance trading. In medieval Europe, the Roman Catholic Church supported wine because the clergy required it for the Mass. Monks in France made wine for years, aging it in caves.[30] An old English recipe that survived in various forms until the 19th century calls for refining white wine from bastard — ad or tainted *bastardo* wine.

4 - Grape varieties

Grape vine yard

Wine is usually made from one or more varieties of the Europeans pecies *Vitis vinifera*, such as Pinot Noir, Chardonnay , Cabernet Sauvignon , Gamay and Merlot. When one of these varieties is used as the predominant grape (usually defined by law as minimums of 75 % to 85 %), the result is a "varietal" as opposed to a "blended" wine. Blended wines are not considered inferior to varietal wines, rather they are a different style of winemaking; some of the world's most highly regarded wines, from regions like Bordeaux and the Rhone Valley, are blended from different grape varieties

Wine can also be made from other species of grape or from hybrids, created by the genetic crossing of two species. *V. labrusca* (of which the Concord grape is acultivar), *V. aestivalis*, *V. ruprestris*, *V. rotundifolia* and *V. riparia* are native North American grapes usually grown to eat fresh or for grape juice, jam, or jelly, and only occasionally made into wine.

Hybridization is different from grafting. Most of the world's vineyards are planted with European *V. vinifera* vines that have been grafted onto North American species' rootstock, a common practice due to their resistance to phylloxera, a root louse that eventually kills the vine. In the late 19th century, most of Europe's vineyards (excluding some of the driest in the south) were devastated by the infestation, leading to widespread vine deaths and eventual replanting. Grafting is done in every wine-producing region in the world except in Argentina, the Canary Islands and Chile - the only places not yet exposed to the insect.

In the context of wine production, *terroir* is a concept that encompasses the varieties of grapes used, elevation and shape of the vineyard, type and chemistry of soil, climate and seasonal conditions, and the local yeast cultures. The range of possible combinations of these factors can result in great differences among wines, influencing the fermentation, finishing, and aging processes as well. Many wineries use growing and production methods that preserve or accentuate the aroma and taste influences of their unique *terroir*. However , flavor differences are less desirable for producers of mass-market table wine or other cheaper wines, where consistency takes precedence. Such producers try to minimize differences in sources of grapes through production techniques such as micro-oxygenation, tannin filtration, cross-flow filtration, thin-film evaporation, and spinning cones.

5 – Classification

Wine grapes on a vine

Regulations govern the classification and sale of wine in many regions of the world. European wines tend to be classified by region (e.g. Bordeaux , Riojaand Chianti), while non-European wines are most often classified by grape (e.g. Pinot Noir and Merlot). Market recognition of particular regions has recently been leading to their increased prominence on non-European wine labels. Examples of recognized non-European locales include Napa Valley and Sonoma Valley in California; Willamette Valley in Oregon; Columbia Valley in Washington; Barossa Valley in South Australia and Hunter Valley in New South Wales; Luján de Cuyo inArgentina; Central Valley in Chile ; Vale dos Vinhedos inBrazil; Hawke's Bay and Marlborough in New Zealand; and Okanagan Valley and Niagara Peninsula in Canada.

Some blended wine names are marketing terms whose use is governed by trade mark law rather than by specific wine laws. For example, Meritage (sounds like "heritage") is generally a Bordeaux-style blend of Cabernet Sauvignon and Merlot, but may also include Cabernet Franc, Petit Verdot, and Malbec. Commercial use of the term Meritage is allowed only via licensing agreements with the Meritage Association.

5 – 1 -European classifications

France has various appellation systems based on the concept of *terroir* , with classifications ranging from *Vin de Table*("table wine") at the bottom, through *Vin de Pays* and *Appellation d' Origine Vin Délimité de Qualité Supérieure* (AOVDQS), up to *Appellation d'Origine Contrôlée* (AOC) or similar, depending on the region. Portugal has developed a system resembling that of France and, in fact, pioneered this concept in 1756 with a royal charter creating the Demarcated Douro Region and regulating the production and trade of wine. Germany created a similar scheme in 2002, although it has not yet achieved the authority of the other countries' classification systems. Spain , Greece and Italy have classifications based on a dual system of region of origin and product quality.

5 – 2 - Beyond Europe

New World wines - those made outside the traditional wine regions of Europe - are usually classified by grape rather than by *terroir* or region of origin, although there have been unofficial attempts to classify them by quality.

6 - Vintages

A "vintage wine" is made from grapes that were all or mostly grown in a particular year, and labeled as such. Some countries allow a vintage wine to include a small portion that is not from the labeled vintage. Variations in a wine's character from year to year can include subtle differences in color, palate, nose, body and development. High-quality wines can improve in flavor with age if properly stored. Consequently, it is not uncommon for wine enthusiasts and traders to save bottles of an especially good vintage wine for future consumption.

In the United States, for a wine to be vintage - dated and labeled with a country of origin or American Viticultural Area (AVA) (e.g. Sonoma Valley), 95 % of its volume must be from grapes harvested in that year. If a wine is not labeled with a country of origin or AVA the percentage requirement is lowered to 85 %.

Vintage wines are generally bottled in a single batch so that each bottle will have a similar taste. Climate's impact on the character of a wine can be significant enough to cause different vintages from the same vineyard to vary dramatically in flavor and quality.[45] Thus, vintage wines are produced to be individually characteristic of the particular vintage and to serve as the flagship wines of the producer. Superior vintages from reputable producers and regions will often command much higher prices than their average ones. Some vintage wines (e.g. Brunello), are only made in better-than-average years.

For consistency, non-vintage wines can be blended from more than one vintage, which helps winemakers sustain a reliable market image and maintain sales even in bad years.[46][47] One recent study suggests that for the average wine drinker, the vintage year may not be as significant for perceived quality as had been thought, although wine connoisseurs continue to place great importance on it.

7 – Tasting

Wine tasting is the sensory examination and evaluation of wine. Wines contain many chemical compounds similar or identical to those in fruits, vegetables, and spices. The sweetness of wine is determined by the amount of residual sugar in the wine after fermentation, relative to the acidity present in the wine. Dry wine, for example, has only a small amount of residual sugar.

Judging color is the first step in tasting a wine.

Some wine labels suggest opening the bottle and letting the wine "breathe" for a couple of hours before serving, while others recommend drinking it immediately . Decanting (the act of pouring a wine into a special container just for breathing) is a controversial subject among wine enthusiasts. In addition to aeration, decanting with a filter allows the removal of bitter sediments that may have formed in the wine. Sediment is more common in older bottles, but aeration may benefit younger wines.

During aeration, a younger wine's exposure to air often "relaxes" the drink, making it smoother and better integrated in aroma, texture, and flavor. Older wines generally "fade" (lose their character and flavor intensity) with extended aeration.[50] Despite these general rules, breathing does not necessarily benefit all wines. Wine may be tasted as soon as the bottle is opened to determine how long it should be aerated, if at all .

When tasting wine, individual flavors may also be detected, due to the complex mix of organic molecules (e.g. esters and terpenes) that grape juice and wine can contain. Experienced tasters can distinguish between flavors characteristic of a specific grape and flavors that result from other factors in winemaking. Typical intentional flavor elements in wine - chocolate, vanilla, or coffee - are those imparted by aging in oak casks rather than the grape itself.

Banana flavors (iso amyl acetate) are the product of yeast metabolism, as are spoilage aromas such as sweaty, barnyard, band-aid (4- ethyl phenol and 4- ethyl guaiacol), and rotten egg (hydrogen sulfide). Some varietals can also exhibit a mineral flavor due to the presence of water-soluble salts as a result of limestone's presence in the vineyard's soil.

Wine aroma comes from volatile compounds released into the air.[54] Vaporization of these compounds can be accelerated by twirling the wine glass or serving at room temperature. Many drinkers prefer to chill red wines that are already highly aromatic, like Chinon and Beaujolais .

The ideal temperature for serving a particular wine is a matter of debate, but some broad guidelines have emerged that will generally enhance the experience of tasting certain common wines. A white wine should foster a sense of coolness, achieved by serving at "cellar temperature" (13°C). Light red wines drunk young should also be brought to the table at this temperature, where they will quickly rise a few degrees. Red wines are generally perceived best when served *chambré* ("at room temperature"). However, this does not mean the temperature of the dining room—often around 70°F/21°C—but rather the coolest room in the house and, therefore, always slightly cooler than the dining room itself. Pinot Noir should be brought to the table for serving at 16°C and will reach its full bouquet at 18°C. Cabernet Sauvignon, zinfandel, and Rhone varieties should be served at 18°C and allowed to warm on the table to 21°C for best aroma .

8 - Collecting

Outstanding vintages from the best vineyards may sell for thousands of dollars per bottle, though the broader term "fine wine" covers those typically retailing in excess of US$30–50.[57] "Investment wines" are considered by some to be Veblen goods: those for which demand increases rather than decreases as their prices rise. The most common wines purchased for investment include those from Bordeaux and Burgundy; cult wines from Europe and elsewhere ; and vintage port. Characteristics of highly collectible wines include :

A proven track record of holding well over time

A drinking-window plateau (i.e., the period for maturity and approachability) that is many years long

A consensus among experts as to the quality of the wines

Rigorous production methods at every stage, including grape selection and appropriate barrel aging

Investment in fine wine has attracted those who take advantage of their victims' relative ignorance of this wine market sector. Such wine fraudsters often profit by charging excessively high prices for off-vintage or lower-status wines from well-known wine regions, while claiming that they are offering a sound investment unaffected by economic cycles. As with any investment, thorough research is essential to making an informed decision.

9 – Production

Wine production by country 2009

Rank	Country	Production (millions of hecto litres)
1	Italy	47,699
2	France	45,558
3	Spain	32,506
4	United States	20,620
5	Argentina	12,135
6	China	12,000
7	Australia	11,600
8	Chile	10,093
9	South Africa	9,788
10	Germany	9,180
11	Russia	7,110
12	Romania	5,600

Wine grapes grow almost exclusively between 30 and 50 degrees latitude north and south of the equator. The world's southernmost vineyards are in the Central Otagoregion of New

Zealand's South Island near the 45th parallel south , and the northernmost are in Flen , Sweden , just north of the 59th parallel north.

10 - Exporting countries

Top ten wine exporting countries in 2006

Rank	Country	000 tonnes
1	Italy*	1,793
2	France	1,462
3	Spain*	1,337
4	Australia	762
5	Chile*	472
6	United States	369
7	Germany	316
8	Argentina	302
9	Portugal	286
10	South Africa	272
World**		**8,363**

* Unofficial figure.
** May include official, semi-official or estimated data.

11 - Consumption

Wine - consumption data from a list of countries by alcohol consumption measured in liters of pure ethyl alcohol consumed per capita in a given year, according to the most recent data from the World Health Organization. The methodology includes persons 15 years of age or older.

12 - Uses

Wine is a popular and important beverage that accompanies and enhances a wide range of European - and Mediterranean - style cuisines , from the simple and traditional to the most sophisticated and complex. Wine is important in cuisine not just for its value as a beverage, but as a flavor agent, primarily in stocks and braising, since its acidity lends balance to rich savory or sweet dishes. Natural wines usually contain from 8 –15 % alcohol by volume. Fortified wines (usually with brandy) are generally 18 to 20 % alcohol.

13 - Religious significance

13 – 1 - Ancient religions

The use of wine in religious ceremonies is common to many cultures and regions. Libations often included wine, and the religious mysteries of Dionysus used wine as a sacramental entheogen to induce a mind - altering state.

13 – 2 - Judaism

Wine is an integral part of Jewish laws and traditions. The *Kiddush* is a blessing recited over wine or grape juice to sanctify the Shabbat. On Pesach (Passover) during the Seder, it is a Rabbinic obligation of adults to drink four cups of wine.[67] In the Tabernacle and in the Temple in Jerusalem, the libation of wine was part of the sacrificial service. Note that this does not mean that wine is a symbol of blood, a common misconception that contributes to the myth of the blood libel. The blessing over wine said before consuming the drink is: *"Baruch atah Hashem* (Adonai) *Eloheinu melech ha-olam, boray p'ree hagafen"*—"Praised be the Lord, our God, King of the universe, Creator of the fruit of the vine."

13 – 3 – Christianity

In Christianity, wine is used in a sacred rite called the Eucharist, which originates in the Gospel account of the Last Supper (Gospel of Luke 22:19) describing Jesus sharing bread and wine with his disciples and commanding them to "do this in remembrance of me." Beliefs about the nature of the Eucharist vary among denominations .

While some Christians consider the use of wine from the grape as essential for the validity of the sacrament, many Protestants also allow (or require) pasteurized grape juice as a substitute. Wine was used in Eucharistic rites by all Protestant groups until an alternative arose in the late 19th century . Methodist dentist and prohibitionist Thomas Bramwell Welch applied new pasteurization techniques to stop the natural fermentation process of grape juice. Some Christians who were part of the growing temperance movement pressed for a switch from wine to grape juice, and the substitution spread quickly over much of the United States, as well as to other countries to a lesser degree . There remains an ongoing debate between some American Protestant denominations as to whether wine can and should be used for the Eucharist or allowed as an ordinary beverage.

	
The bishop elevates the chalice while the deacon fans the Gifts with the ripidion .	Jesus making wine from water in *The Marriage at Cana*, a 14th -century fresco from the Visoki Dečani monastery

12 – 4 - Islam

Alcoholic beverages, including wine, are forbidden under most interpretations of Islamic law. Iran had previously had a thriving wine industry that disappeared after the Islamic Revolution in 1979. In Greater Persia , *mey* (Persian wine) was a central theme of poetry for more than a thousand years, long before the advent of Islam . Some Alevi sects use wine in their religious services.

Certain exceptions to the ban on alcohol apply. Alcohol derived from a source other than the grape (or its byproducts) and the date is allowed in "very small quantities" (loosely defined as a quantity that does not cause intoxication) under the Sunni Hanafi *madhab* , for specific purposes (such as medicines), where the goal is not intoxication. However, modern Hanafi scholars regard alcohol consumption as totally forbidden.

14 - Health effects

Red table wine

Nutritional value per 100 g

Energy	355 kJ (85 kcal)
Carbohydrates	2.6 g
- Sugars	0.6 g
Fat	0.0 g
Protein	0.1 g
Alcohol	10.6 g

Although excessive alcohol consumption has adverse health effects, epidemiological studies have consistently demonstrated that moderate consumption of alcohol and wine is statistically associated with a decrease in cardiovascular illness such as heart failure. Additional news reports on the French paradox also back the relationship. This paradox concerns the comparatively low incidence of coronary heart disease in France despite relatively high levels of saturated fat in the traditional French diet. Some epidemiologists suspect that this difference is due to the higher consumption of wines by the French, but the scientific evidence for this theory is limited. Because the average moderate wine drinker is likely to exercise more often, to be more health conscious, and to be from a higher educational and socioeconomic background, the association between moderate wine drinking and better health may be related to confounding factors or represent a correlation rather than cause and effect.

Population studies have observed a J- curve association between wine consumption and the risk of heart disease: heavy drinkers have an elevated risk, while moderate drinkers (up to 20g of alcohol per day, approximately 120 ml (4 imp fl oz; 4 US fl oz) of 13 % ABV wine) have a lower risk than non-drinkers. Studies have also found that moderate consumption of other alcoholic beverages may be cardio protective, although the association is considerably stronger for wine. Additionally, some studies have found greater health benefits for red than white wine, though other studies have found no difference. Red wine contains more poly phenols than white wine, and these are thought to be particularly protective against cardiovascular disease.

A chemical in red wine called resveratrol has been shown to have both cardio protective and chemo protective effects in animal studies. Low doses of resveratrol in the diet of middle-aged mice has a widespread influence on the genetic factors related to aging and may confer special protection on the heart. Specifically, low doses of resveratrol mimic the effects of caloric restriction—diets with 20–30 % fewer calories than a typical diet. Resveratrol is produced naturally by grape skins in response to fungal infection, including exposure to yeast during fermentation. As white wine has minimal contact with grape skins during this process, it generally contains lower levels of the chemical. Beneficial compounds in wine also include other poly phenols, antioxidants, and flavonoids.

To benefit fully from resveratrol in wine, it is recommended to sip slowly when drinking. Due to inactivation in the gut and liver, most of the resveratrol consumed while drinking red wine does not reach the blood circulation. However, when sipping slowly, absorption via the mucous membranes in the mouth can result in up to 100 times the blood levels of resveratrol.

Red wines from the south of France and from Sardinia in Italy have been found to have the highest levels ofprocyanidins, compounds in grape seeds thought to be responsible for red wine's heart benefits. Red wines from these areas contain between two and four times as much procyanidins as other red wines tested. Procyanidins suppress the synthesis of a peptide called endothelin-1that constricts blood vessels.

A 2007 study found that both red and white wines are effective antibacterial agents against strains of *Streptococcus*. In addition, a report in the October 2008 issue of *Cancer Epidemiology, Biomarkers and Prevention* posits that moderate consumption of red wine may decrease the risk of lung cancer in men.

While evidence from laboratory and epidemiological (observational) studies suggest a cardio protective effect, no controlled studies have been completed on the effect of alcoholic beverages on the risk of developing heart disease or stroke. Excessive consumption of alcohol can cause cirrhosis of the liver and alcoholism ; the American Heart Association cautions people to "consult your doctor on the benefits and risks of consuming alcohol in moderation."

Wine's effect on the brain is also under study. One study concluded that wine made from the Cabernet Sauvignon grape reduces the risk of Alzheimer's Disease. Another study found that among alcoholics, wine damages the hippocampus to a greater degree than other alcoholic beverages.

Sulfites in wine can cause some people, particularly those with asthma, to have adverse reactions. Sulfites are present in all wines and are formed as a natural product of the fermentation process; many winemakers add sulfur dioxide in order to help preserve wine. Sulfur dioxide is also added to foods such as dried apricots and orange juice. The level of added sulfites varies; some wines have been marketed with low sulfite content.

A study of women in the United Kingdom, called The Million Women Study, concluded that moderate alcohol consumption can increase the risk of certain cancers, including breast, pharynx and liver cancer. Lead author of the study, Professor Valerie Beral, has asserted that there is scant evidence that any positive health effects of red wine outweigh the risk of cancer. She said, "It's an absolute myth that red wine is good for you." Professor Roger Corder, author of *The Red Wine Diet*, counters that two small glasses of a very tannic, procyanidin - rich wine would confer a benefit, although "most supermarket wines are low- procyanidin and high-alcohol."

15 - Forgery and manipulation of wines

Incidents of fraud, such as mislabeling the origin or quality of wines, have resulted in regulations on labeling. "Wine scandals" that have received media attention include :

The 1985 Di ethylene Glycol Wine Scandal, in which di ethylene glycol was used as a sweetener in some Austrian wines.

In 1986, methanol (a toxic type of alcohol) was used to alter certain wines manufactured in Italy.

In 2008, some Italian wines were found to includesulfuric acid and hydrochloric acid.

In 2010, some red Chinese wines were found to be adulterated, and as a consequence China's Hebei province has shut down nearly 30 wineries.

16 - Packaging

Most wines are sold in glass bottles and sealed with corks (50% of which come from Portugal). An increasing number of wine producers have been using alternative closures such as screw caps and synthetic plastic" corks". Although alternative closures are less expensive and prevent cork taint, they have been blamed for such problems as excessive reduction

Some wines are packaged in thick plastic bags with in corrugated fiberboard boxes, and are called "box wines", or "cask wine". Tucked inside the package is a tap affixed to the bag in box, or bladder, that is later extended by the consumer for serving the contents. Box wine can stay acceptably fresh for up to a month after opening because the bladder collapses as wine is dispensed, limiting contact with air and, thus, slowing the rate of oxidation. In contrast, bottled wine oxidizes more rapidly after opening because of the increasing ratio of air to wine as the contents are dispensed; it can degrade considerably in a few days.

	
Corrugated box to carry bottles	*Assorted wine corks*

Environmental considerations of wine packaging reveal benefits and drawbacks of both bottled and box wines. The glass used to make bottles is a nontoxic, naturally occurring substance that is completely recyclable, whereas the plastics used for box-wine containers are typically much less environmentally friendly. However, wine-bottle manufacturers have been cited for Clean Air Act violations. A *New York Times* editorial suggested that box wine, being lighter in package weight, has a reduced carbon foot print from its distribution; however, box-wine plastics, even though possibly recyclable, can be more labor-intensive (and therefore expensive) to process than glass bottles. And, while a wine box is recyclable, its plastic bladder most likely is not.

17 - Storage

Wine cellars, or wine rooms, if they are above-ground, are places designed specifically for the storage and aging of wine. In an "active" wine cellar, temperature and humidity are maintained by a climate-control system. "Passive" wine cellars are not climate-controlled, and so must be carefully located. Because wine is a natural, perishable food product, all types—including red, white, sparkling, and fortified—can spoil when exposed to heat, light, vibration or fluctuations in temperature and humidity. When properly stored, wines can maintain their quality and in some cases improve in aroma, flavor, and complexity as they age. Some wine experts contend that the optimal temperature for aging wine is 13°C, others 15°C. Wine refrigerators offer an alternative to wine cellars and are available in capacities ranging from small, 16 - bottle units to furniture - quality pieces that can contain 400 bottles. Wine refrigerators are not ideal for aging, but rather serve to chill wine to the perfect temperature for drinking. These refrigerators keep the humidity low (usually under 50 %), below the optimal humidity of 50 % to 70 %. Lower humidity levels can dry out corks over time, allowing oxygen to enter the bottle, which reduces the wine's quality through oxidation.

Oak wine barrels

Fermentation (Wine)

Fermenting must

Contents

1 - Introduction

The process of fermentation in wine turns grape juice into an alcoholic beverage. During fermentation, yeast interact with sugars in the juice to create ethanol, commonly known as ethyl alcohol, and carbon dioxide (as a by - product) . In winemaking, the temperature and speed of fermentation are important considerations as well as the levels of oxygen present in the must at the start of the fermentation. The risk of stuck fermentation and the development of several wine faults can also occur during this stage, which can last anywhere from 5 to 14 days for *primary fermentation* and potentially another 5 to 10 days for a *secondary fermentation*. Fermentation may be done in stainless steel tanks, which is common with many white wines like Riesling, in an open wooden vat, inside a wine barrel and inside the wine bottle itself as in the production of many sparkling wines.

2 - History

The natural occurrence of fermentation means it was probably first observed long ago by humans . The earliest uses of the word "Fermentation" in relation to winemaking was in reference to the apparent "boiling" within the must that came from the anaerobic reaction of the yeast to the sugars in the grape juice and the release of carbon dioxide. The Latin *fervere* means, literally, *to boil*. In the mid-19th century, Louis Pasteur noted the connection between yeast and the process of the fermentation in which the yeast act as catalyst and mediator through a series of a reaction that convert sugar into alcohol. The discovery of the Embden–Meyerhof–Parnas pathway by Gustav Embden, Otto Fritz Meyerhof and Jakub Karol Parnas in the early 20th century contributed more to the understanding of the complex chemical processes involved in the conversion of sugar to alcohol.

3 - Process

"Bloom", visible as a dusting on the berries

In wine making, there are distinctions made between *ambient yeast*s which are naturally present in wine cellars, vineyards and on the grapes themselves (sometimes known as a grape's "bloom" or "blush") and *cultured yeast* which are specifically isolated and inoculated for use in winemaking. The most common genera of wild yeasts found in winemaking include *Candida*, *Klöckera/ Hanseniaspora* , *Metschnikowiaceae* , *Pichia* and *Zygosaccharomyces*. Wild yeasts can produce high-quality, unique-flavored wines; however, they are often unpredictable and may introduce less desirable traits to the wine, and can even contribute to spoilage. It should be noted that few yeast, and lactic and acetic acid bacterial colonies naturally live on the surface of grapes , but traditional wine makers, particularly in Europe, advocate use of ambient yeast as a characteristic of the region's *terroir*; nevertheless, many winemakers prefer to control fermentation with predictable cultured yeast. The cultured yeasts most commonly used in winemaking belong to the *Saccharomyces cerevisiae* (also known as "sugar yeast") species. Within this species are several hundred different strains of yeast that can be used during fermentation to affect the heat or vigor of the process and enhance or suppress certain flavor characteristics of the varietal. The use of different strains of yeasts is a major contributor to the diversity of wine, even among the same grape variety . Non - Saccharomyces cerevisiae yeasts are being used more prevalently in the industry to add greater complexity to wine. After a winery has been in operation for a number of years, few yeast strains are actively involved in the fermentation process. The use of active dry yeasts reduces the variety of strains that appear in spontaneous fermentation by out competing those strains that are naturally present.

The addition of cultured yeast normally occurs with the yeast first in a dried or "inactive" state and is reactivated in warm water or diluted grape juice prior to being added to the must. To thrive and be active in fermentation, the yeast needs access to a continuous supply of carbon, nitrogen, sulfur, phosphorus as well as access to various vitamins and minerals. These components are naturally present in the grape must but their amount may be corrected by adding nutrients to the wine, in order to foster a more encouraging environment for the yeast. Newly formulated time - release nutrients, specifically manufactured for wine fermentations, offer the most advantageous conditions for yeast . Oxygen is needed as well, but in wine making, the risk of oxidation and the lack of alcohol production from oxygenated yeast requires the exposure of oxygen to be kept at a minimum.

Upon the introduction of active yeasts to the grape must, phosphates are attached to the sugar and the six-carbon sugar molecules begin to be split into three - carbon pieces and go through a series of rearrangement reactions. During this process, the carboxylic carbon atom is released in the form of carbon dioxide with the remaining components becoming acetaldehyde. The absence of oxygen in this anaerobic process allows the acetaldehyde to be eventually converted, by reduction, to ethanol. During the conversion of acetaldehyde, a small amount is converted, by oxidation, to acetic acid which, in excess, can contribute to the wine fault known as volatile acidity (vinegar taint). After the yeast has exhausted its life cycle, they fall to the bottom of the fermentation tank as sediment known as lees . Yeast cultures will die - off whenever all of the sugar in must has been converted into other chemicals or whenever the alcohol content has reached 15 % alcohol per unit volume; a concentration strong enough to kill almost all strains of yeast.

3 – 1 - Other compounds involved

The metabolism of amino acids and breakdown of sugars by yeasts has the effect of creating other biochemical compounds that can contribute to the flavor and aroma of wine. These compounds can be considered "volatile" like aldehydes, ethyl acetate, ester, fatty acids, fusel oils, hydrogen sulfide, ketones and mercaptans) or "non-volatile" like glycerol, acetic acid and succinic acid. Yeast also has the effect during fermentation of releasing glycoside hydrolase which can hydrolyse the flavor precursors of aliphatics (a flavor component that reacts with oak), benzene derivatives, mono terpenes (responsible for floral aromas from grapes like Muscat and Traminer), norisoprenoids (responsible for some of the spice notes in Chardonnay), and phenols.

Some strains of yeasts can generate volatile thiols which contribute to the fruity aromas in many wines such as the gooseberry scent commonly associated with Sauvignon blanc.

Brettanomyces yeasts are responsible for the "barnyard aroma" characteristic in some red wines like Burgundy and Pinot noir.

Methanol is not a major constituent of wine. The usual concentration range is between 0.1 g/liter and 0.2 g/liter. These small traces have no adverse affect on people and no direct affect on the senses.

4 - Winemaking considerations

During fermentation, there are several factors that winemakers take into consideration, with the most influential to ethanol production being sugar content in the must, the yeast strain used, and the fermentation temperature .

The biochemical process of fermentation itself creates a lot of residual heat which can take the must out of the ideal temperature range for the wine. Typically, white wine is fermented between 18 - 20 °C though a wine maker may choose to use a higher temperature to bring out some of the complexity of the wine. Red wine is typically fermented at higher temperatures up to 29 °C .

Fermentation at higher temperatures may have adverse effect on the wine in stunning the yeast to inactivity and even "boiling off" some of the flavors of the wines. Some winemakers may ferment their red wines at cooler temperatures, more typical of white wines, in order to bring out more fruit flavors.

To control the heat generated during fermentation, the winemaker must choose a suitable vessel size or else use a cooling device. Various kinds of cooling devices are available, ranging from the ancient Bordeaux practice of placing the fermentation vat atop blocks of ice to sophisticated fermentation tanks that have built-in cooling rings.

A risk factor involved with fermentation is the development of chemical residue and spoilage which can be corrected with the addition of sulfur dioxide (SO_2), although excess SO_2 can lead to a wine fault. A winemaker who wishes to make a wine with high levels of residual sugar (like a dessert wine) may stop fermentation early either by dropping the temperature of the must to stun the yeast or by adding a high level of alcohol (like brandy) to the must to kill off the yeast and create a fortified wine.

The ethanol produced through fermentation acts as an important co - solvent to the non-polar compound that water cannot dissolve, such as pigments from grape skins, giving wine varieties their distinct color, and other aromatics. Ethanol and the acidity of wine act as an inhibitor to bacterial growth, allowing wine to be safely kept for years in the absence of air.

5 - Other types of fermentation

In wine making, there are different processes that fall under the title of "Fermentation" but might not follow the same procedure commonly associated with wine fermentation.

5 - 1 - Bottle fermentation

Bottle fermentation is a method of sparkling wine production, originating in the Champagne region where after the cuvee has gone through a primary yeast fermentation the wine is then bottled and goes through a secondary fermentation where sugar and additional yeast known as *liqueur de tirage* is added to the wine. This secondary fermentation is what creates the carbon dioxide bubbles that sparkling wine is known for.

5 - 2 - Carbonic maceration

The process of carbonic maceration is also known as whole grape fermentation where instead of yeast being added, the grapes fermentation is encouraged to take place inside the individual grape berries. This method is common in the creation of Beaujolais wine and involves whole clusters of grapes being stored in a closed container with the oxygen in the container being replaced with carbon dioxide . Unlike normal fermentation where yeast converts sugar into alcohol, carbonic maceration works by enzymes within the grape breaking down the cellular matter to form ethanol and other chemical properties. The resulting wines are typically soft and fruity.

5 - 3 - Malolactic fermentation

Instead of yeast, bacteria play a fundamental role in malolactic fermentation which is essentially the conversion of malic acid into lactic acid. This has the benefit of reducing some of the tartness and making the resulting wine taste softer. Depending on the style of wine that the winemaker is trying to produce, malolactic fermentation may take place at the very same time as the yeast fermentation. Alternatively, some strains of yeast may be developed that can convert L- malate to L-lactate during alcohol fermentation. For example, *Saccharomyces cerevisiae* strain ML01 (*S. cerevisiae strain* ML01), which carries a gene encoding malolactic enzyme from *Oenococcus oeni* and a gene encoding malate permease from S*chizosaccharomyces pombe*. *S. cerevisiae strain* ML01 has received regulatory approval in both Canada and the United States.

History of Wine

Wine boy at a Greek symposium

Contents

1 - Introduction

The history of wine spans thousands of years and is closely intertwined with the history of agriculture, cuisine, civilization and humanity itself. Archaeological evidence suggests that the earliest known wine production occurred in what is now the country of Georgia around 7000 BCE , with other notable sites in Greater Iran dated 4500 BCE and Armenia 4100 BCE, respectively. The world's oldest known winery (dated to 3000

BCE) was discovered in Areni-1 cave in a mountainous area of Armenia . Increasingly clear archaeological evidence indicates that domestication of the grapevine took place during the Early Bronze Age in the Near East, Sumer and Egypt from around the third millennium BCE.

Evidence of the earliest wine production in Balkans has been uncovered at archaeological sites in northern Greece (Macedonia), dated to 4500 BC. These same sites also contain remnants of the world's earliest evidence of crushed grapes. In Egypt, wine became a part of recorded history, playing an important role in ancient ceremonial life. Traces of wild wine dating from the second and first millennia BCE have also been found in China.

Wine, linked in myth to Dionysus / Bacchus, was common in ancient Greece and Rome, and many of today's major wine-producing regions of Western Europe were established with Phoenician and, later, Roman plantations . Winemaking technology improved considerably during the time of the Roman Empire: many grape varieties and cultivation techniques were known; the design of the wine press advanced; and barrels were developed for storing and shipping wine.

Following the decline of Rome and its industrial-scale wine production for export, the Christian Church in medieval Europe became a firm supporter of wine, necessary for celebration of the Catholic Mass. Whereas wine was forbidden in medieval Islamic cultures, its use in Christian libation was widely tolerated. Geber and other Muslim chemists pioneered the distillation of wine for Islamic medicinal and industrial purposes such as perfume. Wine production gradually increased, with consumption burgeoning from the 15th century onwards. Wine production survived the devastating Phylloxera louse of 1887 and eventually spread to numerous regions throughout the world.

2 - Prehistory and antiquity

Little is actually known of the early history of wine. It is plausible that early foragers and farmers made alcoholic beverages from wild fruits, including grapes of the species *Vitis vinifera subsp. sylvestris*, ancestor to modern wine grapes (*V. vinifera*). This would have become easier following the development of pottery vessels in the later Neolithic of the Near East, about 11,000 BCE.

Archaeological sites of the Neolithic, Copper Age and early Bronze Age in which vestiges of wine-growing or olive-growing have been found.

In his book *Ancient Wine: The Search for the Origins of Viniculture* (Princeton: Princeton University Press, 2003), Patrick McGovern argues that the domestication of the Eurasian wine grape and winemaking could have originated in the territory of the modern-day country of Georgia, spreading south from there.

The oldest known winery is located in the "Areni-1" cave in the Vayots Dzor Province of Armenia. Dated around 4100 BCE, the winery contains a wine press, fermentation vats, jars, and cups. Archaeologists also found grape seeds and vines of the species *V. vinifera*. Commenting on the importance of the find, McGovern said, "The fact that winemaking was already so well developed in 4000 BCE suggests that the technology probably goes back much earlier."

Domesticated grapes were abundant in the Near East from the beginning of the Early Bronze Age, starting in 3200 BCE. There is also increasingly abundant evidence for winemaking in Sumer and Egypt in the third millennium BCE. The ancient Chinese made wine from native wild "mountain grapes" like *V. thunbergii* for a time, until they imported domesticated grape seeds from Central Asia in the second century. Grapes were also an important food. There is slender evidence for earlier domestication of the grape, in the form of pips from Chalcolithic Tell Shuna in Jordan, but this evidence remains unpublished.

Exactly where wine was first made is still unclear. It could have been anywhere in a vast region stretching from North Africa to Central/South Asia, where wild grapes grow. However, the first large-scale production of wine must have been in the region where grapes were first domesticated: the Southern Caucasus and the Near East. Wild grapes grow in Georgia, the northern Levant, coastal and southeastern Turkey, northern Iran and Armenia. None of these areas can yet be definitively singled out.

2 – 1 - Legends of discovery

In Iran (Persia), the Persian wine "mey" has been a theme of poetry for more than a thousand years

There are many apocryphal tales about the origins of wine. Biblical accounts tell of Noah and his sons producing wine at the base of Mount Ararat.

According to a Persian tale, legendary King Jamshid banished one of his harem ladies from the kingdom, causing her to become despondent and wishing to commit suicide. Going to the king's warehouse, the woman sought out a jar marked "poison" containing the remnants of grapes that had spoiled and deemed undrinkable. Unknown to her, the "spoilage" was actually the result of fermentation (the breakdown of the grapes' sugar by yeast into alcohol). She discovered the effects after drinking to be pleasant and her spirits were lifted. She took her discovery to the king, who became so enamored of this new "wine" beverage that he not only accepted the woman back into his harem but also decreed that all grapes grown in Persepolis would be devoted to winemaking. While most wine historians view this story as pure legend, there is archaeological evidence that wine was known and extensively traded by the early Persian kings.

2 – 2 - Phoenicia and wine

As recipients of winemaking knowledge from areas to the east, the Phoenicians were instrumental in distributing wine, wine grapes and winemaking technology throughout the Mediterranean region through their extensive trade network. Their use of amphoras for transporting wine was widely adopted and Phoenician-distributed grape varieties were important in the development of the wine industries of Rome and Greece.

2 – 3 - Ancient Greece and wine

Much of modern wine culture derives from the practices of the ancient Greeks. While the exact arrival of wine in Greek territory remains obscure, it was certainly known to both the Minoan and Mycenaean cultures. Many of the grapes grown in modern Greece are grown there exclusively and are similar or identical to varieties grown in ancient times. Indeed, the most popular modern Greek wine, a strongly aromatic white called retsina, is thought to be a carryover from the ancient practice of lining wine jugs with tree resin, which imparted a distinct flavor to the drink.

Dionysus in a vineyard; late 6th-century BCE amphora

Evidence from archaeological sites in Greece, in the form of 6,500 – year - old grape remnants, represents the earliest known appearance of wine production in Europe. The "feast of the wine" (*me-tu-wo ne-wo*) was a festival in Mycenaean Greece celebrating the "month of the new wine." Several ancient sources, such as the Roman writer Pliny the Elder, describe the ancient Greek method of using partly dehydrated gypsum before fermentation, and some type of lime after fermentation, to reduce acidity. The Greek writer Theophrastus provides the oldest known description of this aspect of Greek winemaking.

Dionysus, the Greek god of revelry and wine — frequently referred to in the works of Homer and Aesop — was sometimes given the epithet "Acratophorus," by which he was designated as the giver of unmixed wine. Dionysus was also known as Bacchus (the name later adopted by ancient Romans) and the frenzy he induces as *bakkheia*. In Homeric mythology, wine is usually served in "mixing bowls"—it was not traditionally consumed in an undiluted state—and was referred to as "Juice of the Gods." Homer frequently refers to the "wine-dark sea" ; under the intensely blue Greek sky, the Aegean Sea as seen from aboard a boat can appear deep purple.

The earliest reference to a named wine is from the lyrical poet Alkman (7th century BCE), who praises "Dénthis," a wine from the western foothills of Mount Taygetus in Messenia, as "*anthosmías*" ("smelling of flowers"). Aristotle mentions Lemnian wine, which was probably the same as the modern-day Lemnió varietal, a red wine with a bouquet of oregano and thyme. If so, this makes Lemnió the oldest known varietal still in cultivation.

Greek wine was widely known and exported throughout the Mediterranean basin, as amphoras with Greek styling and art have been found throughout the area. The Greeks may have been involved in the first appearance of wine in ancient Egypt. They introduced the *V. vinifera* vine and made wine in their numerous colonies in modern-day Italy, Sicily, southern France and Spain.

2 – 4 - Ancient Egypt and wine

Grape cultivation, winemaking, and commerce in ancient Egypt ca. 1500 BCE

Wine played an important role in ancient Egyptian ceremonial life. A thriving royal winemaking industry was established in the Nile Delta following the introduction of grape cultivation from the Levant to Egypt c. 3000 BCE. The industry was most likely the result of trade between Egypt and Canaan during the Early Bronze Age, commencing from at least the Third Dynasty (2650 – 2575 BCE), the beginning of the Old

Kingdom period (2650 – 2152 BCE). Winemaking scenes on tomb walls, and the offering lists that accompanied them, included wine that was definitely produced in the deltaic vineyards. By the end of the Old Kingdom, five wines, all probably produced in the Delta, constitute a canonical set of provisions, or fixed "menu," for the afterlife.

Wine in ancient Egypt was predominantly red; however, a recent discovery has revealed the first evidence of white wine there. Residue from five clay amphoras from Pharaoh Tutankhamun's tomb yielded traces of white wine.[30] Finds in nearby containers led the same study to establish that Shedeh, the most precious drink in ancient Egypt, was made from red grapes, not pomegranates as previously thought.

As with much of the ancient Middle East, Egypt's lower classes preferred beer as a daily drink rather than wine, a taste likely inherited from the Sumerians. However, wine was well-known, especially near the Mediterranean coast, and figures prominently in the ritual life of the Jewish people, going back to the earliest known records of the faith. The Tanakh mentions it prominently in many locations as both a boon and a curse, and wine drunkenness serves as a major theme in a number of Bible stories.

Much superstition surrounded wine - drinking in early Egyptian times, largely due to its resemblance to blood. In Plutarch's Moralia, he mentions that, prior to the reign of Psammetichus , the ancient kings did not drink wine, "nor use it in libation as something dear to the gods, thinking it to be the blood of those who had once battled against the gods and from whom, when they had fallen and had become commingled with the earth, they believed vines to have sprung." This was considered to be the reason why drunkenness "drives men out of their senses and crazes them, inasmuch as they are then filled with the blood of their forbears."

2 – 5 - Roman Empire and wine

The Roman Empire had an immense impact on the development of viticulture and oenology. Wine was an integral part of the Roman diet and winemaking became a precise business. Vitruvius's *De architectura* (I.4.2) noted how wine storage rooms were built facing north, "since that quarter is never subject to change but is always constant and unshifting."

Shipping wine in Roman Gaul: amphoras (top) were the traditional Mediterranean vessels, but the Gauls introduced the use of barrels

As the Roman Empire expanded, wine production in the provinces grew to the point where it was competing with Roman wines. Virtually all of the major wine-producing regions of Western Europe today were established during the Roman Imperial era.

Winemaking technology improved considerably during the time of the Roman Empire. Many grape varieties and cultivation techniques were developed, and barrels (invented by the Gauls) and later, glass bottles (invented by the Syrians) began to compete with terracotta amphoras for storing and shipping wine. Following the Greek invention of the screw, wine presses became common in Roman villas. The Romans also created a precursor to today's appellation systems, as certain regions gained reputations for their fine wines.

Wine, perhaps mixed with herbs and minerals, was assumed to serve medicinal purposes. During Roman times, the upper classes might dissolve pearls in wine for better health. Cleopatra created her own legend by promising Mark Antony she would "drink the value of a province" in one cup of wine, after which she drank an expensive pearl with a cup of the beverage. When the Western Roman Empire fell around 500 AD, Europe entered a period of invasions and social turmoil, with the Roman Catholic Church as the only stable social structure. Through the Church, grape-growing and winemaking technology, essential for the Mass, were preserved.

2 - 6 - Ancient China and wine

	
A Chinese wine vessel from the 18th century BCE	*A bronze wine storage vessel from the Shang Dynasty (1600 –1046 BCE)*

Following the Han Dynasty (202 BCE – 220 AD), emissary Zhang Qian's exploration of the Western Regions in the second century BCE, and contact with Hellenistic kingdoms such as Fergana, Bactria, and the Indo-Greek Kingdom, high-quality grapes (i.e. *V. vinifera*) were introduced into China and Chinese grape wine (called *putao jiu* in Chinese) was first produced . Prior to Zhang Qian's travels, wild mountain grapes were used to make wine, notably *V. thunbergii* and *V. filifolia*, described in the *Classical Pharmacopoeia of the Heavenly Husbandman*. Rice wine remained the most common wine in China, since grape wine was still considered exotic and reserved largely for the emperor's table during the Tang Dynasty (618–907), and was not popularly consumed by the literati gentry class until the Song Dynasty (960 – 1279) . The fact that rice wine was more common than grape wine was noted even by the

Venetian traveler Marco Polo when he ventured to China in the 1280s.[35] As noted by Shen Kuo (1031–1095) in his *Dream Pool Essays*, an old phrase in China amongst the gentry class was having the company of "drinking guests" (*jiuke*), which was a figure of speech for drinking wine, playing the Chinese zither, playing Chinese chess, Zen Buddhist meditation, ink (calligraphy and painting), tea drinking, alchemy, chanting poetry, and conversation.

3 - Medieval period

3 -1 - Medieval Middle East

In the Arabian peninsula before the advent of Islam, wine was traded by Aramaic merchants, as the climate was not well-suited to the growing of vines. Many other types of fermented drinks, however, were produced in the 5th and 6th centuries, including date and honey wines.

The Muslim conquests of the 7 th and 8 th centuries brought many territories under Muslim control. Alcoholic drinks were prohibited by law, but the production of alcohol, wine in particular, seems to have thrived. Wine was a subject for many poets, even under Islamic rule, and many khalifas used to drink alcoholic beverages during their social and private meetings. Egyptian Jews leased vineyards from the Fatimid and Mamluk governments, produced wine for sacramental and medicinal use, and traded wine throughout the Eastern Mediterranean. Christian monasteries in the Levant and Iraq often cultivated grapevines; they then distributed their vintages in taverns located on monastery grounds. Zoroastrians in Persia and Central Asia also engaged in the production of wine. Though not much is known about their wine trade, they did become known for their taverns.

Wine in general found an industrial use in the medieval Middle East as feedstock after advances in distillation by Muslim alchemists allowed for the production of relatively pure ethanol, which was used in the perfume industry. Wine was also for the first time distilled into brandy during this period.

3 – 2 - Medieval Europe

In the Middle Ages, wine was the common drink of all social classes in the south, where grapes were cultivated. In the north and east, where few if any grapes were grown, beer and ale were the usual beverages of both commoners and nobility. Wine was exported to the northern regions, but because of its relatively high expense was seldom consumed by the lower classes. Since wine was necessary, however, for the celebration of the Catholic Mass, assuring a supply was crucial. The Benedictine monks became one of the largest producers of wine in France and Germany, followed closely by the Cistercians. Other orders, such as the Carthusians, the Templars, and the Carmelites, are also notable both historically and in modern times as wine producers. The Benedictines owned vineyards in Champagne (Dom Perignon was a Benedictine monk), Burgundy, and Bordeaux in France, and in the Rheingau and Franconia in Germany. In 1435 Count John IV of Katzenelnbogen , a wealthy member of the Holy Roman high nobility near Frankfurt, was the first to plant Riesling, the most important German grape. The nearby winemaking monks made it into an industry, producing enough wine to ship all over Europe for secular use. In Portugal, a country with one of the oldest wine traditions, the first appellation system in the world was created.

Monastic cellarer tasting wine, from Li Livres dou Santé
(French ms, late 13th century)

A housewife of the merchant class or a servant in a noble household would have served wine at every meal, and had a selection of reds and whites alike. Home recipes for meads from this period are still in existence, along with recipes for spicing and masking flavors in wines, including the simple act of adding a small amount of honey. As wines were kept in barrels, they were not extensively aged, and thus drunk quite young. To offset the effects of heavy alcohol consumption, wine was frequently watered down at a ratio of four or five parts water to one of wine.

One medieval application of wine was the use of snake-stones (banded agate resembling the figural rings on a snake) dissolved in wine as a remedy for snake bites, which shows an early understanding of the effects of alcohol on the central nervous system in such situations.

Jofroi of Waterford, a 13th-century Dominican, wrote a catalogue of all the known wines and ales of Europe, describing them with great relish and recommending them to academics and counselors.

4 - Modern era

4 – 1 - Spread and development in the Americas

European grape varieties were first brought to what is now Mexico by the first Spanish conquistadors to provide the necessities of the Catholic Holy Eucharist. Planted at Spanish missions, one variety came to be known as the Mission grape and is still planted today in small amounts. Succeeding waves of immigrants imported French, Italian and German grapes, although wine from those native to the Americas (whose flavors can be distinctly different) is also produced. Mexico became the most important wine producer starting in the 16th century, to the extent that its output began to affect Spanish commercial production. In this competitive climate, the Spanish king sent an executive order to halt Mexico 's production of wines and the planting of vineyards.

During the devastating phylloxera blight in late-19th-century Europe, it was found that native American vines were immune to the pest. French-American hybrid grapes were developed and saw some use in Europe, but more important was the practice of grafting European grapevines to American rootstocks to protect vineyards from the insect. The practice continues to this day wherever phylloxera is present.

Today, wine in the Americas is often associated with Argentina, California and Chile, all of which produce a wide variety of wines, from inexpensive jug wines to high-quality varietals and proprietary blends. Most of the wine production in the Americas is based on Old World grape varieties, and wine-growing regions there have often "adopted" grapes that have become particularly closely identified with them. California's Zinfandel (from Croatia and Southern Italy), Argentina's Malbec, and Chile's Carmenère (both from France) are well-known examples.

Until the latter half of the 20th century, American wine was generally viewed as inferior to that of Europe. However, with the surprisingly favorable American showing at the Paris Wine tasting of 1976, New World wine began to garner respect in the land of wine's origins.

4 – 2 - Developments in Europe

In the late 19th century, the phylloxera louse brought widespread destruction to grapevines, wine production, and those whose livelihoods depended on them; far-reaching repercussions included the loss of many indigenous varieties. Lessons learned from the infestation led to the positive transformation of Europe's wine industry. Bad vineyards were uprooted and their land turned to better uses. Some of France's best butter and cheese, for example, is now made from cows that graze on Charentais soil, which was previously covered with vines. *Cuvées* were also standardized, important in creating certain wines as they are known today; Champagne and

Bordeaux finally achieved the grape mixes that now define them. In the Balkans, where phylloxera had had little impact, the local varieties survived. However, the uneven transition from Ottoman occupation has meant only gradual transformation in many vineyards. It is only in recent times that local varieties have gained recognition beyond "mass - market" wines like retsina.

4 – 3 - Australia, New Zealand and South Africa

In the context of wine, Australia, New Zealand, South Africa and other countries without a wine tradition are considered New World producers. Wine production began in the Cape Province of what is now South Africa in the 1680s as a business for supplying ships. Australia's First Fleet (1788) brought cuttings of vines from South Africa, although initial plantings failed and the first successful vineyards were established in the early 19th century. Until quite late in the 20th century, the product of these countries was not well known outside their small export markets. For example, Australia exported mainly to the United Kingdom; New Zealand retained most of its wine for domestic consumption; and South Africa was often isolated from the world market because of apartheid). However, with the increase in mechanization and scientific advances in winemaking, these countries became known for high-quality wine. A notable exception to the foregoing is that the Cape Province was the largest exporter of wine to Europe in the 18th century.

Arak (drink)

Contents

1 - Introduction

Arak, or araq, is an alcoholic spirit (~50 – 63% Alc. Vol./~100–126 proof) from the anis drinks family. It is a clear, colorless, unsweetened anise-flavored distilled alcoholic drink (also labeled as an Apéritif). It is the traditional alcoholic beverage in Iraq, Syria, Lebanon, Palestine, Jordan, and Israel.

2 - Etymology

The word arak comes from Arabic *'araq* عرق, meaning "sweat", its pronunciation varies depending on local varieties of Arabic: /ʕaraʔ, ʕaraɡ/. Arak is not to be confused with the similarly named liquor, arrack (which in some cases, such as in Indonesia—especially Bali, also goes by the name arak) . Another similarly sounding word is *aragh*, which in Armenia, Iran, Azerbaijan and Georgia is the colloquial name of vodka, and not an aniseed - flavored drink. Raki and ouzo are aniseed - flavored alcoholic drinks, related to arak, popular in Turkey and Cyprus, and Greece, respectively.

3 - Consumption

Arak is usually mixed in approximately 1/3 arak and 2/3 water in a traditional Levantine water vessel called *ibrik*, Arabic *'ibrīq* إبريق; then the mixture is poured in small ice filled cups, like in the picture. This dilution causes the clear liquor to turn a translucent milky-white color; this is because anethole, the essential oil of anise, is soluble in alcohol but not in water. This results in an emulsion, whose fine droplets scatter the light and turn the liquid translucent, a phenomenon known as louching. Arak is commonly served with mezza, which could include dozens of small traditional dishes. Most arak drinkers prefer to consume it this way, rather than alone. It is also well consumed with barbecues, along with garlic sauce.

Arak with water and ice

If ice is added after pouring in the cup, it results in the formation of an aesthetically unpleasant skin on the surface of the drink, because the ice causes the oils to solidify out in the arak. If water is added first, the ethanol causes the fat to emulsify, leading to the characteristic milky color. To avoid the precipitation of the anise (instead of emulsion), drinkers prefer not to reuse an arak-filled glass. In restaurants, when a bottle of arak is ordered, the waiter will usually bring a number of glasses along with it for this reason, whilst at home with regular drinkers it is deemed unnecessary.

4 - Major brands

The most commonly known Arak brands are :

4 – 1 – Iraq :

Asriyah
Tayyara

4 – 2 – Syria :

"Arak Rayan" from Syria

Batta my grand father(البطة)
Dinan (دنان)
Al-Hayat (الحياة)
Al Mimas (الميماس)
Rayan (الريان)
Al Jaraa (الجرة)
Jododona (جدودنا)
Brdone (بردوني)
Al Reef (الريف)

4 – 3 – Lebanon :

As Samir (السمير)
Arak el Rif (عرق الريف)
Batroun Mountains (جبال البترون)
Brun (بران)
Al-Laytany (الليطاني)
El Massaya (مسايا)
Fakra (فقرا)
Ghantous and Abi Raad (غنطوس و أبي رعد)
Kefraya (كفرَيا)
Ksarak (كساراك)
Layali Loubnan (ليالي لبنان)
Nakd (نكد)
Riachi (رياشي)
Tazka (تزكا)

Touma (توما)
Wardy (ورده)
عرق ملحم يوسف (نخب أول من نبتة الملفوف والصبار)

4 - 4 - Palestine

Palestinian Arak

Ramallah Golden Arak (عرق رام الله الذهبي)
Sabat Arak (عرق صابات)

4 – 5 - Jordan :

Haddad (حداد)
Zumout (زعمط)

4 – 5 - Israel

Elite Ha'arak (עלית הארק)
Arak Askalon (ארק אשקלון)
Aluf Ha'arak (אלוף הערק)
Arak El Namroud (ערק אל-נמרוד)

5 - Preparation

Distillation begins with the vineyards, and quality grapevines are the key to making good arak . The vines should be very mature and usually of a golden color. Instead of being irrigated, the vineyards are left to the care of the Mediterranean climate and make use of the natural rain and sun. The grapes, which are harvested in late September and October, are crushed and put in barrels together with the juice (in Arabic *El romeli*) and left to ferment for three weeks. Occasionally the whole mix is stirred to release the CO_2.

Numerous stills exist including stainless steel or copper, pot and column stills that will affect the final taste and specificity of the arak. The authentic copper with a Moorish shape are the most searched after.

Aniseed

The finished product is made during the second distillation. The alcohol collected in the first distillation is distilled again but this time it is mixed with aniseed. The ratio of alcohol to aniseed may vary and it is one of the major factors in the quality of the final product. Another distillation takes place, usually on the lowest possible temperature.

For a quality arak, the finished spirit is aged in clay amphoras to allow the angel's share to evaporate and thus the remaining liquid is the most suitable for consumption. The aging process is around twelve months at El Massaya that owns the largest aging capacity in Lebanon.

6 - Variations

Numerous varieties of arak are popular in all the countries bordering the Mediterranean. In the Levant (Israel, Palestine, Jordan, Lebanon, and Syria) it is distilled from fermented grape juice or, at times, sugar, and is considered by the inhabitants to be greatly superior to similar hard liquors in other countries. Other similar drinks are the arak of Iraq, made from fermented date juice, and the zibib of Egypt, a peasant-made drink. The same spirit is called Ouzo in Greece, Mastika in Republic of Macedonia and Bulgaria and Rakı in Turkey; they are made from a variety of products like grain, molasses, plums, figs and potatoes. An Iranian variant called *Aragh-e Sagi* (Persian: عرق سگی, literally *dog's sweat*) is produced without anise, and has a higher alcohol content than other varieties.

Further west, along the northern shores of the Mediterranean, anisette, French pastis and Spanish ojén, served as aperitifs or refreshers, are all sweeter versions of arak.

Arrack

Contents

1 - Introduction

Arrack, also spelled **arak** , is a distilled alcoholic drink typically produced in South Asia and Southeast Asia, made from either the fermented sap of coconut flowers, sugarcane, grain (e.g. red rice) or fruit, depending upon the country of origin. The clear distillate may be blended, aged in wooden barrels, or repeatedly distilled and filtered depending upon the taste and color objectives of the manufacturer. Arrack is not to be confused with *arak*, an anise-flavored alcoholic beverage traditionally consumed in Eastern Mediterranean and North African countries.

2 - Etymology

The word Arak originated from Sinhalese word "Arakku" in Sri Lanka. Some modern authorities believe the word is derived from the Arabic word *arak* (عرق, *arq*), meaning 'distillate'. In the Middle East and Near East, the term *arak* is usually used for liquor distilled from grapes and flavored with anise. However, coconut 'arrack' is considered by some Muslims as a "loophole" in the prohibition against alcohol because it is made from neither grain nor fruit, thus allowing its consumption.

Unlike arak, the word arrack has been considered by old experts to derived from *areca nut*, a palm seed originating in India from the areca tree and used as the basis for many varieties of arrack. In 1838, Samuel Morewood's work on the histories of liquiors was published. On the topic of arrack he said:

The word arrack is decided by philologers to be of Indian origin ; and should the conjecture be correct, that it is derived from the areca-nut, or the arrack-tree, as Kcempfer calls it, J it is clear, that as a spirit was extracted from that fruit, the name was given to all liquors having similar intoxicating effects. The term arrack being common in eastern countries where the arts of civilized life have been so early cultivated, it is more reasonable to suppose that the Tartars received this word through their eastern connexions with the Chinese, or other oriental nations, than to attribute it to a derivation foreign to their language, or as a generic term of their own. The great source of all Indian literature, and the parent of almost every oriental dialect, is the Sanscrit, a language of the most venerable and unfathomable antiquity, though now confined to the libraries of the Brahmins, and solely appropriated to religious laws and records. Mr. Halhed, in the preface to his Grammar of the Bengal language, says, that he was astonished to find a strong similitude between the Persian, Arabian, and even the Latin and Greek languages, not merely in technical and metaphorical terms, which the mutation of refined arts or improved manners might have incidentally introduced, but in the very groundwork of language in monosyllables in the names of numbers, and the appellations which would be first employed on the immediate dawn of civilisation. Telinga is a dialect of the Sanscrit, in which the word areca is found, it is used by the Brahmins in writing Sancrit, and since to the latter all the other tongues of India are more or less indebted, the term areca, or arrack, may be fairly traced through the different languages of the East, so that the general use and application of this word in Asiatic countries cannot appear strange. To these considerations may be added, that in Malabar the tree which *yields the material from which this oriental beverage is produced is termed areca, and, among the Tungusians, Calmucks, Kirghizes, and other hordes, koumiss, in its ardent state, is known by the general term, " Arrack or Rak." Klaproth says, that the Ossetians, (anciently Alans,) a Caucasian people, applied the word " Arak" to denote all distilled liquorsf a decided confirmation of the foregoing observations and opinions.*

Regardless of the exact origin, arrack has come to symbolize a multitude of largely unrelated, distilled alcohols produced throughout Asia and the eastern Mediterranean. This is largely due to the proliferation of distillation knowledge throughout the Middle East during the 14th century. Each country named its own alcohol by using various Latin alphabet forms of the same word which was synonymous with distillation at the time (*arak, araka, araki, ariki, arrack, arack, raki, raque, racque, rac, rak, araka*).

3 - Coconut arrack

Milky sap is taken from the flowers of coconut palm trees before the flowers bloom. The sap quickly ferments to become a mildly alcoholic drink called *tuak*, "toddy" or "palm wine", which is then distilled in vats made of wood (usually halmilla or teak). The end product is a spirit with a taste usually described as "somewhere between whisky and rum". It is generally distilled to between 33% and 50% alcohol by volume (ABV) or 66 to 100 proof). Coconut arrack is traditionally consumed by itself or with ginger beer, a popular soda in Sri Lanka. It also may be mixed in cocktails as a substitute for the required portions of either rum or whiskey. Arrack is often combined with popular mixers such as cola, soda water, and lime juice.

4 - Arrack in different countries

4 – 1 - India

Arrack was banned in the state of Kerala in 1996.

4 – 2 - Sri Lanka

Sri Lanka is the world's largest producer of coconut arrack.

Other than water, the entire manufacturing process revolves around the fermentation and distillation of a single ingredient, the sap of unopened flowers from a coconut palm (*Cocos nucifera*). Each morning at dawn, men known as toddy tappers move among the tops of coconut trees using connecting ropes not unlike tightropes. A single tree may contribute up to two liters per day.

Due to its concentrated sugar and yeast content, the captured liquid naturally and immediately ferments into a mildly alcoholic drink called "toddy", *tuak*, or occasionally "palm wine". Within a few hours after collection, the toddy is poured into large wooden vats, called "wash backs", made from the wood of teak or halmilla trees. The natural fermentation process is allowed to continue in the wash backs until the alcohol content reaches 5-7% and deemed ready for distillation.

Distillation is generally a two-step process involving either pot stills, continuous stills, or a combination of both. The entire distillation process is completed within 24 hours. The first step results in "low wine", a liquid with an alcohol content between 20 and 40%.[5] The second step results in the final distillate with an alcohol content of 60 to 90%. Various blends of coconut arrack diverge in processing, yet the extracted spirit may also be sold raw, repeatedly distilled or filtered, or transferred back into halmilla vats for maturing up to 15 years, depending on flavor, color and fragrance requirements.

Premium blends of arrack add no other ingredients, while the inexpensive and common blends are mixed with neutral spirits before bottling. Most people describe the taste as resembling "…a blend between whiskey and rum", similar, but distinctively different at the same time.

4 – 2 – 1 - Production types

According to the Alcohol and Drug Information Centre's 2008 report on alcohol in Sri Lanka, the types of arrack are

:

Special arrack is produced in the highest volume, nearly doubling in production between 2002 and 2007. Molasses arrack is the least-produced kind and considered the common kind. Nevertheless, as a whole, arrack is the most popular local alcoholic beverage consumed in Sri Lanka and produced as a wide variety of brands that fit into the following three categories:

Premium aged, after distillation, is aged in halmilla vats for up to 15 years to mature and mellow the raw spirit before blending. Premium brands include VSOA, VX, Old Reserve and Extra Special.

Premium clear is generally not aged, but often distilled and/or filtered multiple times to soften its taste. Premium clear brands include Double Distilled and Blue Label.

Common is blended with other alcohols produced from molasses or mixed with neutral spirits as filler.

4 – 2 – 2 - Producers

Sri Lanka's largest manufacturers, listed in order based on their 2007 annual production of arrack, are:

DCSL (Distilleries Company of Sri Lanka), 37.25 million litres

IDL (International Distilleries Ltd), 3.97 million litres

Rockland, 2.18 million liters

Mendis, 0.86 million liters

Sri Lankan arrack was recently launched in the UK , and will be imported to the US for an American launch.

4 – 3 –Indonesia

Batavia arrack is distilled in Indonesia. It is the "rum" of Indonesia, because like rum, it is distilled from sugarcane. It is a pot still distillation. To start the fermentation, local fermented red rice is combined with local yeast to give a unique flavor and smell of the distillate. It is distilled to approx. 70 % ABV. Like rum, Batavia arrack is often a blend of different original parcels. It is used as a component in liqueurs and *punsch*, and also in the confectionery and flavor industries. It is said to enhance the flavor when used as a component in other products, as in the herbal and bitter liqueurs. Arrack is often created as a form of moonshine in Indonesia.

Some arracks reported to be methanol-tainted arrack have resulted in deaths in Indonesia.

4 – 4 – Philippines

The Filipino term for wine (and by extension alcoholic beverages in general) is *alak*, derived from the word "arak".

Lambanóg is commonly described as coconut wine or coconut vodka. Distilled from the sap of the unopened coconut flower, it is particularly potent, having a typical alcohol content of 80 to 90 proof (40 to 45 %) after a single distillation; this may go as high as 166 proof (83 %) after the second distillation. As with coconut arrack, the process begins with the sap from the coconut flower. The sap is harvested into bamboo receptacles similar to rubber tapping, then cooked or fermented to produce a coconut toddy called *tubà*. The *tubà*, which by itself is also a popular beverage, is further distilled to produce lambanóg.

Until recently, lambanóg was considered a local analogue to moonshine and other home-brewed alcoholic drinks due to the process's long history as a cottage industry. Though usually served pure, it is traditionally flavoured with raisins, but lambanóg has recently been marketed in several flavours such as mango, blueberry, bubblegum and cinnamon in an effort to appeal to all age groups.

Quezon province is the major producer of lambanog wine in the Philippines because of the abundance of coconut plantations in the area. The three main distilleries in the country are also located in Quezon province - the Mallari Distillery, the Buncayo Distillery, and the Capistrano Distillery (Vito, 2004).

4 – 5 – Finland

Cloetta Polly 'Original' and 'Milkchoco' chocolates contain "a taste of arrack". The famous Runeberg tart has spoonfuls of arrack in it.

4 – 6 – Sweden

A popular beverage in Sweden based on arrack is *punsch*, often consumed during the winter month or drizzled on top of ice cream.

Raki

The top two brands of rakı in Turkey by popularity, shown here mixed with chilled water in a typical rakı glass.

Contents

1 - Introduction

Raki (Turkish: *rakı*, Ottoman Turkish: راقى, pronounced is a Turkish unsweetened, anise - flavored hard alcoholic drink that is popular in Turkey and in the Balkan countries as an apéritif. It is often served with seafood or Turkish meze. It is similar to several other alcoholic beverages available around the Mediterranean, Albanian regions, the Middle East e.g., pastis, ouzo, sambuca, arak, and aguardiente. It is considered as the *National* alcoholic beverage of Turkey.

The term is also used for a wide variety of non-anise-flavored brandies made from distilled pomace which are popular in the Balkans and Southern Europe: Bulgarian ракия (rakia), Greek tsipouro, Cretan tsikoudia (which is also known locally as raki), Cypriot zivania, and Spanish orujo.

2 - Serving and drinking

In Turkey, raki is the national drink and is traditionally consumed either straight (*sek*, from the French "sec" meaning neat or dry), with chilled water on the side or partly mixed with chilled water, according to personal preference. Ice cubes are sometimes added. Dilution with water causes raki to turn a milky-white color, similar to the louche of absinthe. This phenomenon has resulted in the drink being popularly referred to *aslan sütü* ("lion's milk"). Since *aslan* ("lion") is a Turkish colloquial metaphor for a strong, courageous man, this gives the term a meaning close to "the milk for the strong."

Raki is commonly consumed alongside mezze, a selection of hot and cold appetizers, as well as at a *rakı sofrası* ("raki table"), either before a full dinner or instead of it. It is especially popular with seafood, together with fresh arugula, feta and melon. It is an equally popular complement to various red meat dishes like kebabs, where it is often served with a glass of turnip juice.

The secularist Turkish leader, and founder of the Republic of Turkey, Kemal Atatürk was very fond of raki, and his late-night *rakı sofrası* sessions were his favorite place to debate issues with his closest friends and advisors.

3 - Production

Raki is traditionally produced by twice distilling grape pomace (or grape pomace that has been mixed with ethanol) in traditional copper alembics of 5000 liters, and flavoring it with aniseed.

4 - Etymology

The term *raki* entered English from Turkish *rakı*. The word *rakı* is derived from the Arabic عرق [ʕaraq], other variants being *araka*, *araki*, *ariki*. *Araq* means perspiration in Arabic, which is believed to metaphorically refer to condensation , which likely refers to the condensation that forms outside of the chilled glass, the drop-by-drop manner in which Raki is distilled that is reminiscent of sweating, or the phenomenon of unexpected sweating observed in individuals engaging in excessive Raki consumption . Raki is sometimes referred to as "Lion's Milk".

5 - History

In the Ottoman Empire, until the 19 th century, meyhanes run by Greeks and Albanians would mainly serve wine along with meze, due to religious restrictions imposed by various sultans. Although there were many Muslims among meyhane attendants, sharia authorities could, at times, prosecute them. With the relatively liberal atmosphere of the Tanzimat Period (1839 – 1876), meyhane attendance among Muslims rose considerably, and raki became a favorite among meyhane - goers. By the end of the 20th century, raki took its current standard form and its consumption surpassed that of wine.

During this period, rakı was produced by distillation of grapes pomace (*cibre*) obtained during wine fermentation. When the amount of pomace was not sufficient, alcohol imported from Europe would be added. If anise was not added, it would take the name *düz rakı* (Straight Raki), whereas raki prepared with the addition of gum mastic was named *sakız rakısı* (gum raki) or *mastikha*, especially if produced on the island of Chios.

With the collapse of the Ottoman Empire and the establishment of the modern - day Republic of Turkey, grape - based rakı began to be distilled by the state-owned spirits monopoly Tekel, with the first factory production taking place in 1944 in Izmir. With increasing sugar beet production, Tekel also began to distill the alcohol from molasses, and a new brand of raki made from sugar-beet alcohol was introduced under the name *Yeni Rakı* 'New Rakı'. Molasses gave *Yeni Rakı* a distinctive bitter taste and helped increase the drink's popularity.

Today, with increased competition from the private sector, and the privatization of Tekel in 2004, several new brands and types of raki have emerged, each with its own distinct composition and production method, although the overall qualities of the drink have generally been kept consistent. These include *Efe Rakı*, *Çilingir Rakı*, *Mercan Rakı*, *Fasıl Rakı*, *Burgaz Rakı*, *Ata Rakı*, and *Anadolu Rakı*. *Sarı Zeybek Rakısı*, another recent brand, is aged in oak casks, which gives it a distinctive golden color.

6 - Types and brands

The standard Raki is a grape product, though it may be produced from figs as well. Raki produced from figs, particularly popular in the southern provinces of Turkey, is called *incir boğması, incir rakısı* (Fig Raki), or in Arabic, *tini*.

There are two methods of Turkish raki production. One method uses raisins and other uses grapes. *Yeni Rakı* is produced from raisins and *Tekirdağ Rakısı* is produced from grapes. Fresh grape rakı is like Ouzo but it has a higher alcohol content.

Suma Raki, i.e. distilled Raki prior to the addition of Aniseed, is generally produced from raisins but Raki factories around established wine-producing areas like Tekirdağ, Nevşehir, and İzmir may also use fresh grapes for higher quality. Recently, *yaş üzüm rakısı* (Fresh-Grape Raki) has become more popular in Turkey. A recent brand, *Efe Rakı*, was the first company to produce Raki exclusively of fresh grape suma, called *Efe Yaş Üzüm Rakısı* (Efe Fresh Grape Raki). *Tekirdağ Altın Seri* (Tekirdağ Golden Series) followed the trend and many others have been produced by other companies.

The best-known and popular brands of Raki, however, remain *Yeni Rakı*, originally produced by Tekel, which has transferred production rights to Mey Alkol upon the 2004 privatization of Tekel, and *Tekirdağ Rakısı* from the region of

Tekirdağ, which is famous for its characteristic flavor, believed to be due to the artesian waters of Çorlu used in its production. *Yeni Rakı* has an alcohol content of 45% and 1.5 grams of anise per liter; *Tekirdağ Rakısı* is 45% ABV and has 1.7 grams of anise per liter. There are also two top-quality brands called *Kulüp Rakısı* and *Altınbaş*, with 50 % alcohol.

Dip rakısı (Bottom Raki) is the Raki that remains in the bottom of the tanks during production. Bottom Raki is thought to best capture the dense aroma and flavor of the spirit, and is called *özel rakı* (Special Raki). It is not generally available commercially; instead, Raki factories reserve it as a prestigious gift for large clients.

Anise

Contents

1 - Introduction

Anise ***Pimpinella anisum***, also called **aniseed**, is a flowering plant in the family Apiaceae native to the eastern Mediterranean region and Southwest Asia. Its flavor has similarities with some other spices, such as star anise , fennel and liquor ice.

Scientific classification	
Kingdom:	Plantae
(unranked):	Angiosperms
(unranked):	Eudicots
(unranked):	Asterids

Order:	Apiales
Family:	Apiaceae
Genus:	*Pimpinella*
Species:	***P. anisum***
Binomial name	
Pimpinella anisum L.	

2 - Biology

Anise is a herbaceous annual plant growing to 1 m (3 ft) or more tall. The leaves at the base of the plant are simple, 1-5 cm (⅜-2 in.) long and shallowly lobed, while leaves higher on the stems are feathery pinnate, divided into numerous leaves. The flowers are white, approximately 3 mm in diameter, produced in dense umbels. The fruit is an oblong dry schizocarp, 3 – 6 mm long, usually called "aniseed".

Anise is a food plant for the larvae of some Lepidoptera species (butterflies and moths), including the lime-speck pug and wormwood pug.

3 - Cultivation

Anise plants grow best in light, fertile, well drained soil. The seeds should be planted as soon as the ground warms up in spring. Because the plants have a taproot, they do not transplant well after being established, so they should be started either in their final location or transplanted while the seedlings are still small.

4 - Production

Western cuisines have long used anise to flavor some dishes, drinks, and candies, and the word is used for both the species of herb and its licorice-like flavor. The most powerful flavor component of the essential oil of anise, anethole, is found in both anise and an unrelated spice called star anise (*Illicium verum*) widely used in South Asian, South east Asian, and East Asian dishes. Star anise is considerably less expensive to produce, and has gradually displaced *Pimpinella anisum* in Western markets. While formerly produced in larger quantities, by 1999 world production of the essential oil of anise was only 8 tones, compared to 400 tones from star anise.[4]

5 - Composition

As with all spices, the composition of anise varies considerably with origin and cultivation method. These are typical values for the main constituents.

Moisture:	9 -13 %
Protein:	18 %
Fatty oil:	8 -23 %
Essential oil:	2 - 7 %
Starch:	5 %
N-free extract:	22 - 28 %
Crude fiber :	12 – 25 %

Essential oil yielded by distillation is generally around 2 - 3 % and anethole makes up 80 - 90% of this.

6 - Uses

Anise seeds

6 – 1 - Culinary

Anise is sweet and very aromatic, distinguished by its characteristic flavor. The seeds, whole or powdered, are used in a wide variety of regional and ethnic confectioneries, including the black jelly bean, British aniseed balls, Australian humbugs, New Zealand aniseed wheels, Italian pizzelle, German *Pfeffernüsse* and *Springerle*, Austrian *Anisbögen*, Netherland *muisjes*, Norwegian *knotts*, New Mexican *Bizcochitos*, and Peruvian *picarones*. It is a key ingredient in Mexican *atole de anís* or *champurrado*, which is similar to hot chocolate, and it is taken as a digestive after meals in India. Anise is also used in the Vietnamese noodle soup Pho.

The *Ancient Romans* often served spiced cakes with aniseseed, called mustaceoe at the end of feasts as a digestive. This tradition of serving cake at the end of festivities is the basis for the tradition of serving cake at weddings.

6 – 2 - Liquor

Anise is used to flavor Middle Eastern *arak*, Colombian *aguardiente*, French spirits *absinthe*, *anisette* and *pastis*[*citation needed*], Greek *ouzo*, Bulgarian *mastika*, Macedonian *Мастика*, German *Jägermeister*, Italian *sambuca*, Dutch *Brokmöpke*, Portuguese, Peruvian and Spanish *anís*, Mexican *Xtabentún* and Turkish *rakı*. In these liquors, it is clear, but on addition of water becomes cloudy, a phenomenon known as the ouzo effect. It is believed to be one of the secret ingredients in the French liqueur Chartreuse. It is also used in some root beers, such as Virgil's in the United States.

6 – 3 – Medicinal

> *The seed wasteth and consumeth winde, and is good against belchings and upbraidings of the stomacke, alaieth gripings of the belly, provoketh urine gently, maketh abundance of milke, and stirreth up bodily lust: it staieth the laske, (diarrhea) and also the white flux in women.*

Anise, like fennel, contains anethole, a phytoestrogen.

Anise has been used to treat menstrual cramps.

The main use of anise in European herbal medicine was for its carminative effect, as noted by John Gerard in his "Great Herball," an early encyclopedia of herbal medicine.

The essential oil has reportedly been used as an insecticide against head-lice and mites.

Anise seed infusion made by pouring 1 cup of boiling water over 1 tablespoon anise seed and sweeten with honey has been used to treat smoker's cough.

6 – 4 - Miscellaneous

In the 1860s, American Civil War nurse Maureen Hellstrom used anise seeds as an early form of antiseptic. This method was later found to have caused high levels of toxicity in the blood and was discontinued shortly thereafter.

According to Pliny the Elder, anise was used as a cure for sleeplessness, chewed with alexanders and a little honey in the morning to freshen the breath, and, when mixed with wine, as a remedy for asp bites (N.H. 20.72).

In Pakistani and Indian cuisine, no distinction is made between anise and fennel. Therefore, the same name (*saunf*) is usually given to both of them. Some use the term *patli* (thin) *saunf* or *velayati* (foreign) *saunf* to distinguish anise from fennel, although Gujarati has the term *anisi*.

In the Middle East, water is boiled with about a tablespoon of aniseed per teacup to make a special hot tea called *yansoon*. This tea is given to mothers in Egypt when they are nursing.

Builders of steam locomotives in Britain incorporated capsules of aniseed oil into white metal plain bearings, so the distinctive smell would give warning in case of overheating.

Anise can be made into a liquid scent and is used for both drag hunting and fishing. It is put on fishing lures to attract fish.

Anise is frequently used to add flavor to mu'assel, particularly the double apple flavor.

Breathalyzer

A law enforcement grade Breathalyzer

Contents

1 - Introduction

A **breathalyzer** (a portmanteau of *breath* and *analyzer / analyser*) is a device for estimating blood alcohol content (BAC) from a breath sample. *Breathalyzer* is the brand name of a series of models made by one manufacturer of breath alcohol testing instruments (originally Smith and Wesson, later sold to National Draeger), and is a registered trademark for such instruments. In Canada, a preliminary non-evidentiary screening device can be approved by Parliament as an approved screening device, and an evidentiary breath instrument can be similarly designated as an approved instrument. The U.S. National Highway Traffic Safety Administration maintains a Conforming Products List of breath alcohol devices approved for evidentiary use, as well as for preliminary screening use.

2 - Origins

A 1927 paper produced by Emil Bogen, who collected air in a football bladder and then tested this air for traces of alcohol, discovered that the alcohol content of 2 liters of expired air was a little greater than that of 1 cc of urine. However, research into the possibilities of using breath to test for alcohol in a person's body dates as far back as 1874, when Anstie made the observation that small amounts of alcohol were excreted in breath.

Also, in 1927 a Chicago chemist, W.D. McNalley, invented a breathalizer in which the breath moving through chemicals in water would change color. One use for his invention was for house wives to test whether their husbands had been drinking before letting them in the house.

The first practical roadside breath-testing device intended for use by the police was the **drunkometer**. The drunkometer was developed by Professor Rolla N. Harger in 1938. he drunkometer collected a motorist's breath sample directly into a balloon inside the machine. The breath sample was then pumped through an acidified potassium permanganate solution. If there was alcohol in the breath sample, the solution changed colour. The greater the colour change, the more alcohol there was present in the breath.

In late 1927, in a case in Marlborough, England, a Dr. Gorsky, Police Surgeon, asked a suspect to inflate a football bladder with his breath. Since the 2 liters of the man's breath contained 1.5 ml of ethanol . Dr. Gorsky testified before the court that the defendant was "50 % drunk". Though technologies for detecting alcohol vary, it is widely accepted that Dr. Robert Borkenstein (1912–2002), a captain with the Indiana State Police and later a professor at Indiana University at Bloomington, is regarded as the first to create a device that measures a subject's blood alcohol level based on a breath sample. In 1954, Borkenstein invented his Breathalyzer, which used chemical oxidation and photometry to determine alcohol concentration. Subsequent breath analyzers have converted primarily to infrared spectroscopy. The invention of the Breathalyzer provided law enforcement with a non-invasive test providing immediate results to determine an individual's breath alcohol concentration at the time of testing. Also, the breath alcohol concentration test result itself can vary between individuals consuming identical amounts of alcohol due to gender, weight, and genetic pre-disposition.

It was in Britain, in 1967, that Tom Parry Jones developed and marketed the first electronic breathalyzer. He established Lion Laboratories in Cardiff with his colleague, electrical engineer Bill Dulcie. The Road Safety Act 1967 introduced the first legally enforceable maximum blood alcohol level for drivers in the UK, above which it became an offence to be in charge of a motor vehicle; and introduced the roadside breathalyzer, made available to police forces across the country. In 1979, Lion Laboratories' version of the breathalyser, known as the Alcolyser and incorporating crystal-filled tubes that changed colour above a certain level of alcohol in the breath, was approved for police use. Lion Laboratories won the Queen's Award for Technological Achievement for the product in 1980, and it began to be marketed worldwide.[9] The Alcolyser was superseded by the Lion Intoximeter 3000 in 1983, and later by the Lion Alcolmeter and Lion Intoxilyser. These later models used a fuel cell alcohol sensor rather than crystals, providing a more reliable kerbside test and removing the need for blood or urine samples to be taken at a police station. In 1991, Lion Laboratories was sold to the American company MPD, Inc.

3 - Chemistry

When the user exhales into a breath analyzer, any ethanol present in their breath is oxidized to acetic acid at the anode :

$$CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3CO_2H(l) + 4H^+(aq) + 4e^-$$

At the cathode, atmospheric oxygen is reduced:

$$O_2\,(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

The overall reaction is the oxidation of ethanol to acetic acid and water.

$$CH_3CH_2OH\ (l) + O_2\ (g) \rightarrow CH_3COOH\ (l) + H_2O\ (l)$$

The electrical current produced by this reaction is measured by a microprocessor, and displayed as an approximation of overall blood alcohol content (BAC) by the Alco sensor .

People who have drunk alcohol will release special gases. It will approach silica gel of strong oxidizing agent K2Cr2O7 .If the released gas contains ethanol (CH3CH2OH) steam , ethanol will be oxidized by chromium trioxide to form acetaldehyde. Meanwhile, CrO3 is restored as acetic acid [CH3COOH].

4 - Law enforcement

Breath analyzers do not directly measure blood alcohol content or concentration, which requires the analysis of a blood sample. Instead, they estimate BAC indirectly by measuring the amount of alcohol in one's breath. Two breathalyzer technologies are most prevalent. Desktop analyzers generally use infrared spectrophotometer technology, electrochemical fuel cell technology, or a combination of the two. Hand-held field testing devices are generally based on electrochemical platinum fuel cell analysis and, depending upon jurisdiction, may be used by officers in the field as a form of "field sobriety test" commonly called PBT (preliminary breath test) or PAS (preliminary alcohol screening) or as evidential devices in POA (point of arrest) testing.

5 - Consumer use

There are many models of consumer or personal breath alcohol testers on the market. These hand-held devices are generally less expensive than the devices used by law enforcement. Most retail consumer breath testers use semiconductor-based sensing technology, which is less expensive, less accurate, and less reliable than fuel cell and infrared devices.

All breath alcohol testers sold to consumers in the United States are required to be certified by the Food and Drug Administration , while those used by law enforcement must be approved by the Department of Transportation's National Highway Traffic Safety Administration.

Manufacturers of over-the-counter consumer breath analyzers must submit an FDA 510(k) Premarket Clearance to demonstrate that the device to be marketed is at least as safe and effective, that is, substantially equivalent, to a legally marketed device (21 CFR 807.92(a) (3)) that is not subject to Premarket Approval (PMA). Submitters must compare their device to one or more similar legally marketed devices and make and support their substantial equivalency claims. The devices are cleared as "screeners" which means they have met the requirements used by the FDA for detecting the presence of alcohol in the breath. Screener certification does not mean that the device can measure breath alcohol content accurately. Many breath analyzers cleared by the FDA are very inaccurate when it comes to BAC measurement. No semiconductor device has ever been approved for evidential use (to stand-up in a court of law) by any State Law Enforcement Agencies or the U.S. Department of Transportation.

Public Breathalyzers are starting to become a popular method for consumers to test themselves at the source of alcohol consumption. They are now able to be found in almost any type of licensed business. Canadian Breath Analyzer Company[16] and ACS Corporation manufacture and distribute two separate and competing fuel cell models for public use. Canadian Breath Analyzer's unit utilizes a electrochemical fuel cell sensor which is the latest representation of public and mobile scanner technology. Fuel Cells are more expensive and also much more reliable than their semiconductor counterparts. CBA Company's unit is the CBA-FC-Multi and ACS Corp manufactures the Alcolab. These units are tested by the R.C.M.P. and endorsed to be as accurate as their handheld, roadside scanners.

In France, possession of such a device is a legal obligation from 1 July 2012. All drivers of terrestrial motor vehicles (with the exception of mopeds) must be in possession of an unexpired device, and be able to show that it is immediately available for use. Drivers of vehicles that are equipped with an electronic immobilizer breathalyzer are exempt from this requirement. Failure to carry a breathalyzer becomes a punishable offence from 1 November 2012 . To be in compliance with this decree, the breathalyzer must conform to NF (NFX 20702).

6 - Breath test evidence in the United States

A Breathalyzer in action.

The breath alcohol content reading is used in criminal prosecutions in two ways. The operator of a vehicle whose reading indicates a BAC over the legal limit for driving will be charged with having committed an illegal *per se* offense: that is, it is automatically illegal throughout the United States to drive a vehicle with a BrAC of 0.08 or higher. One exception is the state of Wisconsin, where a first time drunk driving offense is normally a civil ordinance violation . The uniformity is due to federal guidelines, since motor vehicle laws are states'; in earlier years the range of the threshold varied considerably between States. The breath analyzer reading will be offered as evidence of that crime, although the issue is what the BrAC was at the time of driving rather than at the time of the test. Some jurisdictions now allow the use of breath analyzer test results without regard as to how much time passed between operation of the vehicle and the time the test was administered. The suspect will also be charged with driving under the influence of alcohol (sometimes referred to as driving or operating while intoxicated). While BrAC tests are not necessary to prove a defendant was under the influence, laws in most states require the jury to presume that he was under the influence if his BrAC is found and believed to be over 0.08 (grams of alcohol / 210 liters breath) when driving. This is a rebuttable presumption, however: the jury can disregard the test if they find it unreliable or if other evidence establishes a reasonable doubt.

Infrared instruments are also known as "evidentiary breath testers" and generally produce court-admissible results. Other instruments, usually hand held in design, are known as "preliminary breath testers" (PBT), and their results, while valuable to an officer attempting to establish probable cause for a drunk driving arrest, are generally not admissible in court. Some states, such as Idaho, permit data or "readings" from hand-held PBTs to be presented as evidence in court. If at all, they are generally only admissible to show the presence of alcohol or as a pass-fail field sobriety test to help determine probable cause to arrest. South Dakota does not permit data from any type of breath tester, and relies entirely on blood tests to ensure accuracy.

7 - Common sources of error

Breath testers can be very sensitive to temperature, for example, and will give false readings if not adjusted or recalibrated to account for ambient or surrounding air temperatures. The temperature of the subject is also very important.

Breathing pattern can also significantly affect breath test results. One study found that the BAC readings of subjects decreased 11–14 % after running up one flight of stairs and 22 – 25 % after doing so twice Another study found a 15 % decrease in BAC readings after vigorous exercise or hyperventilation . Hyperventilation for 20 seconds has been shown to lower the reading by approximately 11 %. On the other hand, holding one's breath for 30 seconds can increase the breath test result by about 16 % .

Some breath analysis machines assume a hematocrit (cell volume of blood) of 47 %· However, hematocrit values range from 42 to 52 % in men and from 37 to 47 % in women. It has been theorized that a person with a lower hematocrit will have a falsely high BAC reading .

Research indicates that breath tests can vary at least 15% from actual blood alcohol concentration . An estimated 23 % of individuals tested will have a BAC reading higher than their true BAC . Police in Victoria, Australia, use breathalyzers that give a recognized 20% tolerance on readings. Noel Ashby, former Victoria Police Assistant Commissioner (Traffic & Transport), claims that this tolerance is to allow for different body types.

7 – 1 - Calibration

Many handheld breath analyzers sold to consumers use a silicon oxide sensor (also called a semiconductor sensor) to determine the blood alcohol concentration. These sensors are far more prone to contamination and interference from substances other than breath alcohol. The sensors require recalibration or replacement every six months. Higher end personal breath analyzers and professional-use breath alcohol testers use platinum fuel cell sensors. These too require recalibration but at less frequent intervals than semiconductor devices, usually once a year.

Calibration is the process of checking and adjusting the internal settings of a breath analyzer by comparing and adjusting its test results to a known alcohol standard. Law enforcement breath analyzers are meticulously maintained and re-calibrated frequently to ensure accuracy.

There are two methods of calibrating a precision fuel cell breath analyzer, the Wet Bath and the Dry Gas method. Each method requires specialized equipment and factory trained technicians. It is not a procedure that can be conducted by untrained users or without the proper equipment.

The Dry-Gas Method utilizes a portable calibration standard which is a precise mixture of alcohol and inert nitrogen available in a pressurized canister. Initial equipment costs are less than alternative methods and the steps required are fewer. The equipment is also portable allowing calibrations to be done when and where required.

The Wet Bath Method utilizes an alcohol/water standard in a precise specialized alcohol concentration, contained and delivered in specialized simulator equipment. Wet bath apparatus has a higher initial cost and is not intended to be portable. The standard must be fresh and replaced regularly.

Some semiconductor models are designed specifically to allow the sensor module to be replaced without the need to send the unit to a calibration lab.

7 – 2 - Non - specific analysis

One major problem with older breath analyzers is non-specificity: the machines not only identify the ethyl alcohol (or ethanol) found in alcoholic beverages, but also other substances similar in molecular structure or reactivity.

The oldest breath analyzer models pass breath through a solution of potassium dichromate, which oxidizes ethanol into acetic acid, changing color in the process. A monochromatic light beam is passed through this sample, and a detector records the change in intensity and, hence, the change in color, which is used to calculate the percent alcohol in the breath. However, since potassium dichromate is a strong oxidizer, numerous alcohol groups can be oxidized by it, producing false positives. This source of false positives is unlikely as very few other substances found in exhaled air are oxidizable.

Infrared-based breath analyzers project an infrared beam of radiation through the captured breath in the sample chamber and detect the absorbance of the compound as a function of the wavelength of the beam, producing an absorbance spectrum that can be used to identify the compound, as the absorbance is due to the harmonic vibration and stretching of specific bonds in the molecule at specific wavelengths (see infrared spectroscopy). The characteristic bond of alcohols in infrared is the O - H bond, which gives a strong absorbance at a short wavelength. The more light is absorbed by compounds containing the alcohol group, the less reaches the detector on the other side — and the higher the reading. Other groups, most notably aromatic rings and carboxylic acids can give similar absorbance readings.

7 – 3 - Interfering compounds

Some natural and volatile interfering compounds do exist, however. For example, the National Highway Traffic Safety Administration (NHTSA) has found that dieters and diabetics may have acetone levels hundreds or even thousand of times higher than those in others. Acetone is one of the many substances that can be falsely identified as ethyl alcohol by some breath machines. However, fuel cell based systems are non-responsive to substances like acetone.

Substances in the environment can also lead to false BAC readings. For example, methyl tert-butyl ether (MTBE), a common gasoline additive, has been alleged anecdotally to cause false positives in persons exposed to it. Tests have shown this to be true for older machines; however, newer machines detect this interference and compensate for it.[22] Any number of other products found in the environment or workplace can also cause erroneous BAC results. These include compounds found in lacquer, paint remover, celluloid, gasoline, and cleaning fluids, especially ethers, alcohols, and other volatile compounds.

7 – 4 - Homeostatic variables

Breath analyzers assume that the subject being tested has a 2100-to-1 partition ratio in converting alcohol measured in the breath to estimates of alcohol in the blood. If the instrument estimates the BAC, then it measures weight of alcohol to volume of breath, so it will effectively measure grams of alcohol per 2100 ml of breath given. This measure is in direct proportion to the amount of grams of alcohol to every 1 ml of blood. Therefore, there is a 2100-to-1 ratio of alcohol in blood to alcohol in breath. However, this assumed partition ratio varies from 1300:1 to 3100:1 or wider among individuals and within a given individual over time. Assuming a true (and US legal) blood-alcohol concentration of .07 %, for example, a person with a partition ratio of 1500:1 would have a breath test reading of .10 % — over the legal limit.

Most individuals do, in fact, have a 2100-to-1 partition ratio in accordance with William Henry's law, which states that when the water solution of a volatile compound is brought into equilibrium with air, there is a fixed ratio between the concentration of the compound in air and its concentration in water. This ratio is constant at a given temperature. The human body is 37 degrees Celsius on average. Breath leaves the mouth at a temperature of 34 degrees Celsius. Alcohol in the body obeys Henry's Law as it is a volatile compound and diffuses in body water. To ensure that variables such as fever and hypothermia could not be pointed out to influence the results in a way that was harmful to the accused, the instrument is calibrated at a ratio of 2100:1, underestimating by 9 percent. In order for a person running a fever to significantly overestimate, he would have to have a fever that would likely see the subject in the hospital rather than driving in the first place. Studies suggest that about 1.8 % of the population have a partition ratio below 2100:1. Thus, a machine using a 2100-to-1 ratio could actually overestimate the BAC. As much as 14% of the population has a partition ratio above 2100, thus causing the machine to under-report the BAC. Further, the assumption that the test subject's partition ratio will be average—that there will be 2100 parts in the blood for every part in the breath—means that accurate analysis of a given individual's blood alcohol by measuring breath alcohol is difficult, as the ratio varies considerably.

Variance in how much one breathes out can also give false readings, usually low. This is due to biological variance in breath alcohol concentration as a function of the volume of air in the lungs, an example of a factor which interferes with the liquid-gas equilibrium assumed by the devices. The presence of volatile components is another example of this; mixtures of volatile compounds can be more volatile than their components, which can create artificially high levels of ethanol (or other) vapors relative to the normal biological blood/breath alcohol equilibrium.

7 – 5 - Mouth alcohol

One of the most common causes of falsely high breath analyzer readings is the existence of mouth alcohol. In analyzing a subject's breath sample, the breath analyzer's internal computer is making the assumption that the alcohol in the breath sample came from alveolar air — that is, air exhaled from deep within the lungs. However, alcohol may have come from the mouth, throat or stomach for a number of reasons. To help guard against mouth-alcohol contamination, certified breath-test operators are trained to observe a test subject carefully for at least 15–20 minutes before administering the test.

The problem with mouth alcohol being analyzed by the breath analyzer is that it was not absorbed through the stomach and intestines and passed through the blood to the lungs. In other words, the machine's computer is mistakenly applying the partition ratio (see above) and multiplying the result. Consequently, a very tiny amount of alcohol from the mouth, throat or stomach can have a significant impact on the breath-alcohol reading.

Other than recent drinking, the most common source of mouth alcohol is from belching or burping . This causes the liquids and/or gases from the stomach — including any alcohol—to rise up into the soft tissue of the esophagus and oral cavity, where it will stay until it has dissipated. The American Medical Association concludes in its *Manual for Chemical Tests for Intoxication* (1959): "True reactions with alcohol in expired breath from sources other than the alveolar air (eructation, regurgitation, vomiting) will, of course, vitiate the breath alcohol results." For this reason, police officers are supposed to keep a DUI suspect under observation for at least 15 minutes prior to administering a breath test. Instruments such as the Intoxilyzer 5000 also feature a "slope" parameter. This parameter detects any decrease in alcohol concentration of 0.006 g per 210 L of breath in 0.6 second, a condition indicative of residual mouth alcohol, and will result in an "invalid sample" warning to the operator, notifying the operator of the presence of the residual mouth alcohol. PBT's, however, feature no such safeguard.

Acid reflux, or gastro esophageal reflux disease, can greatly exacerbate the mouth-alcohol problem. The stomach is normally separated from the throat by a valve, but when this valve becomes herniated, there is nothing to stop the liquid contents in the stomach from rising and permeating the esophagus and mouth. The contents — including any alcohol—are then later exhaled into the breathalyzer. Experiments on individuals suffering from this condition did not find any actual increase in Breath Ethanol.

Mouth alcohol can also be created in other ways. Dentures, some have theorized, will trap alcohol, although experiments have shown no difference if the normal 15 minute observation period is observed.[26] Periodontal disease can also create pockets in the gums which will contain the alcohol for longer periods . Also known to produce false results due to residual alcohol in the mouth is passionate kissing with an intoxicated person . Recent use of mouthwash or breath fresheners can skew results upward as they can contain fairly high levels of alcohol

7 – 6 - Testing during absorptive phase

Absorption of alcohol continues for anywhere from 20 minutes (on an empty stomach) to two-and-one-half hours (on a full stomach) after the last consumption. Peak absorption generally occurs within an hour. During the initial absorptive phase, the distribution of alcohol throughout the body is not uniform. Uniformity of distribution, called equilibrium, occurs just as absorption completes. In other words, some parts of the body will have a higher blood alcohol content (BAC) than others. One aspect of the non-uniformity before absorption is complete is that the BAC in arterial blood will be higher than in venous blood. Other false positive of high BAC and also blood reading are related to Patients with proteinuria and hematuria, due to kidney metabolization and failure. The metabolization rate of related patients with kidney damage is abnormal in relation to percent in alcohol in the breath. However, since potassium dichromate is a strong oxidizer, numerous alcohol groups can be oxidized by kidney and blood filtration, producing false positives.

During the initial absorption phase, arterial blood alcohol concentrations are higher than venous. After absorption, venous blood is higher. This is especially true with bolus dosing. With additional doses of alcohol, the body can reach a sustained equilibrium when absorption and elimination are proportional, calculating a general absorption rate of 0.02/drink and a general elimination rate of 0.015 / hour. (One drink is equal to 1.5 ounces of liquor, 12 ounces of beer, or 5 ounces of wine.)

Breath alcohol is a representation of the equilibrium of alcohol concentration as the blood gases (alcohol) pass from the (arterial) blood into the lungs to be expired in the breath. Arterial blood distributes oxygen throughout the body. Breath alcohol concentrations are generally lower than blood alcohol concentrations, because a true representation of blood alcohol concentration is only possible if the lungs were able to completely deflate. Vitreous (eye) fluid provides the most accurate account of blood alcohol concentration .

7 – 7 - Retrograde extrapolation

The breath analyzer test is usually administered at a police station, commonly an hour or more after the arrest. Although this gives the BrAC at the time of the test, it does not by itself answer the question of what it was at the time of driving. The prosecution typically provides an estimated alcohol concentration at the time of driving utilizing retrograde extrapolation, presented by expert opinion. This involves projecting back in time to estimate the BrAC level at the time of driving, by applying the physiological properties of absorption and elimination rates in the human body .

Extrapolation is calculated using five factors and a general elimination rate of 0.015 / hour.

For example: Time of breath test-10:00pm...Result of breath test-0.080...Time of driving-9:00pm (stopped by officer)...Time of last drink-8:00 pm...Last food-12:00 pm .

Using these facts, an expert can say the person's last drink was consumed on an empty stomach, which means absorption of the last drink (at 8:00) was complete within one hour-9:00. At the time of the stop, the driver is fully absorbed. The test result of 0.080 was at 10:00. So the one hour of elimination that has occurred since the stop is added in, making 0.080 + 0.015 = 0.095 the approximate breath alcohol concentration at the time of the stop.

8 - Photovoltaic assay

The photovoltaic assay, used only in the dated Photo Electric Intoximeter (PEI), is a form of breath testing rarely encountered today. The process works by using photocells to analyze the color change of a redox (oxidation-reduction) reaction. A breath sample is bubbled through an aqueous solution of sulfuric acid, potassium dichromate, and silver nitrate. The silver nitrate acts as a catalyst, allowing the alcohol to be oxidized at an appreciable rate. The requisite acidic condition needed for the reaction might also be provided by the sulfuric acid. In solution, ethanol reacts with the potassium dichromate, reducing the dichromate ion to the chromium (III) ion. This reduction results in a change of the solution's color from red-orange to green. The reacted solution is compared to a vial of non-reacted solution by a photocell, which creates an electric current proportional to the degree of the color change; this current moves the needle that indicates BAC.

Like other methods, breath testing devices using chemical analysis are somewhat prone to false readings. Compounds that have compositions similar to ethanol, for example, could also act as reducing agents, creating the necessary color change to indicate increased BAC.

9 - Breath analyzer myths

There are a number of substances or techniques that can supposedly "fool" a breath analyzer (i.e., generate a lower blood alcohol content).

A 2003 episode of the popular science television show *MythBusters* tested a number of methods that supposedly allow a person to fool a breath analyzer test. The methods tested included breath mints, onions, denture cream, mouthwash, pennies and batteries; all of these methods proved ineffective. The show noted that using items such as breath mints, onions, denture cream and mouthwash to cover the smell of alcohol may fool a person, but, since they will not actually reduce a person's BAC, there will be no effect on a breath analyzer test regardless of the quantity used, if any, it appeared that using mouthwash only raised the BAC. Pennies supposedly produce a chemical reaction, while batteries supposedly create an electrical charge, yet neither of these methods affected the breath analyzer results.

The *Mythbusters* episode also pointed out another complication: It would be necessary to insert the item into one's mouth (e.g. eat an onion, rinse with mouthwash, conceal a battery), take the breath test, and then possibly remove the item — all of which would have to be accomplished discreetly enough to avoid alerting the police officers administering the test (who would obviously become very suspicious if they noticed that a person was inserting items into their mouth prior to taking a breath test). It would likely be very difficult, especially for someone in an intoxicated state, to be able to accomplish such a feat.

In addition, the show noted that breath tests are often verified with blood tests (which are more accurate) and that even if a person somehow managed to fool a breath test, a blood test would certainly confirm a person's guilt.[29] However, it is not clear why a negative breath test would be verified by a subsequent blood test.

Other substances that might reduce the BAC reading include a bag of activated charcoal concealed in the mouth (to absorb alcohol vapor), an oxidizing gas (such as N_2O, Cl_2, O_3, etc.) that would fool a fuel cell type detector, or an organic interferent to fool an infrared absorption detector. The infrared absorption detector is more vulnerable to interference than a laboratory instrument measuring a continuous absorption spectrum since it only makes measurements at particular discrete wavelengths. However, due to the fact that any interference can only cause higher absorption, not lower, the estimated blood alcohol content will be overestimated . Additionally, Cl_2 is rather toxic and corrosive.

A 2007 episode of the Spike network's show *Manswers* showed some of the more common and not-so-common ways of attempts to beat the breath analyzer, none of which work. Test 1 was to suck on a copper-coated coin such as a penny. Test 2 was to hold a battery on the tongue. Test 3 was to chew gum. None of these tests showed a "pass" reading if the subject had consumed alcohol.

10 - Products that interfere with testing

On the other hand, products such as mouthwash or breath spray can "fool" breath machines by significantly raising test results. Listerine mouthwash, for example, contains 27% alcohol. The breath machine is calibrated with the assumption that the alcohol is coming from alcohol in the blood diffusing into the lung rather than directly from the mouth, so it applies a partition ratio of 2100:1 in computing blood alcohol concentration — resulting in a false high test reading. To counter this, officers are not supposed to administer a PBT for 15 minutes after the subject eats, vomits, or puts anything in their mouth. In addition, most instruments require that the individual be tested twice at least two minutes apart. Mouthwash or other mouth alcohol will have somewhat dissipated after two minutes and cause the second reading to disagree with the first, requiring a retest. (Also see the discussion of the "slope parameter" of the Intoxilyzer 5000 in the "Mouth Alcohol" section above.)

This was clearly illustrated in a study conducted with Listerine mouthwash on a breath machine and reported in an article entitled "Field Sobriety Testing: Intoxilyzers and Listerine Antiseptic" published in the July 1985 issue of *The Police Chief* (p. 70). Seven individuals were tested at a police station, with readings of 0.00%. Each then rinsed his mouth with

20 milliliters of Listerine mouthwash for 30 seconds in accordance with directions on the label. All seven were then tested on the machine at intervals of one, three, five and ten minutes. The results indicated an average reading of 0.43 blood-alcohol concentration, indicating a level that, if accurate, approaches lethal proportions. After three minutes, the average level was still 0.020, despite the absence of any alcohol in the system. Even after five minutes, the average level was 0.011.

In another study, reported in 8(22) Drinking/Driving Law Letter 1, a scientist tested the effects of Binaca breath spray on an Intoxilyzer 5000. He performed 23 tests with subjects who sprayed their throats and obtained readings as high as 0.81—far beyond lethal levels. The scientist also noted that the effects of the spray did not fall below detectable levels until after 18 minutes.

Beer

Schlenkerla Rauchbier being poured from a cask

Contents

1 - Introduction

Beer is an alcoholic beverage produced by the saccharification of starch and fermentation of the resulting sugar. The starch and saccharification enzymes are often derived from malted cereal grains, most commonly malted barley and malted wheat . Most beer is also flavoured with hops, which add bitterness and act as a natural preservative, though other flavourings such as herbs or fruit may occasionally be included. The preparation of beer is called brewing.

Beer is the world's most widely consumed alcoholic beverage; it is the third - most popular drink overall, after water and tea. It is thought by some to be the oldest fermented beverage.

Some of humanity's earliest known writings refer to the production and distribution of beer: the Code of Hammurabi included laws regulating beer and beer parlours , and "The Hymn to Ninkasi", a prayer to the Mesopotamian goddess of beer, served as both a prayer and as a method of remembering the recipe for beer in a culture with few literate people. Today, the brewing industry is a global business, consisting of several dominant multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries.

The strength of beer is usually around 4% to 6% alcohol by volume (abv) although it may vary between 0.5% (de-alcoholized) and 20 %, with some breweries creating examples of 40% abv and above in recent years.

Beer forms part of the culture of beer-drinking nations and is associated with social traditions such as beer festivals, as well as a rich pub culture involving activities like pub crawling and pub games such as bar billiards.

2 - History of beer

Beer is one of the world's oldest prepared beverages, possibly dating back to the early Neolithic or 9500 BC, when cereal was first farmed,[11] and is recorded in the written history of ancient Egypt and Mesopotamia. Archaeologists speculate that beer was instrumental in the formation of civilizations.

Egyptian wooden model of beer making in ancient Egypt, Rosicrucian Egyptian Museum, San Jose, California

The earliest known chemical evidence of barley beer dates to circa 3500 – 3100 BC from the site of Godin Tepe in the Zagros Mountains of western Iran. Some of the earliest Sumerian writings found in the region contain references to a type of beer; one such example, a prayer to the goddess Ninkasi, known as "The Hymn to Ninkasi", served as both a prayer as well as a method of remembering the recipe for beer in a culture with few literate people . The Ebla tablets, discovered in 1974 in Ebla, Syria and date back to 2500 BC, reveal that the city produced a range of beers, including one that appears to be named "Ebla" after the city. A fermented beverage using rice and fruit was made in China around 7000 BC. Unlike sake, mold was not used to saccharify the rice (amylolytic fermentation); the rice was probably prepared for fermentation by mastication or malting .

Almost any substance containing sugar can naturally undergo alcoholic fermentation. It is likely that many cultures, on observing that a sweet liquid could be obtained from a source of starch, independently invented beer. Bread and beer increased prosperity to a level that allowed time for development of other technology and contributed to the building of civilizations.

Beer was spread through Europe by Germanic and Celtic tribes as far back as 3000 BC , and it was mainly brewed on a domestic scale. The product that the early Europeans drank might not be recognised as beer by most people today. Alongside the basic starch source, the early European beers might contain fruits, honey, numerous types of plants, spices and other substances such as narcotic herbs . What they did not contain was hops, as that was a later addition, first mentioned in Europe around 822 by a Carolingian Abbot and again in 1067 by Abbess Hildegard of Bingen.

In 1516, William IV, Duke of Bavaria, adopted the *Reinheitsgebot* (purity law), perhaps the oldest food-quality regulation still in use in the 21st century, according to which the only allowed ingredients of beer are water, hops and barley-malt. Beer produced before the Industrial Revolution continued to be made and sold on a domestic scale, although by the 7th century AD, beer was also being produced and sold by European monasteries. During the Industrial Revolution, the production of beer moved from artisanal manufacture to industrial manufacture, and domestic manufacture ceased to be significant by the end of the 19th century. The development of hydrometers and thermometers changed brewing by allowing the brewer more control of the process and greater knowledge of the results.

Today, the brewing industry is a global business, consisting of several dominant multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries. As of 2006, more than 133 billion liters (35 billion gallons), the equivalent of a cube 510 metres on a side, of beer are sold per year, producing total global revenues of $294.5 billion (£147.7 billion).

In 2010, China's beer consumption hit 450 million hectoliters (45 billion liters) or nearly twice that of the United States but only 5 percent sold were Premium draught beers, compared with 50 percent in France and Germany.

3 - Brewing

The process of making beer is known as brewing. A dedicated building for the making of beer is called a brewery, though beer can be made in the home and has been for much of its history. A company that makes beer is called either a brewery or a brewing company. Beer made on a domestic scale for non-commercial reasons is classified as home brewing regardless of where it is made, though most homebrewed beer is made in the home. Brewing beer is subject to legislation and taxation in developed countries, which from the late 19th century largely restricted brewing to a commercial operation only. However, the UK government relaxed legislation in 1963, followed by Australia in 1972 and the USA in 1978, allowing home brewing to become a popular hobby.

A 16 th - century brewery

The purpose of brewing is to convert the starch source into a sugary liquid called wort and to convert the wort into the alcoholic beverage known as beer in a fermentation process effected by yeast.

The first step, where the wort is prepared by mixing the starch source (normally malted barley) with hot water, is known as "mashing". Hot water (known as "liquor" in brewing terms) is mixed with crushed malt or malts (known as "grist") in a mash tun. The mashing process takes around 1 to 2 hours, during which the starches are converted to sugars, and then the sweet wort is drained off the grains. The grains are now washed in a process known as "sparging". This washing allows the brewer to gather as much of the fermentable liquid from the grains as possible. The process of filtering the spent grain from the wort and sparge water is called *wort separation*. The traditional process for wort separation is lautering, in which the grain bed itself serves as the filter medium. Some modern breweries prefer the use of filter frames which allow a more finely ground grist.[36] Most modern breweries use a continuous sparge, collecting the original wort and the sparge water together. However, it is possible to collect a second or even third wash with the not quite spent grains as separate batches. Each run would produce a weaker wort and thus a weaker beer. This process is known as second (and third) runnings. Brewing with several runnings is called parti gyle brewing.

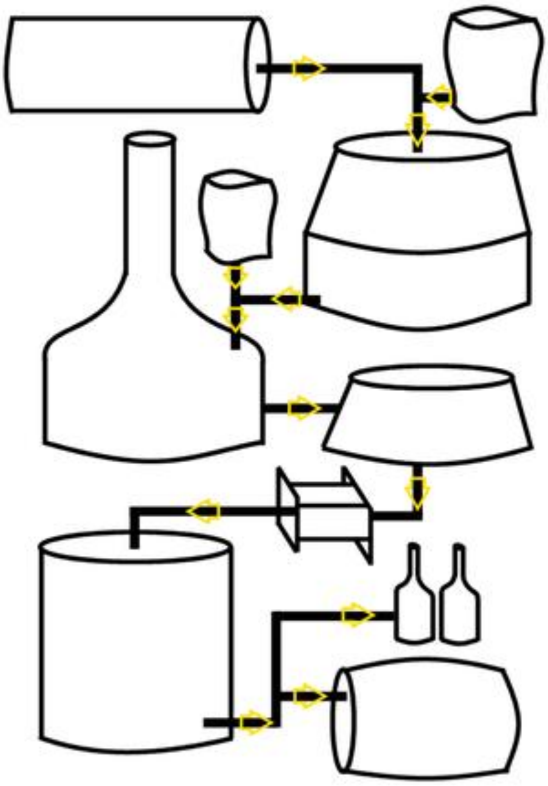


Diagram illustrating the process of brewing beer

Hot Water Tank - Mash Tun - Malt - Hops - Copper – Hop back

Add Yeast to Fermenter – Heat exchanger - Bottling - Cask or Keg

The sweet wort collected from sparging is put into a kettle, or "copper", (so called because these vessels were traditionally made from copper) and boiled, usually for about one hour. During boiling, water in the wort evaporates, but the sugars and other components of the wort remain; this allows more efficient use of the starch sources in the beer. Boiling also destroys any remaining enzymes left over from the mashing stage. Hops are added during boiling as a source of bitterness, flavour and aroma. Hops may be added at more than one point during the boil. The longer the hops are boiled, the more bitterness they contribute, but the less hop flavour and aroma remains in the beer.

After boiling, the hopped wort is now cooled, ready for the yeast. In some breweries, the hopped wort may pass through a hopback, which is a small vat filled with hops, to add aromatic hop flavouring and to act as a filter; but usually the hopped wort is simply cooled for the fermenter, where the yeast is added. During fermentation, the wort becomes beer in a process which requires a week to months depending on the type of yeast and strength of the beer. In addition to producing alcohol, fine particulate matter suspended in the wort settles during fermentation. Once fermentation is complete, the yeast also settles, leaving the beer clear.

Fermentation is sometimes carried out in two stages, primary and secondary. Once most of the alcohol has been produced during primary fermentation, the beer is transferred to a new vessel and allowed a period of secondary fermentation. Secondary fermentation is used when the beer requires long storage before packaging or greater clarity. When the beer has fermented, it is packaged either into casks for cask ale or kegs, aluminium cans, or bottles for other sorts of beer.

4 – Ingredients

Malted barley before roasting

The basic ingredients of beer are water; a starch source, such as malted barley, able to be saccharified (converted to sugars) then fermented (converted into alcohol and carbon dioxide); a brewer's yeast to produce the fermentation; and a flavouring such as hops. A mixture of starch sources may be used, with a secondary starch source, such as maize (corn), rice or sugar, often being termed an adjunct, especially when used as a lower-cost substitute for malted barley. Less widely used starch sources include millet, sorghum and cassava root in Africa, and potato in Brazil, and agave in Mexico, among others . The amount of each starch source in a beer recipe is collectively called the grain bill.

Water

Beer is composed mostly of water. Regions have water with different mineral components; as a result, different regions were originally better suited to making certain types of beer, thus giving them a regional character. For example, Dublin has hard water well-suited to making stout, such as Guinness; while Plzeň has soft water well - suited to making pale lager, such as Pilsner Urquell. The waters of Burton in England contain gypsum, which benefits making pale ale to such a degree that brewers of pale ales will add gypsum to the local water in a process known as Burtonisation.

Starch source

The starch source in a beer provides the fermentable material and is a key determinant of the strength and flavour of the beer. The most common starch source used in beer is malted grain. Grain is malted by soaking it in water, allowing it to begin germination, and then drying the partially germinated grain in a kiln. Malting grain produces enzymes that convert starches in the grain into fermentable sugars. Different roasting times and temperatures are used to produce different colours of malt from the same grain. Darker malts will produce darker beers.

Nearly all beer includes barley malt as the majority of the starch. This is because its fibrous hull remains attached to the grain during threshing. After malting, barley is milled, which finally removes the hull, breaking it into large pieces. These pieces remain with the grain during the mash, and act as a filter bed during lautering, when sweet wort is separated from insoluble grain material. Other malted and unmalted grains (including wheat, rice, oats, and rye, and less frequently, corn and sorghum) may be used. In recent years, a few brewers have produced gluten-free beer, made with sorghum with no barley malt, for those who cannot consume gluten-containing grains like wheat, barley, and rye.

Hops

Flavouring beer is the sole major commercial use of hops. The flower of the hop vine is used as a flavouring and preservative agent in nearly all beer made today. The flowers themselves are often called "hops".

Hop cone in a Hallertau, Germany, hop yard

The first historical mention of the use of hops in beer was from 822 AD in monastery rules written by Adalhard the Elder, also known as Adalard of Corbie , though the date normally given for widespread cultivation of hops for use in beer is the thirteenth century. Before the thirteenth century, and until the sixteenth century, during which hops took over as the dominant flavouring, beer was flavoured with other plants; for instance, *Glechoma hederacea*. Combinations of various aromatic herbs, berries, and even ingredients like wormwood would be combined into a mixture known as gruit and used as hops are now used. Some beers today, such as Fraoch' by the Scottish Heather Ales company and Cervoise Lancelot by the French Brasserie-Lancelot company, use plants other than hops for flavouring.

Hops contain several characteristics that brewers desire in beer. Hops contribute a bitterness that balances the sweetness of the malt; the bitterness of beers is measured on the International Bitterness Units scale. Hops contribute floral, citrus, and herbal aromas and flavours to beer. Hops have an antibiotic effect that favours the activity of brewer's yeast over less desirable microorganisms and aids in "head retention", the length of time that a foamy head created by carbonation will last. The acidity of hops is a preservative.

Yeast

Yeast is the microorganism that is responsible for fermentation in beer. Yeast metabolises the sugars extracted from grains, which produces alcohol and carbon dioxide, and thereby turns wort into beer. In addition to fermenting the beer, yeast influences the character and flavour. The dominant types of yeast used to make beer are the top-fermenting *Saccharomyces cerevisiae* and bottom-fermenting *Saccharomyces uvarum*. *Brettanomyces* ferments lambics, and *Torulaspora delbrueckii* ferments Bavarian weissbier. Before the role of yeast in fermentation was understood, fermentation involved wild or airborne yeasts. A few styles such as lambics rely on this method today, but most modern fermentation adds pure yeast cultures.

Clarifying agent

Some brewers add one or more clarifying agents to beer, which typically precipitate (collect as a solid) out of the beer along with protein solids and are found only in trace amounts in the finished product. This process makes the beer appear bright and clean, rather than the cloudy appearance of ethnic and older styles of beer such as wheat beers.

Examples of clarifying agents include isinglass, obtained from swim bladders of fish; Irish moss, a seaweed; kappa carrageen , from the seaweed *Kappaphycus cottonii*; Polyclar (artificial); and gelatin . If a beer is marked "suitable for Vegans", it was clarified either with seaweed or with artificial agents.

Production and trade

The brewing industry is a global business, consisting of several dominant multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries. More than 133 billion liters (35 billion gallons) are sold per year — producing total global revenues of $294.5 billion (£147.7 billion) as of 2006 .

A microbrewery, or craft brewery, is a modern brewery which produces a limited amount of beer. The maximum amount of beer a brewery can produce and still be classed as a microbrewery varies by region and by authority, though is usually around 15,000 barrels (18,000 hectoliters/ 475,000 US gallons) a year. A brewpub is a type of microbrewery that incorporates a pub or other eating establishment.

SABMiller became the largest brewing company in the world when it acquired Royal Grolsch, brewer of Dutch premium beer brand Grolsch . InBev was the second - largest beer - producing company in the world and Anheuser-Busch held the third spot, but after the acquisition of Anheuser-Busch by InBev, the new Anheuser-Busch InBev company is currently the largest brewer in the world.

Brewing at home is subject to regulation and prohibition in many countries. Restrictions on homebrewing were lifted in the UK in 1963, Australia followed suit in 1972, and the USA in 1978, though individual states were allowed to pass their own laws limiting production.

Varieties

While there are many types of beer brewed, the basics of brewing beer are shared across national and cultural boundaries. The traditional European brewing regions — Germany, Belgium, England and the Czech Republic — have local varieties of beer.

Michael Jackson, in his 1977 book *The World Guide To Beer*, categorized beers from around the world in local style groups suggested by local customs and names . Fred Eckhardt furthered Jackson's work in *The Essentials of Beer Style* in 1989.

Top - fermented beers are most commonly produced with *Saccharomyces cerevisiae*, a top-fermenting yeast which clumps and rises to the surface, typically between 15 and 24 °C (60 and 75 °F). At these temperatures, yeast produces significant amounts of esters and other secondary flavour and aroma products, and the result is often a beer with slightly "fruity" compounds resembling apple, pear, pineapple, banana, plum, or prune, among others.

Before the introduction of hops into England from the Netherlands in the 15th century, the name "ale" was exclusively applied to un hopped fermented beverages, the term *beer* being gradually introduced to describe a brew with an infusion of hops.[79] The word *ale* may come from the Old English *ealu*, in turn from the Proto-Indo-European base **alut-*, which holds connotations of "sorcery, magic, possession, intoxication".

Real ale is the term coined by the Campaign for Real Ale (CAMRA) in 1973 for "beer brewed from traditional ingredients, matured by secondary fermentation in the container from which it is dispensed, and served without the use of extraneous carbon dioxide". It is applied to bottle conditioned and cask conditioned beers.

Pale ale is a beer which uses a top-fermenting yeast[82] and predominantly pale malt. It is one of the world's major beer styles.

Stout and porter are dark beers made using roasted malts or roast barley, and typically brewed with slow fermenting yeast. There are a number of variations including Baltic porter, dry stout, and Imperial stout. The name Porter was first used in 1721 to describe a dark brown beer popular with the street and river porters of London. This same beer later also became known as stout, though the word stout had been used as early as 1677. The history and development of stout and porter are intertwined.

Mild ale has a predominantly malty palate. It is usually dark coloured with an abv of 3 % to 3.6%, although there are lighter hued milds as well as stronger examples reaching 6% abv and higher.

Wheat beer is brewed with a large proportion of wheat although it often also contains a significant proportion of malted barley. Wheat beers are usually top - fermented (in Germany they have to be by law).[The flavour of wheat beers varies considerably, depending upon the specific style.

Lager is the English name for cool fermenting beers of Central European origin. Pale lagers are the most commonly consumed beers in the world. The name "lager" comes from the German "lagern" for "to store", as brewers around Bavaria stored beer in cool cellars and caves during the warm summer months. These brewers noticed that the beers continued to ferment, and to also clear of sediment, when stored in cool conditions.

Lager yeast is a cool bottom - fermenting yeast (*Saccharomyces pastorianus*) and typically undergoes primary fermentation at 7–12 °C (the fermentation phase), and then is given a long secondary fermentation at 0 – 4 °C (the lagering phase). During the secondary stage, the lager clears and mellows. The cooler conditions also inhibit the natural production of esters and other byproducts, resulting in a "cleaner"-tasting beer.

Modern methods of producing lager were pioneered by Gabriel Sedlmayr the Younger, who perfected dark brown lagers at the Spaten Brewery in Bavaria, and Anton Dreher, who began brewing a lager (now known as Vienna lager), probably of amber-red colour, in Vienna in 1840–1841. With improved modern yeast strains, most lager breweries use only short periods of cold storage, typically 1–3 weeks.

***Lambic*,** a beer of Belgium, is naturally fermented using wild yeasts, rather than cultivated. Many of these are not strains of brewer's yeast (*Saccharomyces cerevisiae*) and may have significant differences in aroma and sourness. Yeast varieties such as *Brettanomyces bruxellensis* and *Brettanomyces lambicus* are common in lambics. In addition, other organisms such as *Lactobacillus* bacteria produce acids which contribute to the sourness.

4 - Measurement

Beer is measured and assessed by bitterness, by strength and by colour. The perceived bitterness is measured by the International Bitterness Units scale (IBU), defined in co-operation between the American Society of Brewing Chemists and the European Brewery Convention.[90] The international scale was a development of the European Bitterness Units scale, often abbreviated as EBU, and the bitterness values should be identical.

4 – 1 - Colour

Beer colour is determined by the malt. The most common colour is a pale amber produced from using pale malts. *Pale lager* and *pale ale* are terms used for beers made from malt dried with coke. Coke was first used for roasting malt in 1642, but it was not until around 1703 that the term *pale ale* was used.

In terms of sales volume, most of today's beer is based on the pale lager brewed in 1842 in the town of Pilsen in the present-day Czech Republic . The modern pale lager is light in colour with a noticeable carbonation (fizzy bubbles) and a typical alcohol by volume content of around 5 %. The Pilsner Urquell, Bitburger, and Heineken brands of beer are typical examples of pale lager, as are the American brands Budweiser, Coors, and Miller.

Dark beers are usually brewed from a pale malt or lager malt base with a small proportion of darker malt added to achieve the desired shade. Other colourants — such as caramel—are also widely used to darken beers. Very dark beers, such as stout, use dark or patent malts that have been roasted longer. Some have roasted un malted barley.

4 - 2 - Strength

Beer ranges from less than 3 % alcohol by volume (abv) to around 14 % abv , though this strength can be increased to around 20% by re-pitching with champagne yeast , and to 55 % abv by the freeze-distilling process. The alcohol content of beer varies by local practice or beer style. The pale lagers that most consumers are familiar with fall in the range of 4–6%, with a typical abv of 5 %. The customary strength of British ales is quite low, with many session beers being around 4% abv. Some beers, such as table beer are of such low alcohol content (1% – 4%) that they are served instead of soft drinks in some schools.

The alcohol in beer comes primarily from the metabolism of sugars that are produced during fermentation. The quantity of fermentable sugars in the wort and the variety of yeast used to ferment the wort are the primary factors that determine the amount of alcohol in the final beer. Additional fermentable sugars are sometimes added to increase alcohol content, and enzymes are often added to the wort for certain styles of beer (primarily "light" beers) to convert more complex carbohydrates (starches) to fermentable sugars. Alcohol is a by-product of yeast metabolism and is toxic to the yeast; typical brewing yeast cannot survive at alcohol concentrations above 12% by volume. Low temperatures and too little fermentation time decreases the effectiveness of yeasts and consequently decreases the alcohol content.

Exceptionally strong beers

The strength of beers has climbed during the later years of the 20th century. Vetter 33, a 10.5% abv (33 degrees Plato, hence Vetter "33") doppelbock, was listed in the 1994 *Guinness Book of World Records* as the strongest beer at that time, though Samichlaus, by the Swiss brewer Hürlimann, had also been listed by the *Guinness Book of World Records* as the strongest at 14% abv. Since then, some brewers have used champagne yeasts to increase the alcohol content of their beers. Samuel Adams reached 20% abv with *Millennium*, and then surpassed that amount to 25.6% abv with Utopias. The strongest beer brewed in Britain was Baz's Super Brew by Parish Brewery, a 23% abv beer. In September 2011, the Scottish brewery BrewDog produced Ghost Deer, which, at 28%, they claim to be the world's strongest beer produced by fermentation alone.

The product claimed to be the strongest beer made is Schorschbräu's 2011 *Schorschbock 57* with 57,5 %. It was preceded by *The End of History*, a 55 % Belgian ale, made by BrewDog in 2010. The same company had previously made *Sink The Bismarck!*, a 41% abv IPA,[114] and *Tactical Nuclear Penguin*, a 32 % abv Imperial Stout. Each of these beers are made using the eisbock method of fractional freezing, in which a strong ale is partially frozen and the ice is repeatedly removed, until the desired strength is reached, a process that may class the product as spirits rather than beer. The German brewery Schorschbräu's *Schorschbock*, a 31% abv eisbock, and Hair of the Dog's *Dave*, a 29 % abv barley wine made in 1994, used the same fractional freezing method. A 60 % abv blend of beer with whiskey was jokingly claimed as the strongest beer by a Dutch brewery in July 2010.

8 - Serving

8 -1 - Draught

Draught beer keg fonts at the Délirium Café in Brussels

Draught beer from a pressurized keg is the most common method of dispensing in bars around the world. A metal keg is pressurized with carbon dioxide (CO_2) gas which drives the beer to the dispensing tap or faucet. Some beers may be served with a nitrogen/carbon dioxide mixture. Nitrogen produces fine bubbles, resulting in a dense head and a creamy mouth feel. Some types of beer can also be found in smaller, disposable kegs called beer balls.

In the 1980s, Guinness introduced the beer widget, a nitrogen-pressurized ball inside a can which creates a dense, tight head, similar to beer served from a nitrogen system . The words *draft* and *draught* can be used as marketing terms to describe canned or bottled beers containing a beer widget, or which are cold-filtered rather than pasteurized.

A selection of cask beers

Cask-conditioned ales (or cask ales) are unfiltered and un pasteurized beers. These beers are termed "real ale" by the CAMRA organization. Typically, when a cask arrives in a pub, it is placed horizontally on a frame called a "stillage" which is designed to hold it steady and at the right angle, and then allowed to cool to cellar temperature (typically between 11–13 °C) , before being tapped and vented — a tap is driven through a (usually rubber) bung at the bottom of one end, and a hard spile or other implement is used to open a hole in the side of the cask, which is now uppermost. The act of stillaging and then venting a beer in this manner typically disturbs all the sediment, so it must be left for a suitable period to "drop" (clear) again, as well as to fully condition — this period can take anywhere from several hours to several days. At this point the beer is ready to sell, either being pulled through a beer line with a hand pump, or simply being "gravity-fed" directly into the glass.

Draught beer's environmental impact can be 68 % lower than bottled beer due to packaging differences . A life cycle study of one beer brand, including grain production, brewing, bottling, distribution and waste management, shows that the CO_2 emissions from a 6-pack of micro - brew beer is about 3 kilograms . The loss of natural habitat potential from the 6-pack of micro - brew beer is estimated to be 2.5 square meters (26 square feet). Downstream emissions from distribution, retail, storage and disposal of waste can be over 45% of a bottled micro-brew beer's CO_2 emissions. Where legal, the use of a refillable jug, reusable bottle or other reusable containers to transport draught beer from a store or a bar, rather than buying pre - bottled beer, can reduce the environmental impact of beer consumption.

8 - 2 - Packaging

Most beers are cleared of yeast by filtering when packaged in bottles and cans. However, bottle conditioned beers retain some yeast—either by being unfiltered, or by being filtered and then reseeded with fresh yeast. It is usually recommended that the beer be poured slowly, leaving any yeast sediment at the bottom of the bottle. However, some drinkers prefer to pour in the yeast; this practice is customary with wheat beers. Typically, when serving a hefeweizen wheat beer, 90 % of the contents are poured, and the remainder is swirled to suspend the sediment before pouring it into the glass. Alternatively, the bottle may be inverted prior to opening. Glass bottles are always used for bottle conditioned beers.

Many beers are sold in cans, though there is considerable variation in the proportion between different countries. In Sweden in 2001, 63.9% of beer was sold in cans. People either drink from the can or pour the beer into a glass. Cans protect the beer from light (thereby preventing "skunked" beer) and have a seal less prone to leaking over time than bottles. Cans were initially viewed as a technological breakthrough for maintaining the quality of a beer, then became commonly associated with less expensive, mass - produced beers, even though the quality of storage in cans is much like bottles. Plastic (PET) bottles are used by some breweries.

8 - 3 -Temperature

The temperature of a beer has an influence on a drinker's experience; warmer temperatures reveal the range of flavours in a beer but cooler temperatures are more refreshing. Most drinkers prefer pale lager to be served chilled, a low- or medium-strength pale ale to be served cool, while a strong barley wine or imperial stout to be served at room temperature.

Beer writer Michael Jackson proposed a five-level scale for serving temperatures: well chilled (7 °C) for "light" beers (pale lagers); chilled (8 °C) for Berliner Weisse and other wheat beers; lightly chilled (9 °C) for all dark lagers, altbier and German wheat beers; cellar temperature (13 °C) for regular British ale, stout and most Belgian specialties; and room temperature (15.5 °C) for strong dark ales (especially trappist beer) and barley wine.

Drinking chilled beer began with the development of artificial refrigeration and by the 1870s, was spread in those countries that concentrated on brewing pale lager. Chilling beer makes it more refreshing, though below 15.5 °C the chilling starts to reduce taste awareness and reduces it significantly below 10 °C . Beer served un chilled — either cool or at room temperature, reveal more of their flavours. Cask Marque, a non-profit UK beer organization, has set a temperature standard range of 12°-14 °C for cask ales to be served.

8 – 4 - Vessels

Beer is consumed out of a variety of vessels, such as a glass, a beer stein, a mug, a pewter tankard, a beer bottle or a can. The shape of the glass from which beer is consumed can influence the perception of the beer and can define and accent the character of the style. Breweries offer branded glassware intended only for their own beers as a marketing promotion, as this increases sales.

The pouring process has an influence on a beer's presentation. The rate of flow from the tap or other serving vessel, tilt of the glass, and position of the pour (in the centre or down the side) into the glass all influence the end result, such as the size and longevity of the head, lacing (the pattern left by the head as it moves down the glass as the beer is drunk), and turbulence of the beer and its release of carbonation.

9 - Beer and society

In most societies, beer is the most popular alcoholic beverage.

Various social traditions and activities are associated with beer drinking, such as playing cards, darts, or other pub games; attending beer festivals; visiting a series of pubs in one evening; joining an organization such as CAMRA; visiting breweries; beer-oriented tourism; or rating beer. Drinking games, such as beer pong, are also popular. A relatively new profession is that of the beer sommelier, who informs restaurant patrons about beers and food pairings.

Beer is considered to be a social lubricant in many societies[149] and is consumed in countries all over the world. There are breweries in Middle Eastern countries such as Iran and Syria, and in African countries. Sales of beer are four times those of wine, which is the second most popular alcoholic beverage.

9 – 1 - Health effects

The main active ingredient of beer is alcohol, and therefore, the health effects of alcohol apply to beer. The moderate consumption of alcohol, including beer, is associated with a decreased risk of cardiac disease, stroke and cognitive decline . The long term health effects of continuous, heavy alcohol consumption can, however, include the risk of developing alcoholism and alcoholic liver disease.

Brewer's yeast is known to be a rich source of nutrients; there fore, as expected, beer can contain significant amounts of nutrients, including magnesium, selenium, potassium, phosphorus, biotin, chromium and B vitamins. In fact, beer is sometimes referred to as "liquid bread". Some sources maintain that filtered beer loses much of its nutrition.

A 2005 Japanese study found that low alcohol beer may possess strong anti-cancer properties. Another study found nonalcoholic beer to mirror the cardiovascular benefits associated with moderate consumption of alcoholic beverages . However, much research suggests that the primary health benefit from alcoholic beverages comes from the alcohol they contain.

It is considered that overeating and lack of muscle tone is the main cause of a beer belly, rather than beer consumption. A recent study, however, found a link between binge drinking and a beer belly. But with most overconsumption, it is more a problem of improper exercise and overconsumption of carbohydrates than the product itself . Several diet books quote beer as having an undesirably high glycemic index of 110, the same as maltose; however, the maltose in beer undergoes metabolism by yeast during fermentation so that beer consists mostly of water, hop oils and only trace amounts of sugars, including maltose.

10 - Nutritional information

1 can of beer (356 ml) contains :
Calories :153
Fat(g): 0
Carbohydrates(g): 12.64
Fibers (g): 0
Protein (g): 1.64
Cholesterol (mg): 0

11 - Related beverages

Around the world, there are a number of traditional and ancient starch-based beverages classed as beer. In Africa, there are various ethnic beers made from sorghum or millet, such as Oshikundu in Namibia and Tella in Ethiopia . Kyrgyzstan also has a beer made from millet; it is a low alcohol, somewhat porridge - like drink called "Bozo". Bhutan, Nepal, Tibet and Sikkim also use millet in Chhaang, a popular semi-fermented rice/millet drink in the eastern Himalayas. Further east in China are found Huangjiu and Choujiu — traditional rice-based beverages related to beer.

The Andes in South America has Chicha, made from germinated maize (corn); while the indigenous peoples in Brazil have Cauim, a traditional beverage made since pre-Columbian times by chewing manioc so that enzymes present in human saliva can break down the starch into fermentable sugars ; this is similar to Masato in Peru.

Some beers which are made from bread, which is linked to the earliest forms of beer, are Sahti in Finland, Kvass in Russia and Ukraine, and Bouza in Sudan.

12 - Chemistry

Hops, and beer made with it, contain 8-prenylnaringenin which is a potent phytoestrogen . Hop also contains myrcene, humulene, xanthohumol, isoxanthohumol, myrcenol, linalool, tannins and resin. The alcohol 2M2B is a component of hops brewing.

History of Beer

Contents

1 - Introduction

Ale is one of the oldest beverages humans have produced, dating back to at least the 5th millennium BC and recorded in the written history of Ancient Egypt and Mesopotamia. As almost any cereal containing certain sugars can undergo spontaneous fermentation due to wild yeasts in the air, it is possible that beer-like beverages were independently developed throughout the world soon after a tribe or culture had domesticated cereal. Chemical tests of ancient pottery jars reveal that beer was produced about 7,000 years ago in what is today Iran, and was one of the first-known biological engineering tasks where the biological process of fermentation is used in a process. In Mesopotamia, the oldest evidence of beer is believed to be a 6,000-year-old Sumerian tablet depicting people drinking a beverage through reed straws from a communal bowl. A 3900-year-old Sumerian poem honoring Ninkasi, the patron goddess of brewing, contains the oldest surviving beer recipe, describing the production of beer from barley via bread.

The invention of bread and/or beer has been argued to be responsible for humanity's ability to develop technology and build civilization . The earliest chemically confirmed barley beer to date was discovered at Godin Tepe in the central Zagros Mountains of Iran, ca. 3500-3100 B.C. (Chalcolithic / Late Uruk Period).

Beer may have been known in Neolithic Europe as far back as 3000 BC, and was mainly brewed on a domestic scale.

Ale produced before the Industrial Revolution continued to be made and sold on a domestic scale, although by the 7th century AD beer was also being produced and sold by European monasteries. During the Industrial Revolution, the production of beer moved from artisanal manufacture to industrial manufacture, and domestic manufacture ceased to be significant by the end of the 19th century. The development of hydrometers and thermometers changed brewing by allowing the brewer more control of the process, and greater knowledge of the results.

Today, the brewing industry is a global business, consisting of several dominant multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries. More than 133 billion liters are sold per year —producing total global revenues of $ 294.5 billion in 2006.

2 - History

In ancient Mesopotamia, clay tablets indicate that brewing was a fairly well respected occupation during the time, and that the majority of brewers were women . It was discovered early that reusing the same container for fermenting the mash would produce more reliable results: brewers on the move carried their tubs with them.

The Ebla tablets, discovered in 1974 in Ebla, Syria, which date to 2500 BC, reveal that the city produced a range of beers, including one that appears to be named "Ebla" after the city. Early traces of beer and the brewing process have been found in ancient Babylonia as well. At the time, brewers were women as well, but also priestesses. Some types of beers were used especially in religious ceremonies. In 2100 BC, the Babylonian king Hammurabi included regulations governing tavern keepers in his law code for the kingdom.

Beer was part of the daily diet of Egyptian Pharaohs over 5,000 years ago. Then, it was made from baked barley bread, and was also used in religious practices.

The role of beer in Egyptian society was far greater than just a drink. Often, beer was prescribed to treat various illnesses. Beer was considered to be the most proper gift to give to Egyptian Pharaohs, and it was also offered as a sacrifice to the gods.

Based on historical evidence, it appears that the Egyptians taught the Greeks the beer brewing process. The Greek writer Sophocles (450 BC) discussed the concept of moderation when it came to consuming beer in Greek culture, and believed that the best diet for Greeks consisted of bread, meats, various types of vegetables, and beer or (*zythos*) as they called it. The ancient Greeks also made barley wine (Greek : *krithinos oinos*, "barley wine") mentioned by Greek historian Polybius in his work *The Histories*, where he states that Phaeacians kept barleywine in silver and golden kraters.

In contrast to the Egyptians and Sumerians, "beer never played an important role among the drinking customs of the land of Israel." This is the current state of archaeology pronounced by the Jewish Museum, New York and Jerusalem, relating to the practices of Ancient Israelites.

The process of brewing beer grew tremendously during the rise of Christianity. This was primarily because of the roles that monks had in the production of beer. Monasteries were some of the first organizations to brew beer as a trade. Monks built breweries as part of their efforts to provide food, shelter and drink to various travelers and pilgrims.

A large number of Christian saints are patrons of brewing. Saint Augustine of Hippo, Saint Arnulf of Metz, Saint Luke the Evangelist, and Saint Nicholas all are considered to be patrons of brewing.

Emperor Charlemagne, the ruler of the Christian kingdom around 770 AD considered beer to be an important part of living, and is often thought to have trained Christian brewers himself.

As in ancient times, women were the primary brewers during the Middle Ages. Women took over brewing after the monasteries had really established the process.

3 - Early beers

A replica of ancient Egyptian beer, brewed from emmer wheat by the Courage brewery in 1996

As almost any cereal containing certain sugars can undergo spontaneous fermentation due to wild yeasts in the air, it is possible that beer-like beverages were independently developed throughout the world soon after a tribe or culture had domesticated cereal. Chemical tests of ancient pottery jars reveal that beer was produced about 3,500 BC in what is today Iran, and was one of the first-known biological engineering tasks where the biological process of fermentation is used. Also recent archaeological findings showing that Chinese villagers were brewing fermented alcoholic drinks as far back as 7000 BC on small and individual scale, with the production process and methods similar to that of ancient Egypt and Mesopotamia.

In Mesopotamia (Ancient Iraq), early evidence of beer is a 3900 - year - old Sumerian poem honoring Ninkasi, the patron goddess of brewing, which contains the oldest surviving beer recipe, describing the production of beer from barley via bread.

Beer is also mentioned in the *Epic of Gilgamesh*, in which the 'wild man' Enkidu is given beer to drink. "...he ate until he was full, drank seven pitchers of beer, his heart grew light, his face glowed and he sang out with joy."

Confirmed written evidence of ancient beer production in Armenia can be obtained from Xenophon in his work Anabasis (5th century B.C.) when he was in one of the ancient Armenian villages in which he wrote :

> "*There were stores within of wheat and barley and vegetables, and wine made from barley in great big bowls; the grains of barley malt lay floating in the beverage up to the lip of the vessel, and reeds lay in them, some longer, some shorter, without joints; when you were thirsty you must take one of these into your mouth, and suck. The beverage without admixture of water was very strong, and of a delicious flavour to certain palates, but the taste must be acquired.*
> "

Beer became vital to all the grain-growing civilizations of Eurasian and North African antiquity, including Egypt—so much so that in 1868 James Death put forward a theory in *The Beer of the Bible* that the manna from heaven that God gave the Israelites was a bread - based, porridge - like beer called *wusa*.

These beers were often thick, more of a gruel than a beverage, and drinking straws were used by the Sumerians to avoid the bitter solids left over from fermentation. Though beer was drunk in Ancient Rome, it was replaced in popularity by wine.[24] Tacitus wrote disparagingly of the beer brewed by the

Germanic peoples of his day. Thracians were also known to consume beer made from rye, even since the 5th century BC, as Hellanicus of Lesbos says. Their name for beer was *brutos*, or *brytos*. The Romans called their brew *cerevisia*, from the Celtic word for it.

Ancient Nubians had used beer as an antibiotic medicine.

4 - Medieval Europe

Beer was one of the most common drinks during the Middle Ages. It was consumed daily by all social classes in the northern and eastern parts of Europe where grape cultivation was difficult or impossible. Though wine of varying qualities was the most common drink in the south, beer was still popular among the lower classes. Since the purity of water could seldom be guaranteed, alcoholic drinks were a popular choice, having been boiled as part of the brewing process. Beer also provided a considerable amount of the daily calories in the northern regions. In England and the Low Countries, the per capita consumption was 275 – 300 liters a year by the Late Middle Ages, and beer was drunk with every meal. Though probably one of the most popular drinks in Europe, beer was disdained by science as being unhealthy, mostly because ancient Greek and more contemporary Arab physicians had little or no experience with the drink. In 1256, the Aldobrandino of Siena described the nature of beer in the following way :

"*But from whichever it is made, whether from oats, barley or wheat, it harms the head and the stomach, it causes bad breath and ruins the teeth, it fills the stomach with bad fumes, and as a result anyone who drinks it along with wine becomes drunk quickly; but it does have the property of facilitating urination and makes one's flesh white and smooth.*"

The use of hops in beer was written of in 822 by a Carolingian Abbot. Flavoring beer with hops was known at least since the 9th century, but was only gradually adopted because of difficulties in establishing the right proportions of ingredients. Before that, gruit, a mix of various herbs, had been used, but did not have the same conserving properties as hops. Beer flavored without it was often spoiled soon after preparation and could not be exported. The only other alternative was to increase the alcohol content, which was rather expensive. Hopped beer was perfected in the medieval towns of Bohemia in the Czech Republic by the 13th century. German towns pioneered a new scale of operation with standardized barrel sizes that allowed for large - scale export. Previously beer had been brewed at home, but the production was now successfully replaced by medium-sized operations of about eight to ten people. This type of production spread to Holland in the 14 th century and later to Flanders, Brabant and reached England by the late 15 th century.

English ale and beer brewing were carried out separately, no brewer being allowed to produce both. The Brewers Company of London stated "no hops, herbs, or other like thing be put into any ale or liquore where of ale shall be made – but only liquor (water), malt, and yeast." This comment is some times misquoted as a prohibition on hopped beer.

5 - Early modern Europe

A 16th century brewery

In Europe, beer largely remained a homemaker's activity, made in the home in medieval times. The oldest still operating commercial brewery is the Weihenstephan (Bavaria) abbey brewery, which obtained the brewing rights from the nearby town of Freising in 1040. By the 14th and 15th centuries, beermaking was gradually changing from a family-oriented activity to an artisan one, with pubs and monasteries brewing their own beer for mass consumption.

In 15th century England, an unhopped beer would have been known as an ale, while the use of hops would make it a beer. Hopped beer was imported to England from the Netherlands as early as 1400 in Winchester, and hops were being planted on the island by 1428. The popularity of hops was at first mixed—the Brewers Company of London went so far as to state *"no hops, herbs, or other like thing be put into any ale or liquore wherof ale shall be made—but only liquor (water), malt, and yeast."* However, by the 16th century, "ale" had come to refer to any strong beer, and all ales and beers were hopped, giving rise to the verse noted by the curious antiquary John Aubrey

In 1516, William IV, Duke of Bavaria, adopted the *Reinheitsgebot* (purity law), perhaps the oldest food regulation still in use through the 20th century (the Reinheitsgebot passed formally from German law in 1987). The *Gebot* ordered that the ingredients of beer be restricted to water, barley, and hops; yeast was added to the list after Louis Pasteur's discovery in 1857. The Bavarian law was applied throughout Germany as part of the 1871 German unification as the German Empire under Otto von Bismarck, and has since been updated to reflect modern trends in beer brewing. To this day, the *Gebot* is considered a mark of purity in beers, although this is controversial.

Most beers until relatively recent times were top-fermented. Bottom-fermented beers were discovered by accident in the 16th century after beer was stored in cool caverns for long periods; they have since largely outpaced top-fermented beers in terms of volume.

6 - Asia

There is pre - historic evidence that shows brewing began around 5400 BC in Sumer (southern Iraq). However, as with the history of corn whiskey, the production of other alcoholic beverages is often seen as a way to preserve excess grain, rather than an occupation in and of itself.

Documented evidence and recently excavated tombs indicate that the Chinese brewed alcoholic beverages from both malted grain and grain converted by mold from prehistoric times, but that the malt conversion process was largely considered inefficient in comparison with the use of molds specially cultivated on rice carrier (the resulting molded rice eing called (Jiǔ qū) in Chinese and Koji in Japanese) to convert cooked rice into fermentable sugars, both in the amount of resulting fermentable sugars and the residual by products (the Chinese use the dregs left after fermenting the rice, called 酒糟 (Jiǔzāo), as a cooking ingredient in many dishes, frequently as an ingredient to sauces where Western dishes would use wine), because the rice undergoes starch conversion after being hulled and cooked, rather than whole and in husks like barley malt. Furthermore, the hop plant being unknown in East Asia, malt-based alcoholic beverages did not preserve well over time, and the use of malt in the production of alcoholic beverages gradually fell out of favor in China until disappearing from Chinese history by the end of the Tang Dynasty. The use of rice became dominant, such that wines from fruits of any type were historically all but unknown except as imports in China.

The production of alcoholic beverage from cooked rice converted by microbes continues to this day, and some classify such beverages (米酒 (Mĭjiǔ) in Chinese and Sake in Japanese) as beers since they are made from converted starch rather than fruit sugars. However, this is a debatable point, and such beverages are generally referred to as "rice wine" or "sake" which is really the generic Chinese and Japanese word for all alcoholic beverages.

Some Pacific island cultures ferment starch that has been converted to fermentable sugars by human saliva, similar to the chicha of South America. This practice is also used by many other tribes around the world, who either chew the grain and then spit it into the fermentation vessel or spit into a fermentation vessel containing cooked grain, which is then sealed up for the fermentation. Enzymes in the spittle convert the starch into fermentable sugars, which are fermented by wild yeast. Whether or not the resulting product can be called beer is sometimes disputed, since :

As with Asian rice-based liquors, it does not involve malting.

This method is often used with starches derived from sources other than grain, such as yams, taro, or other such root vegetables.

Some Taiwanese tribes have taken the process a step further by distilling the resulting alcoholic beverage, resulting in a clear liquor. However, as none of the Taiwanese tribes are known to have developed systems of writing, there is no way to document how far back this practice goes, or if the technique was brought from Mainland China by Han Chinese immigrants. Judging by the fact that this technique is usually found in tribes using millet (a grain native to northern China) as the ingredient, the latter seems much more likely.

Asia's first brewery was incorporated in 1855 (although it was established earlier) by Edward Dyer at Kasauli in the Himalayan Mountains in India under the name Dyer Breweries. The company still exists and is known as Mohan Meakin, today comprising a large group of companies across many industries.

7 - The Industrial Revolution

Following significant improvements in the efficiency of the steam engine in 1765, industrialization of beer became a reality. Further innovations in the brewing process came about with the introduction of the thermometer in 1760 and hydrometer in 1770, which allowed brewers to increase efficiency and attenuation.

Prior to the late 18th century, malt was primarily dried over fires made from wood, charcoal, or straw, and after 1600, from coke.

In general, none of these early malts would have been well shielded from the smoke involved in the kilning process, and consequently, early beers would have had a smoky component to their flavors; evidence indicates that maltsters and brewers constantly tried to minimize the smokiness of the finished beer.

Writers of the period describe the distinctive taste derived from wood-smoked malts, and the almost universal revulsion it engendered. The smoked beers and ales of the West Country were famous for being undrinkable – locals and the desperate excepted. This is from "Directions for Brewing Malt Liquors" (1700) :

In most parts of the West, their malt is so stenched with the Smoak of the Wood, with which 'tis dryed, that no Stranger can endure it, though the inhabitants, who are familiarized to it, can swallow it as the Hollanders do their thick Black Beer Brewed with Buck Wheat.

In some places it [malt] is dried at leisure with wood alone, or straw alone, in other with wood and straw together, but, of all, the straw-dried is the most excellent. For the wood-dried malt, when it is brewed, beside that the drink is higher of colour, it doth hurt and annoy the head of him that is not used thereto, because of the smoke. Such also as use both indifferently do bark, cleave, and dry their wood in an oven, thereby to remove all moisture that should procure the fume...

Brown Malts are dryed with Straw, Wood and Fern, etc. The straw- dryed is the best, but the wood sort has a most unnatural Taste, that few can bear with, but the necessitous, and those that are accustomed to its strong smoky tang; yet it is much used in some of the Western Parts of England, and many thousand Quarters of this malt has been formerly used in London for brewing the Butt- keeoing-beers with, and that because it sold for two shillings per Quarter cheaper than Straw-dryed Malt, nor was this Quality of the Wood-dryed Malt much regarded by some of its Brewers, for that its ill Taste is lost in nine or twelve Months, by the Age of the Beer, and the strength of the great Quantity of Hops that were used in its preservation.

The hydrometer transformed how beer was brewed. Before its introduction beers were brewed from a single malt: brown beers from brown malt, amber beers from amber malt, pale beers from pale malt. Using the hydrometer, brewers could calculate the yield from different malts. They observed that pale malt, though more expensive, yielded far more fermentable material than cheaper malts. For example, brown malt (used for Porter) gave 54 pounds of extract per quarter, whilst pale malt gave 80 pounds. Once this was known, brewers switched to using mostly pale malt for all beers supplemented with a small quantity of highly-coloured malt to achieve the correct colour for darker beers.

The invention of the drum roaster in 1817 by Daniel Wheeler allowed for the creation of very dark, roasted malts, contributing to the flavour of porters and stouts. Its development was prompted by a British law of 1816 forbidding the use of any ingredients other than malt and hops. Porter brewers, employing a predominantly pale malt grist, urgently needed a legal colourant. Wheeler's patent malt was the solution.

The discovery of yeast's role in fermentation in 1857 by Louis Pasteur gave brewers methods to prevent the souring of beer by undesirable microorganisms.

6 - Modern beer

Many European nations have unbroken brewing traditions dating back to the earliest historical records. Beer is an especially important drink in countries such as Belgium, Germany, Austria, Ireland, UK, France, the Scandinavian countries, Poland, the Czech Republic, Spain and others having strong and unique brewing traditions with their own history, characteristic brewing methods, and styles of beer.

Unlike in many parts of the world, there is a significant market in Europe (the UK in particular) for beer containing live yeast. These unfiltered, unpasteurized brews are awkward to look after compared to the commonly sold dead beers: live beer quality can suffer with poor care, but many people prefer the taste of a good live beer to a dead one. While beer is usually matured for relatively short times (a few weeks to a few months) compared to wine, some of the stronger so-called real ales have been found to develop character and flavour over the course of as much as several decades.

In some parts of the world, breweries that had begun as a family business by Germans or other European émigrés grew into large companies, often passing into hands with more concern for profits than traditions of quality, resulting in a degradation of the product.

In 1953, New Zealander Morton W. Coutts developed the technique of continuous fermentation. Coutts patented his process which involves beer flowing through sealed tanks, fermenting under pressure, and never coming into contact with the atmosphere, even when bottled. His process was introduced in the US and UK, but is now used for commercial beer production only in New Zealand .

In some sectors brewers are reluctant to embrace new technology for fear of losing the traditional characteristics of their beer. For example Marston's Brewery in Burton on Trent still uses open wooden Burton Union sets for fermentation in order to maintain the quality and flavour of its beers, while Belgium's lambic brewers go so far as to expose their brews to outside air in order to pick up the natural wild yeasts which ferment the wort. Traditional brewing techniques protect the beer from oxidation by maintaining a carbon dioxide blanket over the wort as it ferments into beer.

Modern breweries now brew many different types of beer, ranging from ancient styles such as the spontaneously-fermented lambics of Belgium; the lagers, dark beers, wheat beers and more of Germany; the UK's stouts, milds, pale ales, bitters, golden ale and new modern American creations such as Chili Beer, Cream Ale, and Double India Pale Ales.

Today, the brewing industry is a huge global business, consisting of several multinational companies, and many thousands of smaller producers ranging from brewpubs to regional breweries. Advances in refrigeration, international and transcontinental shipping, marketing and commerce have resulted in an international marketplace, where the consumer has literally hundreds of choices between various styles of local, regional, national and foreign beers.

9 - Mythology

Gambrinus–king of beer

The Finnish epic Kalevala, collected in written form in the 19th century but based on oral traditions many centuries old, devotes more lines to the origin of beer and brewing than it does to the origin of mankind.

The mythical Flemish king Gambrinus (from Jan Primus (John I)), is sometimes credited with the invention of beer.

According to Czech legend, deity Radegast, god of hospitality, invented beer.

Ninkasi was the patron goddess of brewing in ancient Sumer.

In Egyptian mythology, the immense blood-lust of the fierce lioness goddess Sekhmet was only sated after she was tricked into consuming an extremely large amount of red-coloured beer: she became so drunk that she gave up slaughter altogether and became docile.

In Norse mythology the sea god Ægir, his wife Rán, and their nine daughters, brewed ale (or mead) for the gods. In the *Lokasenna*, it is told that Ægir would host a party where all the gods would drink the beer he brewed for them. He made this in a giant kettle that Thor had brought. The cups in Ægir's hall were always full, magically refilling themselves when emptied. Ægir had two servants in his hall to assist him; Eldir [Fire-Kindler] and Fimafeng [Handy].

In Nart sagas, Satanaya (Ubykh [satanaja], Adyghe [setenej], Ossetian [ʃatana]), the mother of the Narts, a fertility figure and matriarch, invented beer.

Humulus (Hop plant)

Contents

1 - introduction

Humulus, **hop**, is a small genus of flowering plants in the family Cannabaceae, which also includes cannabis. The hop is native to temperate regions of the Northern Hemisphere. The species *H. lupulus* is the main flavour ingredient in many types of beer, and as such is widely cultivated for use by the brewing industry.

Scientific classification	
Kingdom:	Plantae
(unranked):	Angiosperms
(unranked):	Eudicots
(unranked):	Rosids
Order:	Rosales
Family:	Cannabaceae
Genus:	*Humulus* L.

2 - Description

Although frequently referred to as the hop "vine", it is technically a bine; unlike vines, which use tendrils, suckers, and other appendages for attaching themselves, bines have stout stems with stiff hairs to aid in climbing. It is a perennial herbaceous plant which sends up new shoots in early spring and dies back to the cold-hardy rhizome in autumn. Hop shoots grow very rapidly, and at the peak of growth can grow 20 to 50 centimeters per week. Hop bines climb by wrapping clockwise (except for *Humulus japonicus*) around anything within reach, and individual bines typically grow between 2 to 15 meters depending on what is available to grow on. The leaves are opposite, with a 7 to 12 cm leafstalk and a heart-shaped, fan-lobed blade 12 to 25 cm long and broad; the edges are coarsely toothed. When the hop bines run out of material to climb, horizontal shoots sprout between the leaves of the main stem to form a network of stems wound round each other.

Male and female flowers of the hop plant develop on separate plants (dioecious). Female plants, which produce the hop flowers used in brewing beer, are often propagated vegetatively and grown in the absence of male plants. This prevents pollination and the development of viable seeds, which are sometimes considered undesirable for brewing beer owing to the potential for off - flavors arising from the introduction of fatty acids from the seeds.

3 - Species

Humulus japonicus leaves

There are three species, one with five varieties:

Humulus japonicus (syn. *H. scandens*). Asian Hop. Leaves with 5–7 lobes. Eastern Asia.

Humulus lupulus. Common Hop. Leaves with 3–5 lobes. Europe, western Asia, North America.

Humulus lupulus var. *lupulus*. Europe, western Asia.

Humulus lupulus var. *cordifolius*. Eastern Asia.

Humulus lupulus var. *lupuloides* (syn. *H. americanus*). Eastern North America.

Humulus lupulus var. *neomexicanus*. Western North America.

Humulus lupulus var. *pubescens*. Midwest North America.

Humulus yunnanensis. Yunnan Hop. Leaves with 3–5 lobes, densely hairy below. Southeast Asia (endemic in Yunnan, China).

Brewers' hops are specific cultivars, propagated by asexual reproduction: see *List of hop varieties*.

4 – 1 - Hop applications

Hops are boiled with the wort in brewing beer and sometimes added post-ferment. They impart a bitterness, flavour, and aroma to the finished product.

In pharmacy *lupulus* is the designation of hop. The dried catkins, commonly referred to as hop cones, of the female plant of *H. lupulus* are used to prepare infusion of hop, tincture of hop, and extract of hop.

5 – 2 - Hop chemistry

The characteristic bitterness imparted by the addition of hops to the brewing process is mainly due to the presence of the bitter acids, which are prenylated acylphloroglucinol derivatives. Bitter acids are divided into the alpha-acids, with humulone the major compound, and the beta-acids, with lupulone the major compound. Alpha-acids isomerize during the brewing process to form iso-alpha acids, which themselves have a bitter taste . Hops also contain xanthohumol, a prenylated chalcone compound, that shows cytoprotective and other health-promoting activities

Malt

	
A handful of malted barley, the white sprouts visible	*Barley is spread out on the floor of a malt house during a traditional malting process*

Contents

1 - Introduction

Malt is germinated cereal grains that have been dried in a process known as "malting". The grains are made to germinate by soaking in water, and are then halted from germinating further by drying with hot air . Malting grains develops the enzymes required to modify the grain's starches into sugars, including the monosaccharide glucose, the disaccharide maltose, the tri saccharide maltotriose, and higher sugars called malto dextrines. It also develops other enzymes, such as proteases, which break down the proteins in the grain into forms that can be used by yeast. Malt also contains small amounts of other sugars, such as sucrose and fructose, which are not products of starch modification but were already in the grain.

Malted grain is used to make beer, whisky, malted shakes, malt vinegar, confections such as Maltesers and Whoppers, flavored drinks such as Horlicks , Ovaltine and Milo, and some baked goods, such as malt loaf, bagels and rich tea biscuits. Malted grain that has been ground into a coarse meal is known as "sweet meal". Various cereals are malted, though barley is the most common. A high-protein form of malted barley is often a label-listed ingredient in blended flours typically used in the manufacture of yeast breads and other baked goods.

The term "malt" refers to several products of the process: the grains to which this process has been applied, for example malted barley; the sugar, heavy in maltose, derived from such grains, such as the baker's malt used in various cereals; or a product based on malted milk, similar to a malted milkshake (i.e., "malts").

2 - Malting

Malting is the process of converting barley into malt, for use in brewing, distilling, or in foods and takes place in a maltings, sometimes called a malthouse, or a malting floor. The sprouted barley is kiln-dried by spreading it on a perforated wooden floor. Smoke, coming from an oasting fire place (via smoke channels) is then used to heat the wooden floor and the sprouted grains. The temperature is usually around 55 °C . A typical floor maltings is a long, single-storey building with a floor that slopes slightly from one end of the building to the other. Floor maltings began to be phased out in the 1940s in favour of "pneumatic plants". Here, large industrial fans are used to blow air through the germinating grain beds and to pass hot air through the malt being kilned. Like floor maltings, these pneumatic plants are batch processes, but of considerably greater size, typically 100 ton batches compared with 20 ton batches for floor malting.

The malting process starts with drying the grains to a moisture content below 14 %, and then storing for around six weeks to overcome seed dormancy. When ready, the grain is immersed or steeped in water two or three times over two or three days to allow the grain to absorb moisture and to start to sprout. When the grain has a moisture content of around 46 %, it is transferred to the malting or germination floor, where it is constantly turned over for around five days while it is air - dried. The grain at this point is called "green malt". The green malt is then kiln - dried to the desired colour and specification. Malts range in colour from very pale through crystal and amber to chocolate or black malts.

3 - Malts

Home brewing malt extracts: liquid in a can and spray dried

Barley is the most commonly malted grain, in part because of its high diastatic power or enzyme content, though wheat, rye, oats and rice are also used. Also very important is the retention of the grain's husk, even after threshing, unlike the bare seeds of threshed wheat or rye. This protects the growing acrospire (developing plant embryo) from damage during malting, which can easily lead to mold growth. It also allows the mash of converted grain to create a filter bed during lautering (see brewing). Malt is often divided into two categories by brewers: base malts and specialty malts. Base malts have enough diastatic power to convert their own starch and usually that of some amount of starch from un malted grain, called adjuncts. Specialty malts have little diastatic power; they are used to provide flavor, color, or "body" (viscosity) to the finished beer. Specialty caramel or crystal malts have been subjected to heat treatment to convert their starches to sugars nonenzymatically.

Within these categories is a variety of types distinguished largely by the kilning temperature (see mash ingredients). In addition, malts are distinguished by the two major species of barley used for malting, two-row and six-row.

4 - Malt extract

Malt extract is also known as extract of malt. It is a sweet, treacly substance used as a dietary supplement. It was popular in the first half of the twentieth century as a supplement for the children of the British urban working - class, whose diet was often deficient in vitamins and minerals. Children were given cod liver oil for the same reason but it proved so unpalatable that it was combined with extract of malt to produce "Malt and Cod - Liver Oil." It was given as a "strengthening medicine" by Kanga to Roo and Tigger in *The House at Pooh Corner*.

Barley malt syrup being slowly added to flour in a bagel recipe

The 1907 British Pharmaceutical Codex's instructions for making nutritional extract of malt do not include a mash-out at the end of extraction, and include the use of lower mash temperatures than is typical with modern beer-brewing practices. The Codex indicates that diastatic activity is to be preserved by the use of temperatures not exceeding 55 °C .

4 – 1 - Malt extract production

Malt extract is frequently used in the brewing of beer. Its production begins by germinating barley grain in a process known as malting. This procedure entails immersing barley in water to encourage the grain to sprout, then drying the barley to halt the progress when the sprouting begins. The drying step stops the sprouting, but the enzymes remain active due to the low temperatures used in base malt production. In one before-and-after comparison, malting decreased barley's extractable starch content by about 7 % on a dry matter basis, and turned that portion into various other carbohydrates.

In the next step, brewers use a process called mashing to extract the sugars. Brewers warm cracked malt in temperature-modulated water, activating the enzymes, which cleave more of the malt's remaining starch into various sugars, the largest percentage of which is maltose.[14] Modern beer mashing practices typically include high enough temperatures at mash-out to deactivate remaining enzymes, thus it is no longer diastatic. The liquid produced from this, wort, is then concentrated by using heat or a vacuum procedure to evaporate water from the mixture.

The concentrated wort is called malt extract. Brewers have the option of using a liquid (LME) or dry (DME) form of it. Each has its pros and cons, so the choice is dependent solely on the individual brewer's preferences.

Liquid malt extract is a thick syrup. Some brewers choose to work only with LME, because they feel it works best for the result they wish to achieve. Also, it requires one less processing step, so it is appealing to those favoring the purest form of product available. However, it is very sticky and, therefore, messier to work with and has a shorter shelf life, and some feel the results are just as good with DME.

A new encapsulating technology permits the production of malt granules. Malt granules are the dried liquid extract from malt used in the brewing or distilling process.

Mash Ingredients

Contents

1 - Introduction

Mash ingredients, mash bill, or grain bill are those materials used in brewing from which a wort can be obtained for fermenting into alcohol. The act of creating and extracting fermentable and non-fermentable sugars and flavor components from grain by steeping it in hot water, and then allowing it to rest at specific temperature ranges in order to activate enzymes that will convert the starches to sugars is called mashing. The sugars, having been run off from the mash ingredients, will later be converted to alcohol and other fermentation products by yeast in the brewing process.

Malted barley - a primary mash ingredient

A typical primary mash ingredient is grain that has been malted. Modern-day malt recipes generally consist of a large percentage of a light malt and, optionally, smaller percentages of more flavorful or highly colored types of malt. The former is called "base malt"; the latter is known as "specialty malts".

The grain bill of a beer or whisky may vary widely in the number and proportion of ingredients. For example, in beer-making, a simple pale ale might contain a single malted grain, while a complex porter may contain a dozen or more ingredients. In whisky production, Bourbon uses a mash made primarily from corn (often mixed with rye or wheat and a small amount of malted barley), and Single Malt Scotch exclusively uses malted barley.

2 - Variables Mashing

Each particular ingredient has its own flavor which contributes to the final character of the beverage. In addition, different ingredients carry other characteristics, not directly relating to the flavor, which may dictate some of the choices made in brewing: nitrogen content, diastatic power, color, modification, and conversion.

The color of a grain or product is evaluated by the American Society of Brewing Chemists Standard Reference Method (denoted both SRM and ASBC, although the two methods are equivalent); the older Lovibond series 52 standard, (°L), which corresponds closely to SRM; or by the European Brewery Convention (EBC) standard. The British Institute of Brewing (IOB) standard was formally retired in 1991, but is still occasionally seen in the United Kingdom.

Diastatic power also called the "diastatic activity" or "enzymatic power" for a grain is measured in degrees Lintner (°Lintner or °L, although the latter can conflict with the symbol °L for Lovibond color); or in Europe by Windisch-Kolbach units (°WK).

3 - Malts

The oldest and most predominant ingredient in brewing is barley, which has been used in beer-making for thousands of years. Modern brewing predominantly uses malted barley for its enzymatic power, but ancient Babylonian recipes indicate that, without the ability to malt grain in a controlled fashion, baked bread was simply soaked in water Malted barley dried at a sufficiently low temperature contains enzymes such as amylase which convert starch into sugar. Therefore, sugars can be extracted from the barley's own starches simply by soaking the grain in water at a controlled temperature; this is mashing.

3 - 1 - Pale malt

Pale malt is the basis of pale ale and bitter and the precursor in production of most other British beer malts. Dried at temperatures sufficiently low to preserve all the brewing enzymes in the grain, it is light in color and, today, the cheapest barley malt available due to mass production. It can be used as a *base malt*, that is, as the malt constituting the majority of the grist, in many styles of beer. Typically, English pale malts are kilned at 95-105 °C. Color ASBC 2-3/EBC 5-7. Diastatic power (DP) 45 °Lintner.

3 - 2 - Mild malt

Mild malt is often used as the base malt for mild ale, and is similar in color to pale malt. Mild malt is kilned at slightly higher temperatures than pale malt in order to provide a less neutral, rounder flavor generally described as "nutty". ASBC 3/EBC 6.

3 - 3 - Stout malt

Stout malt is sometimes seen as a base malt for stout beer; light in color, it is prepared so as to maximize diastatic power in order to better-convert the large quantities of dark malts and un malted grain used in stouts. In practice, however, most stout recipes make use of pale malt for its much greater availability. ASBC 2-3 / EBC 4- 6 , DP 60 -70 °Lintner.

3 - 4 - Amber malt

Amber malt is a more toasted form of pale malt, kilned at temperatures of 150 -160 °C, and is used in brown porter; older formulations of brown porter use amber malt as a base malt (though this was diastatic and produced in different conditions to a modern amber malt). Amber malt has a bitter flavor which mellows on aging, and can be quite intensely flavored; in addition to its use in porter, it also appears in a diverse range of British beer recipes. ASBC 50-70/EBC 100-140; amber malt has no diastatic power.

3 - 5 - Brown malt

Brown malt is a darker form of pale malt, and is used typically in brown ale as well as in porter and stout. Like amber malt, it can be prepared from pale malt at home by baking a thin layer of pale malt in an oven until the desired color is achieved. 50-70 °L, no enzymes.

3 - 6 - Chocolate malt

Chocolate malt is similar to pale and amber malts but kilned at even higher temperatures. Producing complex undertones of vanilla and caramel (but not chocolate), it is used in porters and sweet stouts as well as dark mild ales. It contains no enzymes . ASBC 450 - 500 / EBC 1100 -1300.

3 - 7 - Black malt

Black malt, also called patent malt or black patent malt, is barley malt that has been kilned to the point of carbonizing, around 200 °C. The term "patent malt" comes from its invention in England in 1817, late enough that the inventor of the process for its manufacture, Daniel Wheeler, was awarded a patent. Black malt provides the color and some of the flavor in black porter, contributing an acrid, ashy undertone to the taste. In small quantities, black malt can also be used to darken beer to a desired color, sometimes as a substitute for caramel color. Due to its high kilning temperature, it contains no enzymes. ASBC 500-600/EBC >1300.

3 - 8 - Crystal malt

A paler example of Crystal malt

Crystal malts are prepared separately from pale malts. They are high-nitrogen malts that are wetted and roasted in a rotating drum before kilning. They produce strongly sweet toffee - like flavors and are sufficiently converted that they can be steeped without mashing to extract their flavor. Crystal malts are available in a range of colors, with darker - colored crystal malts kilned at higher temperatures producing stronger, more caramel-like overtones. Some of the sugars in crystal malts caramelize during kilning and become unfermentable; hence, addition of crystal malt will increase the final sweetness of a beer. They contain no enzymes. ASBC 50 - 165 / EBC 90 – 320 ; the typical British crystal malt used in pale ale and bitter is around ASBC 70 - 80.

3 – 9 - Distillers malt

Standard distillers malt or pot still malt is quite light and very high in nitrogen compared to beer malts. These malts are used in the production of whiskey/whisky and generally originate from northern Scotland.

3 - 10 - Peated malt

Peated malt is also available; this is distillers malt that has been smoked over burning peat, which imparts the aroma and flavor characteristics of Islay whisky and some Irish whiskey. Some recent brewers have also included peated malt in interpretations of Scotch ales, although this is generally ahistorical. When peat is used in large amounts for beer making, the resulting beer tends to have a very strong earthy and smoky flavour which most mainstream beer drinkers would find extremely irregular.

3 - 11 - Pilsner malt

Pilsner malt, the basis of pale lager, is quite pale and strongly flavored. Invented in the 1840s, Pilsner malt is the lightest-colored generally-available malt, and also carries a strong, sweet malt flavor. Usually a pale lager's grain bill consists entirely of this malt, which has enough enzymatic power to be used as a base malt. The commercial desirability of light-colored beers has also led to some British brewers adopting Pilsner malt (sometimes described simply as "lager malt" in Britain) in creating golden ales. In Germany, Pilsner malt is also used in some interpretations of the Kölsch style. ASBC 1-2/EBC 3-4, DP 60 °Lintner.

3 - 12 - Vienna malt

Vienna malt or Helles malt is the characteristic grain of Vienna lager and Märzen; although it generally takes up only ten to fifteen percent of the grain bill in a beer, it can be used as a base malt. It has sufficient enzymatic power to self-convert, and it is somewhat darker and kilned at a higher temperature than Pilsener malt. ASBC 3-4/EBC 7-10, DP 50 °Lintner.

3 - 13 - Munich malt

Munich malt is used as the base malt of the bock beer style, especially doppelbock, and appears in dunkel lager and Märzens in smaller quantities. While a darker grain than pale malt, it has sufficient diastatic power to self-convert, despite being kilned at temperatures around 115 °C. It imparts "malty," although not necessarily sweet characteristics, depending on mashing temperatures. ASBC 4-6/EBC 10-15, DP 40 °Lintner.

3 - 14 - Rauchmalz

Rauchmalz is a German malt that is prepared by being dried over an open flame rather than via kiln. The grain has a smoky aroma and is an essential ingredient in Bamberg Rauchbier.

3 - 15 - Acid malt

Acid malt, whose grains contain lactic acid, can be used as a continental analog to Burtonization. Acid malt lowers mash pH, and provides a rounder, fuller character to the beer, enhancing the flavor of Pilseners and other light lagers. Lowering the pH also helps prevent beer spoilage through oxidation.

Honey malt is an intensely-flavored, lightly colored malt. 18 - 20 °L.

Melanoidin malt, a malt like the Belgian Aromatic malt, adds roundness and malt flavor to a beer with a comparably small addition in the grain bill. It also stabilizes the flavor.

3 - 16 – Un malted barley

Un malted barley kernels are used in mashes in Irish whiskey.

Roast barley are unmalted barley kernels which has been toasted in an oven until almost black. Roast barley is, after base malt, usually the most-used grain in stout beers, contributing the majority of the flavor and the characteristic dark-brown color; undertones of chocolate and coffee are common. ASBC 500 - 600 / EBC >1300 or more, no diastatic activity.

Black barley is like roast barley except even darker.

Flaked barley is unmalted, dried barley which has been rolled into flat flakes. It imparts a rich, grainy flavor to beer and is used in many stouts, especially Guinness stout; it also improves head formation and retention.

Torrefied barley is barley kernels that have been heated until they pop like popcorn.

4 - Other grains

4 – 1 - Wheat

4 – 1 - 1 - Wheat malt

Beer brewed in the German Hefeweizen style relies heavily on malted wheat as a grain. Under the Reinheitsgebot, wheat was treated separately from barley, as it was the more expensive grain.

4 – 1 - 2 - Torrefied wheat

Torrefied wheat is used in British brewing to increase the size and retention of a head in beer. Generally it is used as an enhancer rather than for its flavor.

4 – 1 - 3 - Raw wheat

Belgian witbier and Lambic make heavy use of raw wheat in their grist. It provides the distinctive taste and clouded appearance in a witbier and the more complex carbohydrates needed for the wild yeast and bacteria that make a lambic.

4 – 1 – 4 - Wheat flour

Until the general availability of torrefied wheat, wheat flour was often used for similar purposes in brewing. Wheat flour was also, erroneously, used as a yeast food in medieval and renaissance brewing; flour would be cast into the fermenter to feed top-floating yeasts, which have no means of absorbing the raw flour. Brewer's flour is only rarely available today, and is of a larger grist than baker's flour.

4 - 2 - Rye

The use of rye in a beer typifies the rye beer style, especially the German *Roggenbier*. Rye is also used in the Slavic kvass and Finnish sahti farmhouse styles, as readily-available grains in eastern Europe. However, the use of rye in brewing is considered difficult as rye lacks a hull (like wheat) and contains large quantities of beta-glucans compared to other grains; these long-chain sugars can leach out during a mash, creating a sticky gelatinous gum in the mash tun, and as a result brewing with rye requires a long, thorough beta-glucanase rest. Rye is said to impart a spicy, dry flavor to beer.

4 - 3 - Sorghum and millet

Sorghum and millet are often used in African brewing. As gluten-free grains, they have gained popularity in the Northern Hemisphere as base materials for beers suitable for people with coeliac disease. Sorghum produces a dark, hazy beer, however, and sorghum malt is difficult to prepare and rarely commercially available outside certain African countries. Millet is an ingredient in chhaang and pomba, and both grains together are used in oshikundu.

4 - 4 - Rice and corn

In the US, rice and corn are often used by commercial breweries as a means of adding fermentable sugars to a beer cheaply, due to the ready availability and low price of the grains. Corn is also the base grain in chicha and some caium, as well as Bourbon whiskey and Tennessee Whiskey; while rice is the base grain of happoshu and various mostly Asian fermented beverages often referred to as "rice wines" such as sake and makgeolli; corn is also used as an ingredient in some Belgian beers such as Rodenbach to lighten the body.

Corn was originally introduced into the brewing of American lagers because of the high protein content of the six-row barley; adding corn, which is high in sugar but low in protein, helped thin out the body of the resulting beer. Increased amounts of corn use over time led to the development of the American pale lager style. Corn is generally not malted (although it is in some whiskey recipes) but instead introduced into the mash as flaked, dried kernels. Prior to a brew, rice and corn are cooked to allow the starch to gelatinize and thereby render it convertible.

5 – Non - grain solids

Buck wheat and quinoa, while not grains, both contain high levels of available starch and protein, while containing no gluten. Therefore, some breweries use these plants in the production of beer suitable for people with coeliac disease, either alone or in combination with sorghum.

6 - Syrups and extracts

Another way of adding sugar or flavoring to a malt beverage is the addition of natural or artificial sugar products such as honey, white sugar, Dextrose, and / or malt extract. While these ingredients can be added during the mash, the enzymes in the mash do not act on them. Such ingredients can be added during the boil of the wort rather than the mash, and as such, are also known as *copper sugars*.

One syrup which is commonly used in the mash, however, is dry or dried malt extract or DME. DME is prepared by fully converting base malt, then draining the resulting mash, still including amylases, and evaporating it down to a high density. DME is used exclusively in home brewing as a substitute for base malt. It typically has no diastatic power because it is all used up in the production process.

7 - Regional differences

7 – 1 - Britain

British brewing makes use of a wide variety of malts, with considerable stylistic freedom for the brewer to blend them. Many British malts were developed only as recently as the Industrial Revolution, as improvements in temperature-controlled kilning allowed finer control over the drying and toasting of the malted grains.

The typical British brewer's malt is a well-modified, low-nitrogen barley grown in the east of England or southeast of Scotland. In England, the best-known brewer's malt is made from the Maris Otter strain of barley; other common strains are Halcyon, Pipkin, Chariot, and Fanfare. Most malts in current use in Britain are derived from pale malt and were invented no earlier than the reign of Queen Anne. Brewing malt production in Britain is thoroughly industrialized, with barley grown on dedicated land and malts prepared in bulk in large, purpose-build maltings and distributed to brewers around the country to order.

7 – 2 - Continental Europe

Before controlled - temperature kilning became available, malted grains were dried over wood fires; Rauchmalz (German: *smoked malt*) is malt dried using this traditional process. In Germany, beech is often used as the wood for the fire, imparting a strongly smoky flavor to the malt. This malt is then used as the primary component of rauchbier; alder-smoked malt is used in Alaskan smoked porters. Rauchmalz comes in several varieties, generally named for and corresponding to standard kilned varieties (e.g. Rauchpilsener to Pilsener); color and diastatic power are comparable to those for an equivalent kilned grain.

Similarly to crystal malts in Britain, central Europe makes use of caramel malts, which are moistened and kilned at temperatures around 55 - 65 °C in a rotating drum before being heated to higher temperatures for browning. The lower-temperature moistened kilning causes conversion and mashing to take place in the oven, resulting in a grain's starches becoming mostly or entirely converted to sugar before darkening. Caramel malts are produced in color grades analogous to other lager malts: carapils for pilsener malt, caravienne or carahell for Vienna malt, and caramunch for Munich malt. Color and final kilning temperature are comparable to non-caramel analog malts; there is no diastatic activity. Carapils malt is sometimes also called dextrin malt. 10 -120 °L .

7 – 3 - The United States

American brewing combines British and Central European heritages, and as such uses all the above forms of beer malt; Belgian-style brewing is less common but its popularity is growing. In addition, America also makes use of some specialized malts:

6 - row pale malt is a pale malt made from a different species of barley. Quite high in nitrogen, 6-row malt is used as a "hot" base malt for rapid, thorough conversion in a mash, as well as for extra body and fullness; the flavor is more neutral than 2-row malt. 1.8 °L, 160 °Lintner.

Victory malt is a specialized lightly roasted 2-row malt that provides biscuity, caramel flavors to a beer. Similar in color to amber and brown malt, it is often an addition to American brown ale. 25 °L, no diastatic power.

Other notable American barley malts include Special Roast and coffee malt. Special Roast is akin to a darker variety of victory malt.

7 – 4 - Belgium

Belgian brewing makes use of the same grains as central European brewing. In general, though, Belgian malts are slightly darker and sweeter than their central European counterparts. In addition, Belgian brewing uses some local malts:

Pale malt in Belgium is generally darker than British pale malt. Kilning takes place at temperatures five to ten °C lower than for British pale malt, but for longer periods; diastatic power is comparable to that of British pale malt. ASBC 4/EBC 7.

Special B is a dark, intensely sweet crystal malt providing a strong malt flavor.

Biscuit malt is a lightly flavored roasted malt used to darken some Belgian beers. 45-50 EBC/25 °L.

Aromatic malt, by contrast, provides an intensely malty flavor. Kilned at 115 °C, it retains enough diastatic power to self-convert. 50 - 55 EBC / 20 °L.

Brewing

A 16th - century brewery

Contents

1 - Introduction

Brewing is the production of beer through steeping a starch source (commonly cereal grains) in water and then fermenting with yeast. Brewing has taken place since around the 6th millennium BC, and archaeological evidence suggests that this technique was used in ancient Egypt. Descriptions of various beer recipes can be found in Sumerian writings, some of the oldest known writing of any sort. Brewing is done in a brewery by a brewer, and the brewing industry is part of most western economies.

The basic ingredients of beer are water; a starch source, such as malted barley, which is able to be fermented (converted into alcohol); a brewer's yeast to produce the fermentation; and a flavouring, such as s . A secondary starch source (an adjunct) may be used, such as maize (corn), rice or sugar. Less widely used starch sources include millet, sorghum and cassava root in Africa, potato in Brazil, and agave in Mexico, among others. The amount of each starch source in a beer recipe is collectively called the grain bill.

There are several steps in the brewing process, which include malting, milling, mashing, lautering, boiling, fermenting, conditioning, filtering, and packaging. There are three main fermentation methods, warm, cool and wild or spontaneous. Fermentation may take place in open or closed vessels. There may be a secondary fermentation that can take place in the brewery, in the cask, or in the bottle.

Brewing specifically includes the process of steeping, such as with making tea, sake, and soy sauce. Technically, wine, cider and mead are not brewed but rather vinified as there is no steeping process involving solids.

2 - Ingredients

The basic ingredients of beer are water; a starch source, such as malted barley, able to be fermented (converted into alcohol); a brewer's yeast to produce the fermentation; and a flavouring, such as s , to offset the sweetness of the malt . A mixture of starch sources may be used, with a secondary starch source, such as maize (corn), rice, or sugar, often being termed an adjunct, especially when used as a lower-cost substitute for malted barley. Less widely used starch sources include millet, sorghum, and cassava root in Africa, potato in Brazil, and agave in Mexico, among others. The amount of each starch source in a beer recipe is collectively called the grain bill.

Water

Beer is composed mostly of water. Regions have water with different mineral components; as a result, different regions were originally better suited to making certain types of beer, thus giving them a regional character. For example, Dublin has hard water well suited to making stout, such as Guinness; while Pilsen has soft water well suited to making pale lager, such as Pilsner Urquell . The waters of Burton in England contain gypsum, which benefits making pale ale to such a degree that brewers of pale ales will add gypsum to the local water in a process known as Burtonisation.

Starch source

The starch source in a beer provides the fermentable material and is a key determinant of the strength and flavour of the beer. The most common starch source used in beer is malted grain. Grain is malted by soaking it in water, allowing it to begin germination, and then drying the partially germinated grain in a kiln. Malting grain produces enzymes that will allow conversion from starches in the grain into fermentable sugars during the mash process . Different roasting times and temperatures are used to produce different colours of malt from the same grain. Darker malts will produce darker beers.

Nearly all beer includes barley malt as the majority of the starch. This is because of its fibrous husk, which is important not only in the sparging stage of brewing (in which water is washed over the mashed barley grains to form the wort) but also as a rich source of amylase, a digestive enzyme that facilitates conversion of starch into sugars. Other malted and un malted grains (including wheat, rice, oats, and rye, and, less frequently, corn and sorghum) may be used. In recent years, a few brewers have produced gluten - free beer made with sorghum with no barley malt for people that cannot digest gluten-containing grains like wheat, barley, and rye.

Hops

Hop cone in a Hallertau, Germany, hop yard

Hops are the female flower clusters or seed cones of the hop vine *Humulus lupulus* , which are used as a flavouring and preservative agent in nearly all beer made today. Hops had been used for medicinal and food flavouring purposes since Roman times; by the 7 th century in Carolingian monasteries in what is now Germany, beer was being made with hops , though it isn't until the thirteenth century that widespread cultivation of hops for use in beer is recorded . Before the thirteenth century, beer was flavoured with plants such as yarrow, wild rosemary, and bog myrtle, and other ingredients such as juniper berries, aniseed and ginger, which would be combined into a mixture known as gruit and used as hops are now used; between the thirteenth and the sixteenth century, during which hops took over as the dominant flavouring, beer flavoured with gruit was known as ale, while beer flavoured with hops was known as beer . Some beers today, such as *Fraoch* by the Scottish Heather Ales company and *Cervoise Lancelot* by the French Brasserie-Lancelot company, use plants other than hops for flavouring.

Hops contain several characteristics that brewers desire in beer: they contribute a bitterness that balances the sweetness of the malt; they provide floral, citrus, and herbal aromas and flavours; they have an antibiotic effect that favours the activity of brewer's yeast over less desirable microorganisms; and they aid in "head retention", the length of time that a foamy head will last. The acidity of hops is a preservative . Flavouring beer is the sole major commercial use of hops.

Yeast

Yeast is the microorganism that is responsible for fermentation in beer. Yeast metabolises the sugars extracted from grains, which produces alcohol and carbon dioxide, and thereby turns wort into beer. In addition to fermenting the beer, yeast influences the character and flavor . The dominant types of yeast used to make beer are *Saccharomyces cerevisiae*, known as ale yeast, and *Saccharomyces uvarum*, known as lager yeast; *Brettanomyces* ferments lambics,[26] and *Torulaspora delbrueckii* ferments Bavarian weissbier.[27] Before the role of yeast in fermentation was understood, fermentation involved wild or airborne yeasts, and a few styles such as lambics still use this method today. Emil Christian Hansen, a Danish biochemist employed by the Carlsberg Laboratory, developed pure yeast cultures which were introduced into the Carlsberg brewery in 1883,[28] and pure yeast strains are now the main fermenting source used worldwide.

Clarifying agent

Some brewers add one or more clarifying agents to beer, which typically precipitate (collect as a solid) out of the beer along with protein solids and are found only in trace amounts in the finished product. This process makes the beer appear bright and clean, rather than the cloudy appearance of ethnic and older styles of beer such as wheat beers.

Examples of clarifying agents include isinglass, obtained from swim bladders of fish; Irish moss, a seaweed; kappa carrageenan, from the seaweed *Kappaphycus cottonii*; Polyclar (artificial); and gelatin. If a beer is marked "suitable for Vegans", it was generally clarified either with seaweed or with artificial agents , although the *Fast Cask* method invented by Marston's in 2009 may provide another method.

3 - Brewing process

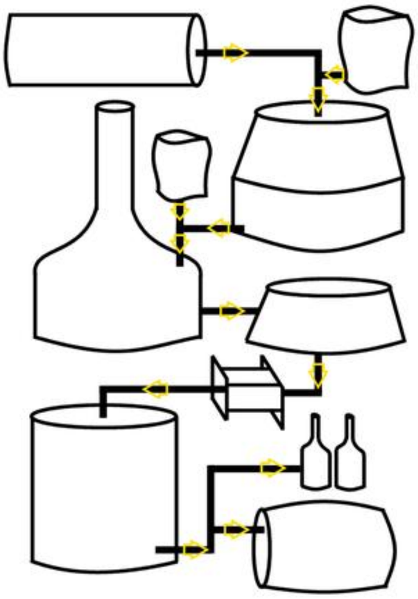


Diagram illustrating the process of brewing beer

Hot Water Tank - Mash Tun - Malt- Hops - Copper –Hop back – Add Yeast to - Fermenter – Heat exchanger- Bottling - Cask or Keg

There are several steps in the brewing process, which may include malting, mashing, lautering, boiling, fermenting, conditioning, filtering, and packaging.

Malting is the process where barley grain is made ready for brewing . Malting is broken down into three steps in order to help to release the starches in the barley. First, during steeping, the grain is added to a vat with water and allowed to soak for approximately 40 hours. During germination, the grain is spread out on the floor of the germination room for around 5 days . The final part of malting is kilning. Here, the malt goes through a very high temperature drying in a kiln. The temperature change is gradual so as not to disturb or damage the enzymes in the grain. When kilning is complete, the grains are now termed malt, and they will be milled or crushed to break apart the kernels and expose the cotyledon, which contains the majority of the carbohydrates and sugars; this makes it easier to extract the sugars during mashing.

Mashing converts the starches released during the malting stage, into sugars that can be fermented. The milled grain is mixed with hot water in a large vessel known as a mash tun. In this vessel, the grain and water are mixed together to create a cereal mash. During the mash, naturally occurring enzymes present in the malt convert the starches (long chain carbohydrates) in the grain into smaller molecules or simple sugars (mono - , di- , and tri - saccharides). This "conversion" is called saccharification. The result of the mashing process is a sugar rich liquid or "wort" (pronounced wert), which is then strained through the bottom of the mash tun in a process known as lautering. Prior to lautering, the mash temperature may be raised to about 75 °C (known as a mash out) to deactivate enzymes. Additional water may be sprinkled on the grains to extract additional sugars (a process known as sparging).

The wort is moved into a large tank known as a "copper" or kettle where it is boiled with hops and sometimes other ingredients such as herbs or sugars. This stage is where many chemical and technical reactions take place, and where important decisions about the flavour, colour, and aroma of the beer are made . The boiling process serves to terminate enzymatic processes, precipitate proteins, isomerize hop resins, and concentrate and sterilize the wort. Hops add flavour, aroma and bitterness to the beer. At the end of the boil, the hopped wort settles to clarify in a vessel called a "whirlpool", where the more solid particles in the wort are separated out.

After the whirlpool, the wort then begins the process of cooling. This is when the wort is transferred rapidly from the whirlpool or brew kettle to a heat exchanger to be cooled. The heat exchanger consists of tubing inside a tub of cold water. It is very important to quickly cool the wort to a level where yeast can be added safely as yeast is unable to grow in high temperatures . After the wort goes through the heat exchanger, the cooled wort goes into a fermentation tank. A type of yeast is selected and added, or "pitched", to the fermentation tank . When the yeast is added to the wort, the fermenting process begins, where the sugars turn into alcohol, carbon dioxide and other components. When the fermentation is complete the brewer may rack the beer into a new tank, called a conditioning tank. Conditioning of the beer is the process in which the beer ages, the flavour becomes smoother, and flavours that are unwanted dissipate. After conditioning for a week to several months, the beer may be filtered and force carbonated for bottling, or fined in the cask.

4 - Mashing

A mash tun full of grain steeping in heated "liquor" (water)

Mashing is the process of combining a mix of milled grain (typically malted barley with supplementary grains such as corn, sorghum, rye or wheat), known as the "grain bill", and water, known as "liquor", and heating this mixture in a vessel called a "mash tun". Mashing is a form of steeping, and defines the act of brewing, such as with making tea, sake, and soy sauce. Technically, wine, cider and mead are not brewed but rather vinified, as there is no steeping process involving solids. Mashing allows the enzymes in the malt to break down the starch in the grain into sugars, typically maltose to create a malty liquid called wort. There are two main methods – infusion mashing, in which the grains are heated in one vessel; and decoction mashing, in which a proportion of the grains are boiled and then returned to the mash, raising the temperature.[48] Mashing involves pauses at certain temperatures (notably 45 °C, 62 °C and 73 °C), and takes place in a "mash tun" – an insulated brewing vessel with a false bottom. The end product of mashing is called a "mash".

Mashing usually takes 1 to 2 hours, and during this time the various temperature rests activate different enzymes depending upon the type of malt being used, its modification level, and the intention of the brewer. The activity of these enzymes convert the starches of the grains to dextrins and then to fermentable sugars such as maltose. A mash rest from 49–55 °C activates various proteases, which break down proteins that might otherwise cause the beer to be hazy. This rest is generally used only with undermodified (i.e. undermalted) malts which are decreasingly popular in Germany and the Czech Republic, or non-malted grains such as corn and rice, which are widely used in North American beers. A mash rest at 60 °C (140 °F) activates β - glucanase, which breaks down gummy β-glucans in the mash, making the sugars flow out more freely later in the process. In the modern mashing process, commercial fungal based β-glucanase may be added as a supplement. Finally, a mash rest temperature of 65–71 °C is used to convert the starches in the malt to sugar, which is then usable by the yeast later in the brewing process. Doing the latter rest at the lower end of the range favours β-amylase enzymes, producing more low-order sugars like maltotriose, maltose, and glucose which are more fermentable by the yeast. This in turn creates a beer lower in body and higher in alcohol. A rest closer to the higher end of the range favours α-amylase enzymes, creating more higher-order sugars and dextrins which are less fermentable by the yeast, so a fuller-bodied beer with less alcohol is the result. Duration and pH variances also affect the sugar composition of the resulting wort.

4 – 1 - Lautering

Lautering is the separation of the wort (the liquid containing the sugar extracted during mashing) from the grains . This is done either in a mash tun outfitted with a false bottom, in a lauter tun, or in a mash filter. Most separation processes have two stages: first wort run-off, during which the extract is separated in an undiluted state from the spent grains, and sparging, in which extract which remains with the grains is rinsed off with hot water. The lauter tun is a tank with holes in the bottom small enough to hold back the large bits of grist and hulls. The bed of grist that settles on it is the actual filter. Some lauter tuns have provision for rotating rakes or knives to cut into the bed of grist to maintain good flow. The knives can be turned so they push the grain, a feature used to drive the spent grain out of the vessel . The mash filter is a plate-and-frame filter. The empty frames contain the mash, including the spent grains, and have a capacity of around one hectoliter. The plates contain a support structure for the filter cloth. The plates, frames, and filter cloths are arranged in a carrier frame like so: frame, cloth, plate, cloth, with plates at each end of the structure. Newer mash filters have bladders that can press the liquid out of the grains between spargings. The grain does not act like a filtration medium in a mash filter.

5 - Boiling

After mashing, the beer wort is boiled with hops (and other flavourings if used) in a large tank known as a "copper" or brew kettle - though historically the mash vessel was used and is still in some small breweries . The boiling process is where chemical and technical reactions take place , including sterilization of the wort to remove unwanted bacteria, releasing of hop flavours, bitterness and aroma compounds through isomerization, stopping of enzymatic processes, precipitation of proteins, and concentration of the wort . Finally, the vapours produced during the boil volatilise off - flavours, including dimethyl sulfide precursors . The boil is conducted so that it is even and intense - a continuous "rolling boil".[59] The boil on average lasts between

45 and 90 minutes, depending on its intensity, the hop addition schedule, and volume of water the brewer expects to evaporate.

At the end of the boil, the hopped wort settles to clarify in a vessel called a "whirlpool", where the more solid particles in the wort are separated out.

5 – 1 - Brew kettles or coppers

Brew kettles

The simplest boil kettles are direct-fired, with a burner underneath. These can produce a vigorous and favourable boil, but are also apt to scorch the wort where the flame touches the kettle, causing caramelization and making clean up difficult. Most breweries use a steam-fired kettle, which uses steam jackets in the kettle to boil the wort . The steam is delivered under pressure by an external boiler. State-of-the-art breweries today use many interesting boiling methods, all of which achieve a more intense boiling and a more complete realisation of the goals of boiling.

Many breweries have a boiling unit outside of the kettle, sometimes called a calandria, through which wort is pumped. The unit is usually a tall, thin cylinder, with many tubes upwards through it. These tubes provide an enormous surface area on which vapor bubbles can nucleate, and thus provides for excellent volitisation. The total volume of wort is circulated seven to twelve times an hour through this external boiler, ensuring that the wort is evenly boiled by the end of the boil. The wort is then boiled in the kettle at atmospheric pressure, and through careful control the inlets and outlets on the external boiler, an overpressure can be achieved in the external boiler, raising the boiling point by a few Celsius degrees. Upon return to the boil kettle, a vigorous vaporisation occurs. The higher temperature due to increased vaporization can reduce boil times up to 30%. External boilers were originally designed to improve performance of kettles which did not provide adequate boiling effect, but have since been adopted by the industry as a sole means of boiling wort.

Modern breweries can also be equipped with internal calandria, which requires no pump. In essence, it works on the same principle as external units, but relies on convection to move wort through the boiler. This can prevent over boiling, as a deflector above the boiler reduces foaming, and also reduces evaporation. In general, internal calandria are difficult to clean.

5 – 2 - Whirl pooling

At the end of the boil, the wort is set into a whirlpool. The so-called tea leaf paradox forces the denser solids (coagulated proteins, vegetable matter from hops) into a cone in the center of the whirlpool tank.

In most large breweries, there is a separate tank for whirl pooling. These tanks have a large diameter to encourage settling, and is flat bottomed or with a slope of 1 or 2° towards the outlet, a tangential inlet near the bottom of the whirlpool, and an outlet on the bottom near the outer edge of the whirlpool. A whirlpool should have no internal protrusions that might slow down the rotation of the liquid. The bottom of the whirlpool is often slightly sloped towards the outlet. Newer whirlpools often have "Denk rings" suspended in the middle of the whirlpool. These rings are aligned horizontally and have about 75 % of the diameter of the whirlpool. The Denk rings prevent the formation of secondary eddies in the whirlpool, encouraging the formation of a cohesive trub cone in the middle of the whirlpool. Smaller breweries often use the brew kettle as a whirlpool. The trub being the solids that the brewer wants to remove from the wort.

5 – 3 - Hop back

A hop back is a sealed chamber that is inserted in between the brewing kettle and counter - flow wort chiller. Hops are added to the chamber, the hot wort from the kettle is run through it, and then immediately cooled in the wort chiller before entering the fermentation chamber. It facilitates maximum retention of volatile hop aroma compounds that would normally be driven off when the hops contact the hot wort. Because it is a sealed chamber, the volatile hop compounds are trapped in the hot wort, and then the wort is immediately cooled, which keeps the volatile compounds in solution.

In the United Kingdom, it is common practice to use a hop back to clear the green wort (green wort is wort to which yeast has not yet been added). This device has the same effect as, but operates in a completely different manner than, a whirlpool. The two devices are often confused but are in function, quite different. While a whirlpool functions through the use of centrifugal forces, a hopback uses a layer of fresh hop flowers in a confined space to act as a filter bed to remove trub (pronounced tr-oo-b, tr-uh-b in the UK). Furthermore, while a whirlpool is useful only for the removal of pelleted hops (as flowers do not tend to separate as easily), in general hopbacks are used only for the removal of whole flower hops (as the particles left by pellets tend to make it through the hop back).

5 – 4 - Wort cooling

After the whirlpool, the wort must be brought down to fermentation temperatures (20–26°Celsius) before yeast is added. In modern breweries this is achieved through a plate heat exchanger. A plate heat exchanger has many ridged plates, which form two separate paths. The wort is pumped into the heat exchanger, and goes through every other gap between the plates. The cooling medium, usually water, goes through the other gaps. The ridges in the plates ensure turbulent flow. A good heat exchanger can drop 95 °C wort to 20 °C while warming the cooling medium from about 10 °C to 80 °C. The last few plates often use a cooling medium which can be cooled to below the freezing point, which allows a finer control over the wort-out temperature, and also enables cooling to around 10 °C. After cooling, oxygen is often dissolved into the wort to revitalize the yeast and aid its reproduction.

While boiling, it is useful to recover some of the energy used to boil the wort. On its way out of the brewery, the steam created during the boil is passed over a coil through which unheated water flows. By adjusting the rate of flow, the output temperature of the water can be controlled. This is also often done using a plate heat exchanger. The water is then stored for later use in the next mash, in equipment cleaning, or wherever necessary.

Another common method of energy recovery takes place during the wort cooling. When cold water is used to cool the wort in a heat exchanger, the water is significantly warmed. In an efficient brewery, cold water is passed through the heat exchanger at a rate set to maximize the water's temperature upon exiting. This now-hot water is then stored in a hot water tank.

6 - Fermenting

Modern fermentation tanks

Fermentation in brewing is the conversion of carbohydrates to alcohols and carbon dioxide or organic acids using yeasts, bacteria, or a combination thereof, under anaerobic conditions. A more restricted definition of fermentation is the chemical conversion of sugars into ethanol. The science of fermentation is known as zymurgy.

After the wort is cooled and aerated – usually with sterile air – yeast is added to it, and it begins to ferment. It is during this stage that sugars won from the malt are metabolized into alcohol and carbon dioxide, and the product can be called beer for the first time. Fermentation happens in tanks which come in all sorts of forms, from enormous cylindro - conical vessels, through open stone vessels, to wooden vats.

Most breweries today use cylindro-conical vessels, or CCVs, which have a conical bottom and a cylindrical top. The cone's aperture is typically around 60°, an angle that will allow the yeast to flow towards the cone's apex, but is not so steep as to take up too much vertical space. CCVs can handle both fermenting and conditioning in the same tank. At the end of fermentation, the yeast and other solids which have fallen to the cone's apex can be simply flushed out of a port at the apex.

Open fermentation vessels are also used, often for show in brewpubs, and in Europe in wheat beer fermentation. These vessels have no tops, which makes harvesting top-fermenting yeasts very easy. The open tops of the vessels make the risk of infection greater, but with proper cleaning procedures and careful protocol about who enters fermentation chambers, the risk can be well controlled.

Fermentation tanks are typically made of stainless steel. If they are simple cylindrical tanks with beveled ends, they are arranged vertically, as opposed to conditioning tanks which are usually laid out horizontally. Only a very few breweries still use wooden vats for fermentation as wood is difficult to keep clean and infection-free and must be repitched more or less yearly.

6 – 1 - Fermentation methods

There are three main fermentation methods, warm, cool and wild or spontaneous. Fermentation may take place in open or closed vessels. There may be a secondary fermentation which can take place in the brewery, in the cask or in the bottle.

Brewing yeasts may be classed as "top - cropping" (or "top-fermenting") and "bottom - cropping" (or "bottom - fermenting"). This distinction was introduced by the Dane Emil Christian Hansen. Top-cropping yeasts are so called because they form a foam at the top of the wort during fermentation. They can produce higher alcohol concentrations and in higher temperatures, typically 16 to 24 °C . produce fruitier, sweeter beers. An example of a top - cropping yeast is *Saccharomyces cerevisiae*. Bottom - cropping yeasts are typically used to produce cool fermented, lager - type beers, though they can also ferment at higher temperatures if kept under 34 C. These yeasts ferment more sugars, creating a dryer beer, and grow well at low temperatures. An example of bottom - cropping yeast is *Saccharomyces pastorianus*, formerly known as *Saccharomyces carlsbergensis*.

For both types, yeast is fully distributed through the beer while it is fermenting, and both equally flocculate (clump together and precipitate to the bottom of the vessel) when fermentation is finished. By no means do all top - cropping yeasts demonstrate this behaviour, but it features strongly in many English yeasts that may also exhibit chain forming (the failure of budded cells to break from the mother cell), which is in the technical sense different from true flocculation.

The most common top - cropping brewer's yeast, *Saccharomyces cerevisiae*, is the same species as the common baking yeast. However, baking and brewing yeasts typically belong to different strains, cultivated to favour different characteristics: Baking yeast strains are more aggressive, in order to carbonate dough in the shortest amount of time; brewing yeast strains act slower, but tend to produce fewer off - flavours and tolerate higher alcohol concentrations (with some strains, up to 22 %).

To ensure purity of strain, a "clean" sample of brewing yeast is sometimes stored, either dried or refrigerated in a laboratory. After a certain number of fermentation cycles, a full scale propagation is produced from this laboratory sample. Typically, it is grown up in about three or four stages using sterile brewing wort and oxygen.

6 – 1 – 1 - Warm - fermenting

In general, yeasts such as *Saccharomyces cerevisiae* are fermented at warm temperatures between 15 and 20 °C (59 and 68 °F), occasionally as high as 24 °C (75 °F),[70] while the yeast used by Brasserie Dupont for saison ferments even higher at 29 °C (84 °F) to 35 °C. They generally form a foam on the surface of the fermenting beer , as during the fermentation process its hydrophobic surface causes the flocs to adhere to CO_2 and rise; because of this, they are often referred to as "top-cropping" or "top-fermenting" – though this distinction is less clear in modern brewing with the use of cylindro-conical tanks. Generally, warm-fermented beers are ready to drink within three weeks after the beginning of fermentation, although some brewers will condition them for several months.

6 – 1 – 2 - Cool fermenting

Lager is beer that has been cool fermented at around 10 °C , compared to typical warm fermentation temperatures of 18 °C . It is then stored for 30 days or longer close to the freezing point, and during this storage sulphur components developed during fermentation dissipate.

Though it is the cool fermenting that defines lager, the main technical difference with lager yeast is its ability to process raffinose (a tri saccharide composed of the sugars galactose, fructose, and glucose), which means that all sugars are fermented, resulting in a well attenuated beer; warm fermenting yeast only cleaves and ferments the fructose portion of raffinose, leaving melibiose, which it cannot further cleave into two mono saccharides due to its lack of melibiase, so ale remains sweeter with a lower conversion of sugar into alcohol. Raffinose is a minor dry component of Carlsberg barley, but once malted is practically nonexistent .

While the nature of yeast was not fully understood until Emil Hansen of the Carlsberg brewery in Denmark isolated a single yeast cell in the 1800s, brewers in Bavaria had for centuries been selecting cold-fermenting lager yeasts by storing ("lagern") their beers in cold alpine caves. The process of natural selection meant that the wild yeasts that were most cold tolerant would be the ones that would remain actively fermenting in the beer that was stored in the caves. Some of these Bavarian yeasts were brought back to the Carlsberg brewery around the time that Hansen did his famous work.

Today, lagers represent the vast majority of beers produced. Examples include Budweiser Budvar, Birra Moretti, Stella Artois, Red Stripe, and Singha. Some lager-style beers market themselves as Pilsner, which originated in Pilsen, Czech Republic *(Plzeň in Czech)*. However, Pilsners are brewed with 100 % barley malt and aggressive hop bitterness, flavor, and aroma.

Lager yeast normally ferments at a temperature of approximately 5 °C . Lager yeast can be fermented at a higher temperature normally used for top-fermenting yeast, and this application is often used in a beer style known as *California Common* or colloquially as "steam beer". *Saccharomyces pastorianus* is used in the brewing of lager.

6 – 1 – 3 - Spontaneous fermentation

These beers are brewed primarily around Brussels, Belgium. They are fermented in oak barrels after being inoculated with wild yeast and bacteria while cooling in a Koelship. Wild yeast and bacteria ferment the wort in the oak barrels. The beers fermented from yeast and bacteria in the Brussels area are called Lambic beers. These bacteria add a sour flavour to the beer. Of the many styles of beer very few use bacteria, most are fermented with yeast alone and bacterial contamination is avoided. However, with the advent of yeast banks and the National Collection of Yeast Cultures, brewing these beers – albeit not through spontaneous fermentation – is possible anywhere. Specific bacteria cultures are also available to reproduce certain styles.

Brettanomyces is a genus of yeast important in brewing lambic, a beer produced not by the deliberate addition of brewer's yeasts, but by spontaneous fermentation with wild yeasts and bacteria.

7 - Conditioning

After initial or primary fermentation, the beer is now conditioned, matured or aged , in one of several ways , which can take from 2 to 4 weeks, several months, or several years, depending on the type of beer. The beer is usually transferred into a second container, so that it is no longer exposed to the dead yeast and other debris (also known as "trub") that have settled to the bottom of the primary fermenter. This prevents the formation of unwanted flavours and harmful compounds such as acetyl aldehydes.

Kräusening

Kräusening is a conditioning method in which fermenting wort is added to the finished beer . The active yeast will restart fermentation in the finished beer, and so introduce fresh carbon dioxide; the conditioning tank will be then sealed so that the carbon dioxide is dissolved into the beer producing a lively "condition" or level of carbonation. The kräusening method may also be used to condition bottled beer.

Lagering

Lagers are aged at near freezing temperatures for 1–6 months depending on style. This cold aging serves to reduce sulphur compounds produced by the bottom - fermenting yeast and to produce a cleaner tasting final product with fewer esters. Unpleasant flavours such as phenolic compounds become insoluble in the cold beer, and the beer's flavour becomes smoother. During this time pressure is maintained on the tanks to prevent the beer from going flat. If the fermentation tanks have cooling jackets on them, as opposed to the whole fermentation cellar being cooled, conditioning can take place in the same tank as fermentation. Otherwise separate tanks (in a separate cellar) must be employed. This is where aging occurs.

Secondary fermentation

During secondary fermentation, most of the remaining yeast will settle to the bottom of the second fermenter, yielding a less hazy product.

Bottle fermentation

Some beers undergo a fermentation in the bottle, giving natural carbonation. This may be a second or third fermentation. They are bottled with a viable yeast population in suspension. If there is no residual fermentable sugar left, sugar may be added. The resulting fermentation generates CO_2 that is trapped in the bottle, remaining in solution and providing natural carbonation.

Cask conditioning

Cask ale or cask-conditioned beer is the term for unfiltered and unpasteurised beer that is conditioned (including secondary fermentation) and served from a cask without additional nitrogen or carbon dioxide pressure.

8 - Filtering

Filtering the beer stabilizes the flavour, and gives beer its polished shine and brilliance. Not all beer is filtered. When tax determination is required by local laws, it is typically done at this stage in a calibrated tank.

Filters come in many types. Many use sheets or candles. Others use a fine powder such as diatomaceous earth, also called kieselguhr. The powder is added to the beer and recirculated past screens to form a filtration bed.

Filters range from rough filters that remove much of the yeast and any solids (e.g., hops, grain particles) left in the beer, to filters tight enough to strain colour and body from the beer. Filtration ratings are divided into rough, fine, and sterile. Rough filtration leaves some cloudiness in the beer, but it is noticeably clearer than unfiltered beer. Fine filtration removes almost all cloudiness. Sterile filtration removes almost all microorganisms.

Sheet (pad) filters

These filters use sheets that allow only particles smaller than a given size to pass through. The sheets are placed into a filtering frame, sterilized (with boiling water, for example) and then used to filter the beer. The sheets can be flushed if the filter becomes blocked. The sheets are usually disposable and are replaced between filtration sessions. Often the sheets contain powdered filtration media to aid in filtration.

Pre-made filters have two sides. One with loose holes, and the other with tight holes. Flow goes from the side with loose holes to the side with the tight holes, with the intent that large particles get stuck in the large holes while leaving enough room around the particles and filter medium for smaller particles to go through and get stuck in tighter holes.

Sheets are sold in nominal ratings, and typically 90% of particles larger than the nominal rating are caught by the sheet.

Kieselguhr filters

Filters that use a powder medium are considerably more complicated to operate, but can filter much more beer before regeneration. Common media include diatomaceous earth and perlite.

9 - Packaging

Packaging is putting the beer into the containers in which it will leave the brewery. Typically, this means putting the beer into bottles, aluminium cans and kegs, but it may include putting the beer into bulk tanks for high-volume customers.

10 - Brewing methods

There are several additional brewing methods, such as barrel aging, double dropping, and Yorkshire Square.

11 - By - products

Brewing by-products are "brewer's grains" and dregs (typically dried and resold as "brewers dried yeast") from the filtration process. Brewer's grains are sold as fodder, and often used as an ingredient in compound feed. Yeast extract is obtained from an additional production process using brewers dried yeast.

12 - Brewing industry

The brewing industry is a global business, consisting of several dominant multinational companies and many thousands of smaller producers known as microbreweries or regional breweries depending on size and region. More than 133 billion liters (35 billion gallons) are sold per year—producing total global revenues of $ 294.5 billion as of 2006. SABMiller became the largest brewing company in the world when it acquired Royal Grolsch, brewer of Dutch premium beer brand Grolsch. InBev was the second-largest beer-producing company in the world and Anheuser - Busch held the third spot, but after the acquisition of Anheuser - Busch by InBev, the new Anheuser - Busch InBev company is currently the largest brewer in the world.

Brewing at home is subject to regulation and prohibition in many countries. Restrictions on home brewing were lifted in the UK in 1963, Australia followed suit in 1972, and the USA in 1978, though individual states were allowed to pass their own laws limiting production.

Neutral Grain Spirit

Contents

1 - Introduction

Neutral grain spirit (also called pure grain alcohol (PGA) or grain neutral spirit (GNS)) is a clear, colorless, flammable liquid that has been distilled from a grain-based mash to a very high level of ethanol content. The term *neutral* refers to the spirit's lacking the flavor that would have been present if the mash ingredients were distilled to a lower level of alcohol purity, and also lacking any flavoring added to it after distillation (as is done, for example, with gin). Other kinds of spirits, such as whisky, are distilled to a lower alcohol percentage in order to preserve the flavor of the mash.

The mash from which neutral grain spirit is produced can be any type or mixture of cereal grains.

As a defined standard of identification under U.S. law, "neutral spirits" or "neutral alcohol" are distilled spirits produced from any material at or above 95% alcohol by volume. Such a product made from grain is "grain neutral spirit," while such a spirit made from grapes is called "grape neutral spirit," and so on.[1] When the term is used in an informal context rather than as a term of U.S. law, any distilled spirit of high alcohol purity (e.g., 170 proof or higher) that does not contain added flavoring may be referred to as neutral alcohol.

The purity of neutral grain spirit has a practical limit of 190 proof because a mixture of ethanol and water becomes an azeotrope at 95.6% ABV .

Neutral grain spirit is only one type of neutral spirit (also called neutral alcohol). Neutral alcohol can also be produced from grapes, sugar beets, sugarcane, or other fermented plant material. In particular, large quantities of neutral alcohol are distilled from wine, a product that is referred to as *vinous alcohol*.

Neutral grain spirit is used in the production of blended whiskey, cut brandy, some liqueurs, and some bitters. As a consumer good, it is almost always mixed with other beverages to create such drinks as punch and various cocktails, or to produce homemade liqueurs.

2 - Availability in market areas

Because of its high alcohol content, neutral grain spirit is illegal, unavailable, or difficult to find in many areas.

2 – 1 - Canada

In Canada, The Luxco product Everclear is only sold in the province of Alberta. In British Columbia, one can purchase neutral grain spirits only with a permit for medical, research, or industrial use. Neutral grain spirits are also sold in Quebec from the producer Alcool Global.

2 – 2 - United States

Everclear, Golden Grain Alcohol, Clear Spring, Graves XXX and Gem Clear are five brands of neutral grain spirit sold in the United States.

It is illegal to sell the 190-proof variety of neutral grain spirit (i.e., Everclear, Golden Grain Alcohol, Clear Spring, Graves XXX, or Gem Clear) in some of the United States — California, Florida, Hawaii, Maine, Massachusetts, Michigan, Minnesota,[4] Nevada, and North Carolina.

In some of these states, the 151-proof variety of Everclear may be sold. Pennsylvania requires an application to purchase it (PLCB-2196).

In the U.S. Commonwealth of Virginia, grain alcohol lacking distinctive color, odor, and flavor, while not illegal, is not sold at any liquor stores owned by the State (compare, for example, that beverages such as Southern Comfort, a flavored liqueur that has grain alcohol as its base, are sold). Because Virginia has a self-legislated monopoly on the sale of hard liquor, independent liquor stores are illegal, and the product is thus mostly unavailable. In some cases, however, liquor stores on U.S. military bases in the Commonwealth do sell grain alcohol, and small quantities may be imported on one's person from nearby states.

2 – 3 - Europe

In Europe, neutral alcohol is sold in some countries. Since it is usually distilled from grain, it is in fact neutral grain spirit. This product contains 95% – 95.6 % ABV and is much used for making homemade liqueurs. In Germany, neutral alcohol is called Neutral alcohol or (colloquially) Primasprit . Primasprit is sold in stores and is most often used for making homemade liqueurs; other uses are rare.

In Italy it is called alcool puro and contains up to 95.6% ABV. It may be legally purchased by anyone over the age of 18.

There are several companies in Poland that sell neutral grain spirit. Most of these are part of a state-owned monopoly called Polmos, which is now being privatized.

2 – 4 - Japan

In Japan, neutral grain spirit is sold in the same manner as other common liquors. It may be purchased by anyone over the age of 20 in both bars and retail stores, or on Internet shopping sites, provided that the retailer possesses a license issued by the National Tax Agency. Handling or storing more than 400 liters also requires a license.

Neutral grain spirit is classified as a hazardous material in Japan due to its flammability, and fire departments advise caution when drinking it while smoking.

3 - Rectified spirit

"Rectified spirit" or "rectified alcohol" is neutral alcohol which has been purified by means of "rectification" (i.e., repeated distillation). It will contain at least 95% ABV. It is normally used for medicinal purposes but can also be used to make homemade liqueurs. It can be a grain spirit or can be made from other plants.

4 - Cultural references

In the 1964 film *Dr. Strangelove* (directed by Stanley Kubrick), base commander General Jack D. Ripper states that he drinks only pure grain alcohol with distilled water or rainwater.

In season 5 of the sitcom *It's Always Sunny in Philadelphia*, during the World Series Defense episode, the gang state that they drink only grain alcohol or "riot punch" before any event where a riot or brawl could occur, such as a Philadelphia Phillies World Series game.

Cellulosic Ethanol Commercialization

Contents

1 Introduction

Cellulosic ethanol commercialization is the process of building an industry out of methods of turning cellulose-containing organic matter into fuel. Companies, such as Iogen, POET, and Abengoa, are building refineries that can process biomass and turn it into bio ethanol. Companies, such as Diversa, Novozymes, and Dyadic, are producing enzymes that could enable a cellulosic ethanol future. The shift from food crop feedstocks to waste residues and native grasses offers significant opportunities for a range of players, from farmers to biotechnology firms, and from project developers to investors.

The cellulosic ethanol industry developed some new commercial - scale plants in 2008. In the United States, plants totaling 12 million liters (3.17 million gal) per year were operational, and an additional 80 million liters (21.1 million gal.) per year of capacity—in 26 new plants — was under construction. In Canada, capacity of 6 million liters per year was operational. In Europe, several plants were operational in Denmark, Germany, Spain, and Sweden, and capacity of 10 million liters per year was under construction.

Italy - based Mossi & Ghisolfi Group broke ground for its 13 million US gallons (49,000 m^3) per year cellulosic ethanol facility in northwestern Italy on April 12, 2011. The project will be the largest cellulosic ethanol project in the world, 10 times larger than any of the other currently operating demonstration-scale facilities.

2 - Cellulosic ethanol production

Cellulosic ethanol can be produced from a diverse array of feed stocks, such as wood pulp from trees or any plant matter. Instead of taking the grain from wheat and grinding that down to get starch and gluten, then taking the starch, cellulosic ethanol production involves the use of the whole crop. This approach should increase yields and reduce the carbon footprint because the amount of energy-intensive fertilizers and fungicides will remain the same, for a higher output of usable material.

3 - Commercialization by country

3 – 1 - Australia

Ethtec is building a pilot plant in Harwood, New South Wales, which uses wood residues as a feed stock.

3 – 2 - Brazil

GraalBio is building a facility projected to produce 82 million litres of cellulosic ethanol per year.

3 – 3 - Canada

In Canada, Iogen Corp. is a developer of cellulosic ethanol process technology. Iogen has developed a proprietary process and operates a demonstration-scale plant in Ontario. The facility has been designed and engineered to process 40 tons of wheat straw per day into ethanol using enzymes made in an adjacent enzyme manufacturing facility. In 2004, Iogen began delivering its first shipments of cellulosic ethanol into the marketplace. In the near term, the company intends to commercialize its cellulose ethanol process by licensing its technology broadly through turnkey plant construction partnerships. The company is currently evaluating sites in the United States and Canada for its first commercial - scale plant.

Lignol Innovations has a pilot plant, which uses wood as a feedstock, in Vancouver.

In March 2009, KL Energy Corporation of South Dakota and Prairie Green Renewable Energy of Alberta announced their intention to develop a cellulosic ethanol plant near Hudson Bay, Saskatchewan. The Northeast Saskatchewan Renewable Energy Facility will use KL Energy’s modern design and engineering to produce ethanol from wood waste.

3 – 4 - China

Cellulosic ethanol production currently exists at "pilot" and "commercial demonstration" scale, including a plant in China engineered by SunOpta Inc. and owned and operated by China Resources Alcohol Corporation that is currently producing cellulosic ethanol from corn stover (stalks and leaves) on a continuous, 24 - hour per day basis.

3 – 5 - Denmark

Inbicon's bio ethanol plant in Kalund borg , with the capacity to produce 5.4 million liters annually, was opened in 2009. Believed to be the world's largest cellulosic ethanol plant as of early 2011, the facility runs on about 30,000 metric tons of straw per year and the plant employs about 30 people. The plant also produces 13,000 metric tons of lignin pellets per year, used as fuel at combined-heat-and-power plants, and 11,100 metric tons of C5 molasses which is currently used for biomethane production via anaerobic digestion, and has been tested as a high carbohydrate animal feed supplement and potential bio-based feedstock for production of numerous commodity chemicals including diols, glycols, organic acids, and biopolymer precursors and intermediates.

Since October 2010, an E5 blend of 95 % gasoline and 5% cellulosic ethanol blend has been available at 100 filling stations across Denmark. Distributed by Statoil, the Bio95 2G mixture uses ethanol derived from wheat straw collected on Danish fields after harvest and produced by Inbicon (a div. of DONG Energy), using enzyme technology from Novozymes.

Commercial or experimental Cellulosic Ethanol Plants in Denmark
(Operational or under construction)

Company	Location	Feedstock	Yearly amount	Operational
Biogasol	Bornholm	Wheat straw	5 mill litre	2012
Ensted-værket	Aabenraa	Wheat straw	? mill litre	2013
Inbicon owned by Dong Energy	Kalundborg, Zealand	Wheat straw	5.4 mill litre	2009
Maabjerg Energy Concept owned by Dong Energy	Maabjerg	Wheat straw	50 - 70 mill litre	??2013

3 – 6 - Germany

The biofuel company Butalco has recently signed a research and development contract with Hohenheim University. The Institute of Fermentation Technology within the Department of Food Science and Biotechnology at Hohenheim University has been concerned with questions on the production of bioethanol for almost 30 years. The focus in recent years has been on the improvement of the material, energy and life cycle assessment of the production of ethanol. Special interest to BUTALCO is the use of the newly built pilot plant, which is equipped with a safety class 1 approved fermentation room with 4 x 1.5 m^3 fermenters . The concept of the plant allows both starch and ligno cellulosic based raw materials to be processed. The collaboration will allow BUTALCO to optimize its C5 sugar fermenting and butanol producing yeast strains on a technical scale and produce first amounts of bioethanol from ligno cellulose. The whole process of the production of biofuel from the choice of cellulosic biomass feedstock to the conversion into sugars and fermentation through to the purification will be optimized under industrial conditions.

3 – 7 - Italy

Italy - based Mossi & Ghisolfi Group broke ground for its 13 million US gallons (49,000 m^3) per year cellulosic ethanol facility in Crescentino in northwestern Italy on April 12, 2011. The project will be the largest cellulosic ethanol project in the world, 10 times larger than any of the currently operating demonstration-scale facilities. The plant is "expected to become operational in 2012 and will use a variety of locally sourced feed stocks, beginning with wheat straw and Arundo donax, a perennial giant cane".

3 – 8 - Japan

Nippon Oil Corporation and other Japanese manufacturers including Toyota Motor Corporation plan to set up a research body to develop cellulose-derived biofuels. The consortium plans to produce 250,000 kilolitres (1.6 million barrels) per year of bio ethanol by March 2014, and produce bioethanol at 40 yen ($ 0.437) per liter by 2015.

In March 2009, Honda Motor announced an agreement for the construction of a new cellulosic ethanol research facility in Japan. The new Kazusa-branch facility of the Honda Fundamental Technology Research Center will be built within the Kazusa Akademia Park, in Kisarazu, Chiba. Construction is scheduled to begin in April 2009, with the aim to begin operations in November 2009.

3 – 9 - Norway

In October 2010, Norway-based cellulosic ethanol technology developer Weyland commenced production at its 200,000 liter (approximately 53,000 gallon) pilot-scale facility in Bergen, Norway. The plant will demonstrate the company's acid hydrolysis production process, paving the way for a commercial - scale project. The company also plans to market its technology world wide.

3 – 10 - Spain

Abengoa continues to invest heavily in the necessary technology for bringing cellulosic ethanol to market. Utilizing process and pre-treatment technology from SunOpta Inc., Abengoa is building a 5 million US gallons (19,000 m^3) cellulosic ethanol facility in Spain and have recently entered into a strategic research and development agreement with Dyadic International, Inc. (AMEX: DIL), to create new and better enzyme mixtures which may be used to improve both the efficiencies and cost structure of producing cellulosic ethanol.

3 – 11 - Sweden

SEKAB has developed an industrial process for production of ethanol from biomass feed-stocks, including wood chips and sugar cane bagasse. The development work is being carried out at an advanced pilot plant in Örnsköldsvik, and has sparked international interest. The technology will be gradually scaled up to commercial production in a new breed of bio-refineries from 2013 to 2015.

3 – 12 - United Kingdom

A $ 400 million investment programme to cover the construction of a world scale ethanol plant and a high technology demonstration plant to advance development work on the next generation of biofuels has been announced by BP, Associated British Foods (ABF) and DuPont. The bioethanol plant will be built on BP's existing chemicals site at Saltend, Hull. Due to be commissioned in late 2009, it will have an annual production capacity of some 420 million litres from wheat feed stock.

3 – 13 - United States

The US government actively supports the development and commercialization of cellulosic ethanol through a variety of mechanisms. In the first decade of the 21st century, a lot of companies announced plans to build commercial cellulosic ethanol plants, but most of those plans eventually fell apart, and many of the small companies went bankrupt. By today (2012), there are many demonstration plants throughout the country, and handful of commercial-scale plants which are in operation or close to it. With the market for cellulosic ethanol in the United States projected to continue growing in the coming years, the outlook for this industry is good.

3 – 13 - 1 - Government support

The US Federal government is actively promoting the development of ethanol from cellulosic feedstocks as an alternative to conventional petroleum transportation fuels. For example, programs sponsored by U.S. Department of Energy (DOE) include research to develop better cellulose hydrolysis enzymes and ethanol-fermenting organisms, to engineering studies of potential processes, to co-funding initial ethanol from cellulosic biomass demonstration and production facilities. This research is conducted by various national laboratories , including the National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL) and Idaho National Laboratory (INL), as well as by universities and private industry. Engineering and construction companies and operating companies are generally conducting the engineering work.

In May 2008, Congress passed a new farm bill that will accelerate the commercialization of advanced biofuels, including cellulosic ethanol. The *Food, Conservation, and Energy Act of 2008* provides for grants covering up to 30% of the cost of developing and building demonstration-scale biorefineries for producing "advanced biofuels," which essentially includes all fuels that are not produced from corn kernel starch. It also allows for loan guarantees of up to $250 million for building commercial-scale bio refineries to produce advanced bio fuels.

Using a newly developed tool known as the "Biofuels Deployment Model", Sandia researchers have determined that 21 billion US gallons (79,000,000 m^3) of cellulosic ethanol could be produced per year by 2022 without displacing current crops. The Renewable Fuels Standard, part of the 2007 Energy Independence and Security Act, calls for an increase in biofuels production to 36 billion US gallons (140,000,000 m^3) a year by 2022 .

In January 2011, the USDA approved $405 million in loan guarantees through the 2008 Farm Bill to support the commercialization of cellulosic ethanol at three facilities owned by Coskata, Enerkem and INEOS New Planet BioEnergy. The projects represent a combined 73 million US gallons (280,000 m^3) per year production capacity and will begin producing cellulosic ethanol in 2012. The USDA also released a list of advanced biofuel producers who will receive payments to expand the production of advanced biofuels. In July 2011, the US Department of Energy gave in $105 million in loan guarantees to POET for a commercial-scale plant to be built Emmetsburg, Iowa.

3 – 13 – 1- Commercial development

The cellulosic ethanol industry in the United States developed some new commercial-scale plants in 2008. Plants totaling 12 million liters (3.17 million gal) per year were operational, and an additional 80 million liters per year of capacity - in 26 new plants - was under construction. (For comparison the estimated US petroleum consumption for all uses was about 816 million gal/day in 2008.)

Cellulosic Ethanol Plants in the U.S. (Operational or under construction)

Company	Location	Feedstock	Capacity (million gal/year)	Began Production	Type
Abengoa Bioenergy	Hugoton, KS	Wheat straw	25 - 30	est. June 2013	Commercial
BlueFire Ethanol	Irvine, CA	Multiple sources	3.9		Commercial
BlueFire Ethanol	Fulton, MS	Multiple sources	19	est. 2012	Commercial
Coskata, Inc.	Boligee, Alabama	Wood waste	16	est. 2013	Commercial
Coskata, Inc.	Madison, Pennsylvania	Multiple sources	0.04	October 2009	Semi - commercial
DuPont	Nevada, IA	Corn stover	30	est. 2014	Commercial
Fulcrum BioEnergy	Reno, NV	Municipal solid waste	10	est. end of 2013	Commercial
Gulf Coast Energy	Livingston, AL	Wood waste	0.3	before 2008	Demonstration
KL Energy Corp.	Upton, WY	Wood waste			
Mascoma	Kinross, MI	Wood waste	20	est. 2014	Commercial
POET LLC	Emmetsburg, IA	Corn stover	20 - 25	est. lat 2013	Commercial
POET LLC[43]	Scotland, SD	Corn stover	0.03	2008	Pilot

5 - Environmental issues

Cellulosic ethanol and grain-based ethanol are, in fact, the same product, but many scientists believe cellulosic ethanol production has distinct environmental advantages over grain-based ethanol production. On a life-cycle basis, ethanol produced from agricultural residues or dedicated cellulosic crops has significantly lower greenhouse gas emissions and a higher sustainability rating than ethanol produced from grain.

According to US Department of Energy studies conducted by the Argonne Laboratories of the University of Chicago, cellulosic ethanol reduces greenhouse gas emissions (GHG) by 85% over reformulated gasoline. By contrast, starch ethanol (e.g., from corn), which usually uses natural gas to provide energy for the process, reduces greenhouse gas emissions by 18% to 29% over gasoline.

Critics such as Cornell University professor of ecology and agriculture David Pimentel and University of California at Berkeley engineer Tad Patzek question the likelihood of environmental, energy, or economic benefits from cellulosic ethanol technology from non-waste.

Time Line of Alcohol Fuel

Ethanol, an alcohol fuel, is an important fuel for the operation of internal combustion engines that are used in cars, trucks, and other kinds of machinery.

Since ancient times ethanol has been used for lamp oil and cooking, along with plant and animal oils. Small alcohol stoves (also called “spirit lamps”) were commonly used by travelers in the 17th century to warm food and themselves.

Before the American Civil War many farmers in the USA had an alcohol still to turn crop waste into free lamp oil and stove fuel for the farmers' family use. Conflict over taxation was not unusual; one example was the Whiskey Rebellion in 1791.

In **1826**, Samuel Morey uses alcohol in the first American internal combustion engine prototype.

In the **1830s,** alcohol blends had replaced increasingly expensive whale oil in most parts of the country. It "easily took the lead as the illuminant" because it was "a decided improvement on other oils then in use."

By **1860,** thousands of distilleries churned out at least 90 million US gallons (340,000 m^3) of alcohol per year for lighting. Camphene / alcohol blends (at $.50 per gallon) were cheaper than whale oil ($1.30 to $2.50 per gallon) and lard oil (90 cents per gallon). It was about the same price as coal oil, which was the product first marketed as "kerosene."

In **1860**, German inventor Nikolaus Otto uses ethyl alcohol as a fuel in an early internal combustion engine.

In **1862** and **1864**, a tax on alcohol was passed in the U.S. to pay for the Civil War, increasing the price of ethanol to over $

2.00 per gallon. A new product from petroleum, called kerosene, is taxed at 10 cents a gallon.

In the 19th century, spirit lamps, Pigeon lamps and others used a variety of blends of alcohol and oils in Europe. Alcohol powered not only automobiles and farm machinery but also a wide variety of lamps, stoves, heaters, laundry irons, hair curlers, coffee roasters and every conceivable household appliance. By one estimate, some 95,000 alcohol fueled stoves and 37,000 spirit lamps had been manufactured in Germany by 1902.

By the **1890s**, alcohol fueled engines are starting to be used in farm machinery in Europe, making countries more fuel independent. Research at the Experimental Mechanical Laboratory of Paris and at the Deutsche Landwirtschaftliche Gesellschaft in Berlin in the 1890s helped pave the way for expanded use of alcohol fuel.

By **1896**, horseless carriages (cars) were showing up on roads in Europe and the United States. Because gasoline is so cheap and abundant, and also because ethanol is taxed at a high level, early US automobiles are adapted to gasoline from the beginning. Racing cars, on the other hand, usually used ethanol (and other alcohols) because more power could be developed in a smaller, lighter engine. Charles Edgar Duryea builds the first U.S. gasoline powered car but is aware of Samuel Morey's ethanol fueled experimental car of 1826. Henry Ford's first car, the Quadracycle, is also built that year. The car runs on gasoline, but Ford is aware of experiments with ethanol in Germany, and subsequently backs the lifting of the U.S. tax on industrial uses of ethanol.

In **1899**, the German government taxed petroleum imports and subsidized domestic ethanol. Kaiser Wilhelm II "was enraged at the Oil Trust of his country, and offered prizes to his subjects and cash assistance ... to adapt [alcohol] to use in the industries."

In **1901**, the French ministry of agriculture offered prizes for the best alcohol fueled engines and household appliances.

In **1902**, the Paris alcohol fuel exposition exhibited alcohol powered cars, farm machinery, lamps, stoves, heaters, laundry irons, hair curlers, coffee roasters, and every conceivable household appliance and agricultural engine powered by alcohol. This exhibit traveled widely through Europe and was featured at the 1907 Jamestown Virginia tricentennial celebrations.

In **1906**, the *Free Alcohol* bill is passed. The USA repeals the alcohol tax under Teddy Roosevelt. At 14 cents per US gallon, corn ethanol was cheaper than gasoline at 22 cents per US gallon. Bills pass that exempt farm stills from government control. In backing the bill, U.S. President Teddy Roosevelt says: “The Standard Oil Company has, largely by unfair or unlawful methods, crushed out home competition... It is highly desirable that an element of competition should be introduced by the passage of some such law as that which has already passed in the House, putting alcohol used in the arts and manufacturers upon the [tax] free list.”

Starting in **1901**, the discovery of new oil fields in Texas causes the price of gasoline to drop to between 18 and 22 cents per US gallon by **1906**, undercutting farm ethanol markets

In **1908**, the Ford Model T is introduced. Early models had adjustable carburetors to run on ethanol or gasoline.

In **1909**, the U.S. Geological Survey reports: "In regard to general cleanliness, such as absence of smoke and disagreeable odors, alcohol has many advantages over gasoline or kerosene as a fuel… The exhaust from an alcohol engine is never clouded with a black or grayish smoke." Overall, alcohol was "a more ideal fuel than gasoline."

In **1914**, the *Free Alcohol* bill is amended again to decrease the regulatory burden and encourage alcohol fuel production in the U.S.

In **1917** Alexander Graham Bell says: "Alcohol makes a beautiful, clean and efficient fuel… Alcohol can be manufactured from corn stalks, and in fact from almost any vegetable matter capable of fermentation… We need never fear the exhaustion of our present fuel supplies so long as we can produce an annual crop of alcohol to any extent desired."

In **1918**, Scientific American says it is "now definitely established that alcohol can be blended with gasoline to produce a suitable fuel …"

Another article notes that the Pasteur Institute of France found it could obtain 10 US gallons (38 L) of ethanol per ton of seaweed.

In **1919**, Prohibition of beverage alcohol in the U.S. leads to suggestions for more ethanol use as an anti-knock blend with gasoline.

Farm belt politicians are split on ethanol as a fuel. While distillers could have a new market for their alcohol, some thought that allowing any distillery to stay open would be a "bargain with the devil."

In the **1920s** and **1930s**, Koolmotor, Benzalcool, Moltaco, Lattybentyl, Natelite, Alcool and Agrol are some of the gasoline-ethanol blends of fuels once found in Britain, Italy, Hungary, Sweden, South Africa, Brazil and the USA (respectively).

In **1920**, David White, chief geologist of US Geological Survey, estimates total oil remaining in the US at 6.7 billion barrels (1.07×10^9 m^3). "In making this estimate, which included both proved reserves and resources still remaining to be discovered, White conceded that it might well be in error by as much as 25 percent."

In **1921**, leaded gasoline is developed at the General Motors research laboratories in Dayton, Ohio. GM researcher Thomas Midgley still maintains: “The most direct route which we now know for converting energy from its source, the sun, into a material that is suitable for use in an internal combustion motor is through vegetation to alcohol… It now appears that alcohol is the only liquid from a direct vegetable source that combines relative cheapness with suitability (although other sources might be found)… Alcohol will stand very high initial compressions without knocking, and at high compressions is smooth and highly satisfactory.”.

In **1921**, British engineer Harry Ricardo patents racing fuels RD1 and RD2 (for Ricardo Discol) that contained methanol and ethanol, acetone and small amounts of water. These were widely used on race tracks throughout Europe and the US in the 1920s and 30s.

In **1923** leaded gasoline it is marketed, and by 1924 GM and Standard Oil Co. form the Ethyl Corp. Ethyl claims it has "solved" the problem of engine knock, but public health scientists (such as Alice Hamilton of Harvard University) are appalled at the prospects for lead poisoning and insist that alternatives such as ethanol blends are available.

In **1923** Rolls-Royce engine designer Harry Ricardo writes: “…It is a matter of absolute necessity to find an alternative fuel. Fortunately, such a fuel is in sight in the form of alcohol; this is a vegetable product whose consumption involves no drain on the world’s storage and which, in tropical countries at all events, can ultimately be produced in quantities sufficient to meet the world's demand, at all events at the present rate of consumption. By the use of a fuel derived from vegetation, mankind is adapting the sun's heat to the development of motive power, as it becomes available from day to day; by using mineral fuels, he is consuming a legacy – and a limited legacy at that – of heat stored away many thousands of years ago. In the one case he is, as it were, living within his income, in the other he is squandering his capital. It is perfectly well known that alcohol is an excellent fuel, and there is little doubt but that sufficient supplies could be produced within the tropical regions of the British empire…" [

In **1923**, the price of alcohol from molasses was less than 20 cents per US gallon, while retail gasoline prices had reached an all-time high of 28 cents per gallon. Standard Oil experiments with a 10% alcohol, 90% gasoline blend for a few months to increase octane and stop engine knock.

In 1923, French assembly passes the Carburant National law requiring gasoline importers to buy alcohol for 10% blends from the State Alcohol Service. The law has a far-reaching impact as many other nations, especially Brazil and other sugar-cane growing countries, were influenced to enact similar laws based on the French and German programs.

By the **mid-1920s**, ethyl alcohol is blended with gasoline in every industrialized nation, and some blends are showing up as experiments in the United States, but the market is dominated by leaded gasoline.

In October of **1924**, a catastrophic miscalculation in the production of leaded gasoline causes at least 17 refinery deaths and many dozens of permanently debilitating injuries. GM and Standard very nearly abandon leaded gasoline, but decide to defend it, claiming (contrary to their own prior published research) that "“So far as science knows at the present time, tetraethyl lead is the only material available which can bring about these [antiknock] results."

In **1925**, Henry Ford tells the New York Times that ethyl alcohol is "the fuel of the future" which “is going to come from fruit like that sumach out by the road, or from apples, weeds, sawdust -- almost anything. There is fuel in every bit of vegetable matter that can be fermented. There's enough alcohol in one year's yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years."

In **1926**, US Public Health Service allows leaded gasoline to return to the market.

In **1928** Harry Ricardo, National Distillers Co. and Shell Oil introduce an alcohol fuel blend in the United Kingdom called “Cleveland Discol.” The ethanol blend is a popular unleaded gasoline brand and is sold through 1968.

In August **1930**, the German government required all gasoline importers to buy 2.5% of the volume of their imports from the German Alcohol Monopoly, and the ratio was increased to 6% and then 10% by 1932. Estimates of alcohol used in 1932 vary from 44 million liters to about 175 million liters. Some 36,000 small farm alcohol stills, owned by the monopoly, were in operation at this time.[24] By 1938, Germany was producing about 267 million liters of ethanol, about two thirds from potatoes and the rest from grain, wood sulfite liquors and beets. Some 89 million liters of methanol were produced from coal, while other synthetic fuels included 550 million liters of benzene and over one billion liters of synthetic gasoline. All told, 54 % of the pre-war German fuel production was derived from non - petroleum sources, of which 8% was ethanol from renewable sources

In the **1930s**, the Dust bowl drought and Great Depression forced many more farmers to move to the cities looking for work, leaving their alcohol fuel stills behind. Henry Ford, a farmer himself, supported ethanol's use over gas.

In **1933**, faced with the 25% unemployment of the Great Depression, the European concept of finding new markets for surplus farm products is widely discussed, with ethanol-gasoline blending among the most significant. Fuel blending experiments begin in Peoria, IL, Spokane WA, Lincoln, NE, and Ames, IA. Federal and state governments consider tax advantages to help ethanol production and increase employment among farmers. By 1935 the Chemurgy movement emerges, supported by farmers, Republicans, and Henry Ford. Along with ethanol, chemurgy research included new products to grow on the farm (such as soybeans and new products from biological materials, such as soybean plastics and inks.

In **1933**, a campaign to end Prohibition in the United States emerges. Concerned about renewed interest in ethanol for fuel, the American Petroleum Institute begins a campaign against ethanol blends, claiming such "will harm the petroleum industry and the automobile industry as well as state and national treasuries by reducing [oil] consumption," the sole beneficiaries allegedly being distillers, railroads (which would transport the alcohol) and bootleggers "to whom would be opened brand new fields of fraud." Prohibition ends with the passage of the Twenty-first Amendment to the United States Constitution on December 5, 1933.

From **1933** to **1939**, various oil companies and the American Petroleum Institute argued that tax incentives for ethanol would hurt the oil industry, reduce state treasuries, and create a bootlegger' atmosphere around fueling stations. They also claimed alcohol fuel was inferior to gasoline.

In **1937**, the farm chemurgy movement finds backers for the Agrol ethanol fuel plant, created at Atchison, Kansas. For two years, ethanol blends were sold at around 2,000 service stations in the U.S. Midwest. Agrol plant managers complained of sabotage and bitter infighting by the oil industry, and the cheaper price of gasoline. Agrol sold for 17 cents per gallon, while leaded gasoline sold for 16 cents.

In **1939**, Agrol production shuts down.

In **1942**, chemists who designed the Agrol ethanol plant, especially Leo Christensen, go to work producing ethanol for aviation fuel and synthetic "Buna-S" rubber for World War II. By 1944, petroleum based synthetic rubber production lags, and three quarters of all tires, raincoats, engine gaskets and other rubber products for the war effort come from ethanol.

In **1942** a war investigating committee led by then-Senator (and future president) Harry Truman makes public evidence that the oil industry had colluded with German chemical companies, especially I.G. Farben, to prevent the development of synthetic rubber production in the United States. Standard Oil (Exxon) had entered a partnership that it described as a "full marriage" designed to "outlast the war" no matter who won.

On **October 14, 1947**, legendary test pilot Chuck Yeager became the first man to fly faster than Mach 1, the speed of sound. He was piloting the Bell X-1, a bullet-shaped rocket plane that was the first in a series of secret high-speed research aircraft. The X-planes came to symbolize the danger and glamour of test flying at California's Edwards Air Force Base in the late 1940s and 50s. Originally known as the XS-1, the X-1 was powered by a Reaction Motors XLR11-RM3 rocket engine. Its four chambers each produced 1,500 pounds (6.7 kN) of thrust. At full power, the engine burned up its 600-US-gallon (2,300 L) supply of liquid oxygen and alcohol fuel in less than three minutes.

In **1949**, S.J.W. Pleeth, chemist for the Cleveland Discol company in Great Britain, writes: "The bias aroused by the use of alcohol as a motor fuel has produced [research] results that are incompatible with each other ... Countries with considerable oil deposits -- such as the US -- or which control oil deposits of other lands -- such as Holland -- tend to produce reports antithetical to the use of fuels alternative to petrol; countries with little or no indigenous oil tend to produce favorable reports. The contrast ... is most marked. One can scarcely avoid the conclusion that the results arrived at are those best suited to the political or economic aims of the country concerned or the industry sponsoring the research. We deplore this partisan use of science, while admitting its existence, even in the present writer."

In **1964**, a seven-car crash kills drivers Dave MacDonald and Eddie Sachs on the second lap of the Indianapolis 500, as over 150 US gallons (570 L) of gasoline burned. Johnny Rutherford, who was also involved in the crash, survived, mainly because his methanol-fueled car had not ignited. The United States Auto Club bans gasoline and switches all cars to methyl alcohol (methanol), a rule which would stay for 41 years before ending after the 2005 race.

During the Nigerian Civil War of **1967 to 1970**, Engineers in the breakaway republic of Biafra resorted to powering vehicles with alcohol. Initially, alcohol was used to supplement the crude oil refining capacity which the fledgling state had under its control, but as the Soviet and UK backed Nigerian army seized the oil producing regions, and with the Nigerian embargo beginning to bite, alcohol became the dominant source of fuel for the economy.

In **1971**, the Nebraska Agricultural Products Industrial Utilization Committee (or "Gasohol" Committee) is formed to find new uses for surplus grain. The commission tests ethanol-gasoline blends in thousands of cars over millions of miles, proving that ethanol can be used as an octane-boosting additive to replace leaded gasoline.

In **1973**, Arab oil embargo creates a worldwide energy crisis, leading to intensified search for alternative energy sources.

In **1979** President Jimmy Carter's administration creates federal incentives for ethanol production. Federal and state subsidies for ethanol amount to about $11 billion between 1979 and 2000, as compared to about $150 billion in tax credits for the oil industry (from 1968–2000), according to the General Accounting Office.

By the **mid-1980s**, over 100 new corn alcohol production plants are built and over a billion US gallons of ethanol for fuel were sold per year. The ethanol program is controversial for several reasons, not the least of which was that the ethanol industry was dominated by one company – Archer Daniels Midland of Peoria, Ill.

In **1984**, the number of ethanol plants peaked at 163 in the U.S., producing 595 million US gallons (2,250,000 m^3) of ethanol that year.

in 1988, the George H.W. Bush administration proposes a clean up of “air toxics” in gasoline, focusing on replacing benzene octane boosters with ethanol. The proposal leads to one part of the 1990 Clean Air Act.

In the late **1980s** and **1990s**, an oil surplus drives gasoline prices down as low as $12 per barrel, driving most of the ethanol industry into bankruptcy.

In 1990 and 1992, Congress passes amendments to the Clean Air Act encouraging the use of ethanol and other oxygenated fuels as replacements for benzene, toluene and xylene octane boosters. MTBE becomes the oil industry's favorite additive, but as water pollution problems were recognized, MTBE is banned in California. Ethanol production rises to the 4-billion-US-gallon (15,000,000 m^3) level.

Between **1997** and **2002**, three million U.S. cars and light trucks are produced which could run on E85, a blend of 85 % ethanol with 15% gasoline. Almost no gas stations sell this fuel however.

In the early **2000s**, the invasion of Iraq makes Americans aware of their dependence on foreign oil. This and worry over climate change causes leading alternative energies like biofuel, solar and wind to expand 20 to 30 % yearly.

In **2003**, California is the first state to ban MTBE. Several other states start switching soon afterward. California consumes 900 million US gallons (3,400,000 m^3) of ethanol a year, about a third of all the ethanol produced in the United States.

In **2004**, Crude oil prices rise by 80 %. Gasoline prices rise 30% in the U.S. Diesel fuel rises almost 50 %. These rises are caused by hurricane damage to oil rigs in the Gulf of Mexico, attacks on Iraqi oil pipelines, disruptions elsewhere, and rising demand for gasoline in Asia, as Asians buy more cars. Alcohol fuel prices are much closer to the price of gasoline. The ethanol industry in the USA makes 225,000 barrels (35,800 m^3) per day in August, an all-time record. Some conventional oil fuel companies are investing in alcohol fuel. Oil reserves are forecast to last about 40 more years. Total use (demand) of ethanol is 3.53 billion US gallons (13,400,000 m^3).

In **2005**, E85 sells for 45 cents (or 30-75 cents wholesale) less than gasoline on average in the U.S. More than 4 million flexible-fuel (runs on E85 and gasoline) vehicles exist in the U.S. About 400 filling stations exist in the U.S that sell E85 fuel, mostly in the Midwest. Gasoline prices rise as ethanol prices stay the same, due to rapidly growing ethanol supply and federal tax subsidies for ethanol. Wholesale ethanol prices drop nearly 30% between January and April, or $1.75 to $1.23 per gallon in the U.S.

In **2006**, the Indy Racing League switches to a 10 % ethanol-90% methanol fuel mixture as part of a phase-in of ethanol as part of a switch to an all - ethanol formula in 2007. Bill Gates buys a quarter of Pacific Ethanol Inc.

In **2007**, United nations Food and Agriculture Organization Special Rapporteur for the Right to Food urges five-year moratorium on food based biofuels, including ethanol, saying its development is a "crime against humanity." [33] The UN Food and Agriculture Organization (FAO) calls this "regrettable," and UN secretary-general Ban Ki-Moon, called for more scientific research. "Clearly biofuels have great potential for good and, perhaps, also for harm."

Diesel Fuel

Contents

1 - Introduction

Diesel fuel in general is any liquid fuel used in diesel engines. The most common is a specific fractional distillate of petroleum fuel oil, but alternatives that are not derived from petroleum, such as biodiesel, biomass to liquid (BTL) or gas to liquid (GTL) diesel, are increasingly being developed and adopted. To distinguish these types, petroleum-derived diesel is increasingly called petro diesel. Ultra-low sulfur diesel (ULSD) is a standard for defining diesel fuel with substantially lowered sulfur contents. As of 2007, almost all diesel fuel available in the United States of America, Canada and Europe is the ULSD type.

In the UK, diesel fuel for on-road use is commonly abbreviated DERV, standing for *Diesel Engined Road Vehicle*, which carries a tax premium over equivalent fuel for non-road use In Australia Diesel fuel is often known as 'distillate'

2 - History

2 – 1 - Etymology

The word "diesel" is derived from the family name of German inventor Rudolf Diesel who in 1892 invented the diesel engine.

2 – 2 - engine

Diesel engines are a type of internal combustion engine. Rudolf Diesel originally designed the diesel engine to use coal dust as a fuel. He also experimented with various oils, including some vegetable oils,[5] such as peanut oil, which was used to power the engines which he exhibited at the 1900 Paris Exposition and the 1911 World's Fair in Paris.

3 - Sources

Diesel fuel is produced from petroleum and from various other sources.

3 – 1 - Petroleum diesel

3 – 1 – 1 - Refining

Petroleum diesel, also called petro diesel, or fossil diesel is produced from the fractional distillation of crude oil between 200 °C and 350 °C at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule.

3 – 1 – 2 - Cetane number

The principal measure of diesel fuel quality is its cetane number. A higher cetane number indicates that the fuel ignites more readily when sprayed into hot compressed air. European (EN 590 standard) road diesel has a minimum cetane number of 51. Fuels with higher cetane numbers, normally "premium" diesel fuels with additional cleaning agents and some synthetic content, are available in some markets.

3 – 1 – 3 - Fuel value and price

As of 2010, the density of petroleum diesel is about 0.832 kg / l about 12 % more than ethanol-free petrol (gasoline), which has a density of about 0.745 kg / l . About 86.1 % of the fuel mass is carbon, and when burned, it offers a net heating value of 43.1 MJ / kg as opposed to 43.2 MJ / kg for gasoline. However, due to the higher density, diesel offers a higher volumetric energy density at 35.86 MJ / L vs . 32.18 MJ/L for gasoline, some 11 % higher, which should be considered when comparing the fuel efficiency by volume. The CO_2 emissions from diesel are 73.25 g / MJ, just slightly lower than for gasoline at 73.38 g / MJ. Diesel is generally simpler to refine from petroleum than gasoline, and contains hydrocarbons having a boiling point in the range of 180 – 360°C .The price of diesel traditionally rises during colder months as demand for heating oil rises, which is refined in much the same way. Because of recent changes in fuel quality regulations, additional refining is required to remove sulfur, which contributes to a some times higher cost. In many parts of the United States and throughout the United Kingdom and Australia,[10] diesel may be priced higher than petrol . Reasons for higher-priced diesel include the shutdown of some refineries in the Gulf of Mexico, diversion of mass refining capacity to gasoline production, and a recent transfer to ultra-low sulfur diesel (ULSD), which causes infrastructural complications . In Sweden, a diesel fuel designated as MK-1 (class 1 environmental diesel) is also being sold; this is a ULSD that also has a lower aromatics content, with a limit of 5%. This fuel is slightly more expensive to produce than regular ULSD.

3 – 1 – 4 - Use as vehicle fuel

Unlike petroleum ether and liquefied petroleum gas engines, diesel engines do not use high-voltage spark ignition (spark plugs). An engine running on diesel compresses the air inside the cylinder to high pressures and temperatures (compression ratios from 14:1 to 18:1 are common in current diesel engines); the engine generally injects the diesel fuel directly into the cylinder, starting a few degrees before top dead center (TDC) and continuing during the combustion event. The high temperatures inside the cylinder cause the diesel fuel to react with the oxygen in the mix (burn or oxidize), heating and expanding the burning mixture to convert the thermal/pressure difference into mechanical work, i.e., to move the piston. Engines have glow plugs to help start the engine by preheating the cylinders to a minimum operating temperature. Diesel engines are lean burn engines,[14] burning the fuel in more air than is required for the chemical reaction. They thus use less fuel than rich burn spark ignition engines which use a Stoichiometric air-fuel ratio (just enough air to react with the fuel). Because they have high compression ratios and no throttle, diesel engines are more efficient than many spark-ignited engines ·

Gas turbine internal combustion engines can also take diesel fuel, as can some other types of internal combustion. External combustion engines can easily use diesel fuel as well.

This efficiency and its lower flammability than gasoline[16] are the two main reasons for military use of diesel in armored fighting vehicles. Engines running on diesel also provide more torque, and are less likely to stall, as they are controlled by a mechanical or electronic governor .

A disadvantage of diesel as a vehicle fuel in cold climates, compared to gasoline or other petroleum-derived fuels, is that its viscosity increases quickly as the fuel's temperature decreases, turning into a non-flowing gel (see Compression Ignition – Gelling) at temperatures as high as −19 °C or −15 °C , which cannot be pumped by regular fuel pumps. Special low-temperature diesel contains additives to keep it in a more liquid state at lower temperatures, but starting a diesel engine in very cold weather may still pose considerable difficulties.

Another disadvantage of diesel engines compared to petrol / gasoline engines is the possibility of runaway failure. Since diesel engines do not require spark ignition, they can sustain operation as long as diesel fuel is supplied. Fuel is typically supplied via a fuel pump. If the pump breaks down in an "open" position, the supply of fuel will be unrestricted, and the engine will runaway and risk terminal failure. (In vehicles or installations that use both diesel engines and bottled gas, a gas leak into the engine room could also provide fuel for a runaway, via the engine air intake.)

3 – 1 – 5 - Use as car fuel

Diesel-powered cars generally have a better fuel economy than equivalent gasoline engines and produce less greenhouse gas emission. Their greater economy is due to the higher energy per-litre content of diesel fuel and the intrinsic efficiency of the diesel engine. While petrodiesel's higher density results in higher greenhouse gas emissions per litre compared to gasoline, the 20 – 40 % better fuel economy achieved by modern diesel-engined automobiles offsets the higher per-litter emissions of greenhouse gases, and a diesel-powered vehicle emits 10 – 20 percent less greenhouse gas than comparable gasoline vehicles. Biodiesel-powered diesel engines offer substantially improved emission reductions compared to petro diesel or gasoline-powered engines, while retaining most of the fuel economy advantages over conventional gasoline-powered automobiles. However, the increased compression ratios mean there are increased emissions of oxides of nitrogen (NO_x) from diesel engines. This is compounded by biological nitrogen in biodiesel to make NO_x emissions the main drawback of diesel versus gasoline engines .

3 – 1 – 6 - Reduction of sulfur emissions

In the past, diesel fuel contained higher quantities of sulfur. European emission standards and preferential taxation have forced oil refineries to dramatically reduce the level of sulfur in diesel fuels. In the United States, more stringent emission standards have been adopted with the transition to ULSD starting in 2006, and becoming mandatory on June 1, 2010 (see also diesel exhaust). U.S. diesel fuel typically also has a lower cetane number (a measure of ignition quality) than European diesel, resulting in worse cold weather performance and some increase in emissions.

3 – 1 – 7 - Environment hazards of sulfur

High levels of sulfur in diesel are harmful for the environment because they prevent the use of catalytic diesel particulate filters to control diesel particulate emissions, as well as more advanced technologies, such as nitrogen oxide ($N\ O_x$) adsorbers (still under development), to reduce emissions. Moreover, sulfur in the fuel is oxidized during combustion, producing sulfur dioxide and sulfur trioxide, that in presence of water rapidly convert to sulfuric acid, one of the chemical processes that results in acid rain. However, the process for lowering sulfur also reduces the lubricity of the fuel, meaning that additives must be put into the fuel to help lubricate engines. Biodiesel and bio diesel / petro diesel blends, with their higher lubricity levels, are increasingly being utilized as an alternative. The U.S. annual consumption of diesel fuel in 2006 was about 190 billion litres (42 billion imperial gallons or 50 billion US gallons).

3 – 1 – 8 - Chemical composition

Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including *n*, *iso*, and cyclo paraffins), and 25 % aromatic hydrocarbons (including naphthalenes and alkyl benzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$.

3 – 1 – 9 - Algae, microbes, and water contamination

There has been much discussion and misunderstanding of algae in diesel fuel . Algae need light to live and grow. As there is no sunlight in a closed fuel tank, no algae can survive, but some microbes can survive and feed on the diesel fuel.

These microbes form a colony that lives at the interface of fuel and water. They grow quite fast in warmer temperatures. They can even grow in cold weather when fuel tank heaters are installed. Parts of the colony can break off and clog the fuel lines and fuel filters.

Water in fuel can damage a fuel injection pump, some diesel fuel filters also trap water.

3 – 1 – 10 - Road hazard

Petro diesel spilled on a road will stay there until washed away by sufficiently heavy rain, whereas gasoline will quickly evaporate. After the light fractions have evaporated, a greasy slick is left on the road which can destabilize moving vehicles. Diesel spills severely reduce tire grip and traction, and have been implicated in many accidents. The loss of traction is similar to that encountered on black ice. Diesel slicks are especially dangerous for two-wheeled vehicles such as motorcycles.

3 - 2 - Synthetic diesel

Synthetic diesel can be produced from any carbonaceous material, including biomass, biogas, natural gas, coal and many others. The raw material is gasified into synthesis gas, which after purification is converted by the Fischer-Tropsch process to a synthetic diesel.

The process is typically referred to as biomass-to-liquid (BTL), gas-to-liquid (GTL) or coal-to-liquid (CTL), depending on the raw material used.

Paraffinic synthetic diesel generally has a near-zero content of sulfur and very low aromatics content, reducing unregulated emissions of toxic hydrocarbons, nitrous oxides and PM.[28]

3 – 2 – FAME

Fatty-acid methyl ester (FAME), perhaps more widely known as biodiesel, is obtained from vegetable oil or animal fats (biolipids) which have been trans esterified with methanol. It can be produced from many types of oils, the most common being rapeseed oil (rapeseed methyl ester, RME) in Europe and soybean oil (soy methyl ester, SME) in the USA. Methanol can also be replaced with ethanol for the trans esterification process, which results in the production of ethyl esters. The trans esterification processes use catalysts, such as sodium or potassium hydroxide, to convert vegetable oil and methanol into FAME and the undesirable byproducts glycerine and water, which will need to be removed from the fuel along with methanol traces. FAME can be used pure (B100) in engines where the manufacturer approves such use, but it is more often used as a mix with diesel, BXX where XX is the biodiesel content in percent.

FAME as a fuel is regulated under DIN EN 14214 and ASTM D6751.

FAME has a lower energy content than diesel due to its oxygen content, and as a result, performance and fuel consumption can be affected. It also can have higher levels of N Ox emissions, possibly even exceeding the legal limit. FAME also has lower oxidation stability than diesel, and it offers favorable conditions for bacterial growth, so applications which have a low fuel turnover should not use FAME. The loss in power when using pure biodiesel is 5 to 7 %.

Fuel equipment manufacturers (FIE) have raised several concerns regarding FAME fuels: free methanol, dissolved and free water, free glycerin, mono and diglycerides, free fatty acids, total solid impurity levels, alkaline metal compounds in solution and oxidation and thermal stability. They have also identified FAME as being the cause of the following problems: corrosion of fuel injection components, low-pressure fuel system blockage, increased dilution and polymerization of engine sump oil, pump seizures due to high fuel viscosity at low temperature, increased injection pressure, elastomeric seal failures and fuel injector spray blockage.

Unsaturated fatty acids are the source for the lower oxidation stability; they react with oxygen and form peroxides and result in degradation byproducts, which can cause sludge and lacquer in the fuel system.

As FAME contains low levels of sulfur, the emissions of sulfur oxides and sulfates, major components of acid rain, are low. Use of biodiesel also results in reductions of unburned hydrocarbons, carbon monoxide (CO), and particulate matter. CO emissions using biodiesel are substantially reduced, on the order of 50% compared to most petrodiesel fuels. The exhaust emissions of particulate matter from biodiesel have been found to be 30 percent lower than overall particulate matter emissions from petro diesel. The exhaust emissions of total hydrocarbons (a contributing factor in the localized formation of smog and ozone) are up to 93 percent lower for biodiesel than diesel fuel.

Biodiesel also may reduce health risks associated with petroleum diesel. Biodiesel emissions showed decreased levels of polycyclic aromatic hydrocarbon (PAH) and nitrited PAH compounds, which have been identified as potential cancer-causing compounds. In recent testing, PAH compounds were reduced by 75 to 85 percent, except for benz (a) anthracene, which was reduced by roughly 50 percent. Targeted n PAH compounds were also reduced dramatically with biodiesel fuel, with 2-nitrofluorene and 1-nitropyrene reduced by 90 percent, and the rest of the nPAH compounds reduced to only trace levels.

3 – 4 – Hydrogenated oils and fats

This category of diesel fuels involves converting the triglycerides in vegetable oil and animal fats into alkanes by refining and hydrogenation. The produced fuel has many properties that are similar to synthetic diesel, and are free from the many disadvantages of FAME.

3 – 5 – DME

Di methyl ether, DME, is a synthetic, gaseous diesel fuel that results in clean combustion with very little soot and reduced NOx emissions.

4 - Transportation and storage

Diesel fuel is widely used in most types of transportation. The gasoline-powered passenger automobile is the major exception.

4 – 1 - Railroad

Diesel displaced coal and fuel oil for steam-powered vehicles in the latter half of the 20th century, and is now used almost exclusively for the combustion engines of self-powered rail vehicles (locomotives and railcars).

4 – 2 - Aircraft

The first diesel-powered flight of a fixed-wing aircraft took place on the evening of September 18, 1928, at the Packard Motor Company proving grounds at Utica, USA, with Captain Lionel M. Woolson and Walter Lees at the controls (the first "official" test flight was taken the next morning). The engine was designed for Packard by Woolson, and the aircraft was a Stinson SM1B, X7654. Later that year, Charles Lindbergh flew the same aircraft. In 1929, it was flown 621 miles (999 km) nonstop from Detroit to Langley Field, near Norfolk, Virginia. This aircraft is now owned by Greg Herrick, and is at the Golden Wings Flying Museum near Minneapolis, Minnesota. In 1931, Walter Lees and Fredrick Brossy set the nonstop flight record flying a Bellanca powered by a Packard diesel for 84 hours and 32 minutes. The Hindenburg rigid airship was powered by four 16-cylinder diesel engines, each with approximately 1,200 horsepower (890 kW) available in bursts, and 850 horsepower (630 kW) available for cruising.

The most-produced aviation diesel engine in history has been the Junkers Jumo 205 , which, along with its similar developments from the Junkers Motorenwerke, had approximately 1000 examples of the unique opposed piston, two-stroke design power plant built in the 1930s leading into World War II in Germany.

4 – 3 - Storage

In the US, diesel is recommended to be stored in a yellow container to differentiate it from kerosene and gasoline, which are typically kept in blue and red containers, respectively.

In the UK, diesel is normally stored in a black container, to differentiate it from unleaded petrol (which is commonly stored in a green container) or, in the past, leaded petrol (which was stored in a red container).

5 - Other uses

Poor quality (high sulfur) diesel fuel has been used as an extraction agent for liquid-liquid extraction of palladium from nitric acid mixtures. Such use has been proposed as a means of separating the fission product palladium from PUREX raffinate which comes from used nuclear fuel. In this system of solvent extraction, the hydrocarbons of the diesel act as the diluent while the dialkyl sulfides act as the extractant. This extraction operates by a solvation mechanism. So far, neither a pilot plant nor full scale plant has been constructed to recover palladium, rhodium or ruthenium from nuclear wastes created by the use of nuclear fuel.

Diesel fuel is also often used as the main ingredient in oil-base mud drilling fluid. The advantage of using diesel is its low cost and that it delivers excellent results when drilling a wide variety of difficult strata including shale, salt and gypsum formations. Diesel-oil mud is typically mixed with up to 40% brine water. Due to health, safety and environmental concerns, Diesel-oil mud is often replaced with vegetable, mineral, or synthetic food-grade oil-base drilling fluids, although diesel-oil mud is still in widespread use in certain regions.

6 - Taxation

Diesel fuel is very similar to heating oil, which is used in central heating. In Europe, the United States, and Canada, taxes on diesel fuel are higher than on heating oil due to the fuel tax, and in those areas, heating oil is marked with fuel dyes and trace chemicals to prevent and detect tax fraud. Similarly, "untaxed" diesel (sometimes called "off-road diesel") is available in some countries for use primarily in agricultural applications, such as fuel for tractors, recreational and utility vehicles or other noncommercial vehicles that do not use public roads. Additionally, this fuel may have sulphur levels that exceed the limits for road use in some countries (e.g. USA).

This untaxed diesel is dyed red for identification, and should a person be found to be using this untaxed diesel fuel for a typically taxed purpose (such as "over-the-road", or driving use), the user can be fined (e.g. US $ 10,000 in the USA). In the United Kingdom, Belgium and the Netherlands, it is known as red diesel (or gas oil), and is also used in agricultural vehicles, home heating tanks, refrigeration units on vans/trucks which contain perishable items such as food and medicine and for marine craft. Diesel fuel, or marked gas oil is dyed green in the Republic of Ireland and Norway. The term "diesel-engined road vehicle" (DERV) is used in the UK as a synonym for unmarked road diesel fuel. In India, taxes on diesel fuel are lower than on petrol, as the majority of the transportation for grains and other essential commodities across the country runs on diesel.

In some countries, such as Germany and Belgium, diesel fuel is taxed lower than petrol (gasoline) (typically around 20% lower), but the annual vehicle tax is higher for diesel vehicles than for petrol vehicles . This gives an advantage to vehicles that travel longer distances (which is the case for trucks and utility vehicles) because the annual vehicle tax depends only on engine displacement, not on distance driven. The point at which a diesel vehicle becomes less expensive than a comparable petro vehicle is around 20,000 km a year (12,500 miles per year) for an average car. However, due to a rise in oil prices from about 2009, the advantage point started to drop, causing more people opting to buy a diesel car where they would have opted for a gasoline car a few years ago. Such an increased interest in diesel has resulted in slow but steady "dieseling" of the automobile fleet in the countries affected, sparking concerns in certain authorities about the harmful effects of diesel.

Taxes on biodiesel in the U.S. vary between states; some states (Texas, for example) have no tax on biodiesel and a reduced tax on biodiesel blends equivalent to the amount of biodiesel in the blend, so that B20 fuel is taxed 20 % less than pure petro diesel. Other states, such as North Carolina, tax biodiesel (in any blended configuration) the same as petrodiesel, although they have introduced new incentives to producers and users of all biofuels.

Fossil Fuel

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Coal, one of the fossil fuels.

Contents

1 - Introduction

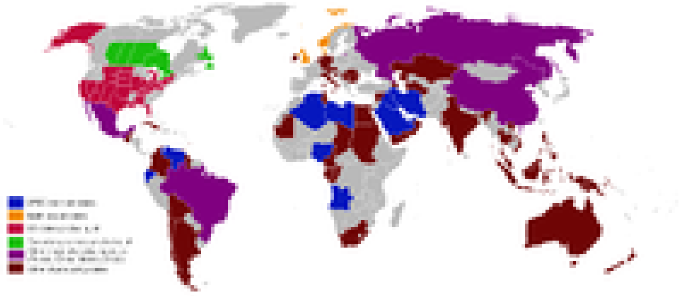
Fossil fuels are fuels formed by natural processes such as anaerobic decomposition of buried dead organisms. The age of the organisms and their resulting fossil fuels is typically millions of years, and sometimes exceeds 650 million years. Fossil fuels contain high percentages of carbon and include coal, petroleum, and natural gas.[2] They range from volatile materials with low carbon : hydrogen ratios like methane, to liquid petroleum to nonvolatile materials composed of almost pure carbon, like anthracite coal. Methane can be found in hydrocarbon fields, alone, associated with oil, or in the form of methane clathrates. Fossil fuels formed from the fossilized remains of dead plants by exposure to heat and pressure in the Earth's crust over millions of years. This biogenic theory was first introduced by Georg Agricola in 1556 and later by Mikhail Lomonosov in the 18th century.

It was estimated by the Energy Information Administration that in 2007 primary sources of energy consisted of petroleum 36.0%, coal 27.4 %, natural gas 23.0 %, amounting to an 86.4 % share for fossil fuels in primary energy consumption in the world. Non-fossil sources in 2006 included hydroelectric 6.3 % , nuclear 8.5 %, and others (geothermal, solar, tidal, wind, wood, waste) amounting to 0.9 %. World energy consumption was growing about 2.3 % per year.

Fossil fuels are non-renewable resources because they take millions of years to form, and reserves are being depleted much faster than new ones are being made. The production and use of fossil fuels raise environmental concerns. A global movement toward the generation of renewable energy is therefore under way to help meet increased energy needs.

The burning of fossil fuels produces around 21.3 billion tones (21.3 giga tones) of carbon dioxide (CO_2) per year, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tonnes of atmospheric carbon dioxide per year (one tone of atmospheric carbon is equivalent to 44 / 12 or 3.7 tones of carbon dioxide). Carbon dioxide is one of the greenhouse gases that enhances radiative forcing and contributes to global warming, causing the average surface temperature of the Earth to rise in response, which the vast majority of climate scientists agree will cause major adverse effects.

2 - Origin



Since oil fields are located only at certain places on earth, only a select group of countries are oil-independent, the other countries are dependent on the oil production capacities of these countries

Petroleum and natural gas are formed by the anaerobic decomposition of remains of organisms including phytoplankton and zooplankton that settled to the sea (or lake) bottom in large quantities under anoxic conditions, millions of years ago. Over geological time, this organic matter, mixed with mud, got buried under heavy layers of sediment. The resulting high levels of heat and pressure caused the organic matter to chemically alter, first into a waxy material known as kerogen which is found in oil shales, and then with more heat into liquid and gaseous hydrocarbons in a process known as catagenesis.

There is a wide range of organic, or hydrocarbon, compounds in any given fuel mixture. The specific mixture of hydrocarbons gives a fuel its characteristic properties, such as boiling point, melting point, density, viscosity, etc. Some fuels like natural gas, for instance, contain only very low boiling, gaseous components. Others such as gasoline or diesel contain much higher boiling components.

Terrestrial plants, on the other hand, tend to form coal and methane. Many of the coal fields date to the Carboniferous period of Earth's history. Terrestrial plants also form type III kerogen, a source of natural gas.

3 - Importance

Fossil fuels are of great importance because they can be burned (oxidized to carbon dioxide and water), producing significant amounts of energy per unit weight. The use of coal as a fuel predates recorded history. Coal was used to run furnaces for the melting of metal ore. Semi-solid hydrocarbons from seeps were also burned in ancient times , but these materials were mostly used for waterproofing and embalming.

Commercial exploitation of petroleum, largely as a replacement for oils from animal sources (notably whale oil), for use in oil lamps began in the 19th century.

Natural gas, once flared-off as an unneeded byproduct of petroleum production, is now considered a very valuable resource.[12]

Heavy crude oil, which is much more viscous than conventional crude oil, and tar sands, where bitumen is found mixed with sand and clay, are becoming more important as sources of fossil fuel.[13] Oil shale and similar materials are sedimentary rocks containing kerogen, a complex mixture of high-molecular weight organic compounds, which yield synthetic crude oil when heated (pyrolyzed). These materials have yet to be exploited commercially.[14] These fuels can be employed in internal combustion engines, fossil fuel power stations and other uses.

Prior to the latter half of the 18th century, windmills and watermills provided the energy needed for industry such as milling flour, sawing wood or pumping water, and burning wood or peat provided domestic heat. The wide scale use of fossil fuels, coal at first and petroleum later, to fire steam engines enabled the Industrial Revolution. At the same time, gas lights using natural gas or coal gas were coming into wide use. The invention of the internal combustion engine and its use in automobiles and trucks greatly increased the demand for gasoline and diesel oil, both made from fossil fuels. Other forms of transportation, railways and aircraft, also required fossil fuels. The other major use for fossil fuels is in generating electricity and as feedstock for the petrochemical industry. Tar, a leftover of petroleum extraction, is used in construction of roads.

3 – 1 - Reserves

Levels of primary energy sources are the reserves in the ground. Flows are production. The most important part of primary energy sources are the carbon based fossil energy sources. Coal, oil, and natural gas provided 79.6 % of primary energy production during 2002 (in million tones of oil equivalent (mtoe)) (34.9+23.5+21.2).

Levels (proved reserves) during 2005–2006

Coal : 905 billion metric tonnes , 4,416 billion barrels of oil equivalent

Oil : 1,119 billion barrels to 1,317 billion barrels

Natural gas : 175 – 181 trillion cubic meters , 1,161 billion barrels of oil equivalent

Flows (daily production) during 2006

Coal : 16,761,260 metric tones , 52,000,000 barrels n of oil equivalent per day
Oil: 84,000,000 barrels per day
Natural gas : 2,963 billion cubic meters , 19,000,000 barrels of oil equivalent per day

Years of production left in the ground with the current proved reserves and flows above
Coal: 148 years
Oil: 43 years
Natural gas: 61 years

Years of production left in the ground with the most optimistic proved reserve estimates .

Coal: 417 years
Oil: 43 years
Natural gas: 167 years

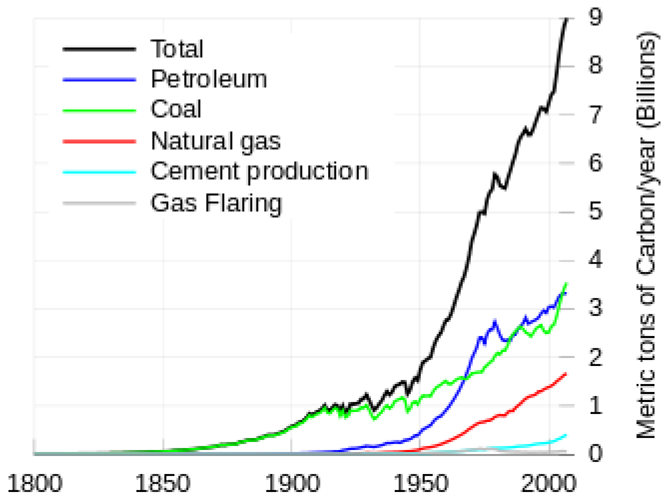
The calculation above assumes that the product could be produced at a constant level for that number of years and that all of the proved reserves could be recovered. In reality, consumption of all three resources has been increasing. While this suggests that the resource will be used up more quickly, in reality, the production curve is much more akin to a bell curve. At some point in time, the production of each resource within an area, country, or globally will reach a maximum value, after which, the production will decline until it reaches a point where is no longer economically feasible or physically possible to produce.

The above discussion emphasizes worldwide energy balance. It is also valuable to understand the ratio of reserves to annual consumption (R/C) by region or country. For example, energy policy of the United Kingdom recognizes that Europe's R/C value is 3.0, very low by world standards, and exposes that region to energy vulnerability. Alternatives to fossil fuels are a subject of intense debate worldwide.

4 - Limits and alternatives

The principle of supply and demand suggests that as hydrocarbon supplies diminish, prices will rise. Therefore higher prices will lead to increased alternative, renewable energy supplies as previously uneconomic sources become sufficiently economical to exploit. Artificial gasolines and other renewable energy sources currently require more expensive production and processing technologies than conventional petroleum reserves, but may become economically viable in the near future. See Energy development. Different alternative sources of energy include nuclear, hydroelectric, solar, wind, and geothermal.

5 - Environmental effects

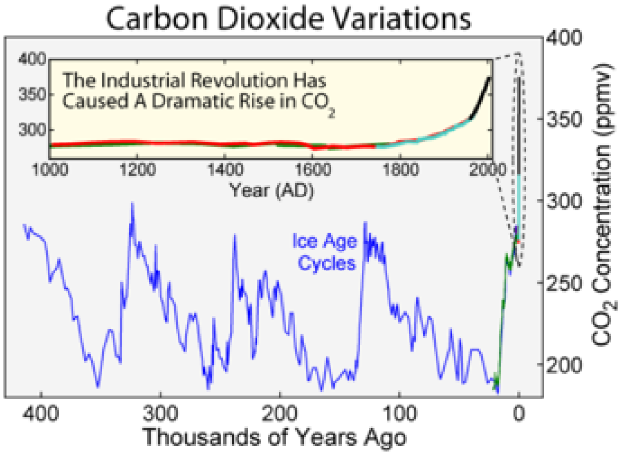


Global fossil carbon emission by fuel type, 1800–2007. Note: Carbon only represents 27% of the mass of CO_2

The U.S. holds less than 5 % of the world's population but, due to large houses and private cars, uses more than a quarter of the world's supply of fossil fuels. In the United States, more than 90 % of greenhouse gas emissions come from the combustion of fossil fuels.[21] Combustion of fossil fuels also produces other air pollutants, such as nitrogen oxides, sulfur dioxide, volatile organic compounds and heavy metals.

According to Environment Canada:

"The electricity sector is unique among industrial sectors in its very large contribution to emissions associated with nearly all air issues. Electricity generation produces a large share of Canadian nitrogen oxides and sulphur dioxide emissions, which contribute to smog and acid rain and the formation of fine particulate matter. It is the largest uncontrolled industrial source of mercury emissions in Canada. Fossil fuel-fired electric power plants also emit carbon dioxide, which may contribute to climate change. In addition, the sector has significant impacts on water and habitat and species. In particular, hydro dams and transmission lines have significant effects on water and biodiversity."



Carbon dioxide variations over the last 400,000 years, showing a rise since the industrial revolution.

According to U.S. Scientist Jerry Mahlman and USA Today: Mahlman, who crafted the IPCC language used to define levels of scientific certainty, says the new report will lay the blame at the feet of fossil fuels with "virtual certainty," meaning 99% sure. That's a significant jump from "likely," or 66% sure, in the group's last report in 2001, Mahlman says. His role in this year's effort involved spending two months reviewing the more than 1,600 pages of research that went into the new assessment.

Combustion of fossil fuels generates sulfuric, carbonic, and nitric acids, which fall to Earth as acid rain, impacting both natural areas and the built environment. Monuments and sculptures made from marble and limestone are particularly vulnerable, as the acids dissolve calcium carbonate.

Fossil fuels also contain radioactive materials, mainly uranium and thorium, which are released into the atmosphere. In 2000, about 12,000 tones of thorium and 5,000 tones of uranium were released worldwide from burning coal. It is estimated that during 1982, US coal burning released 155 times as much radioactivity into the atmosphere as the Three Mile Island incident.

Burning coal also generates large amounts of bottom ash and fly ash. These materials are used in a wide variety of applications, utilizing, for example, about 40 % of the US production.

Harvesting, processing, and distributing fossil fuels can also create environmental concerns. Coal mining methods, particularly mountaintop removal and strip mining, have negative environmental impacts, and offshore oil drilling poses a hazard to aquatic organisms. Oil refineries also have negative environmental impacts, including air and water pollution. Transportation of coal requires the use of diesel-powered locomotives, while crude oil is typically transported by tanker ships, each of which requires the combustion of additional fossil fuels.

Environmental regulation uses a variety of approaches to limit these emissions, such as command-and-control (which mandates the amount of pollution or the technology used), economic incentives, or voluntary programs.

An example of such regulation in the USA is the "EPA is implementing policies to reduce airborne mercury emissions. Under regulations issued in 2005, coal - fired power plants will need to reduce their emissions by 70 percent by 2018.".

In economic terms, pollution from fossil fuels is regarded as a negative externality. Taxation is considered one way to make societal costs explicit, in order to 'internalize' the cost of pollution. This aims to make fossil fuels more expensive, thereby reducing their use and the amount of pollution associated with them, along with raising the funds necessary to counteract these factors.

According to Rodman D. Griffin, "The burning of coal and oil have saved inestimable amounts of time and labor while substantially raising living standards around the world". Although the use of fossil fuels may seem beneficial to our lives, this act is playing a role on global warming and it is said to be dangerous for the future.[28]

Ethanol Fuel

Contents

1 - Introduction

Ethanol fuel is ethanol (ethyl alcohol), the same type of alcohol found in alcoholic beverages. It is most often used as a motor fuel, mainly as a biofuel additive for gasoline. World ethanol production for transport fuel tripled between 2000 and 2007 from 17 billion to more than 52 billion litres. From 2007 to 2008, the share of ethanol in global gasoline type fuel use increased from 3.7 % to 5.4 %. In 2011 worldwide ethanol fuel production reached 22.36 billion U.S. liquid gallons (bg) (84.6 billion liters), with the United States as the top producer with 13.9 bg (52.6 billion liters), accounting for 62.2 % of global production, followed by Brazil with 5.6 bg (21.1 billion liters). Ethanol fuel has a "gasoline gallon equivalency" (GGE) value of 1.5 US gallons (5.7 L), which means 1.5 gallons of ethanol produce the energy of one gallon of gasoline.

Ethanol fuel is widely used in Brazil and in the United States, and together both countries were responsible for 87.1 % of the world's ethanol fuel production in 2011. Most cars on the road today in the U.S. can run on blends of up to 10% ethanol, and ethanol represented 10 % of the U.S. gasoline fuel supply in 2011. Since 1976 the Brazilian government has made it mandatory to blend ethanol with gasoline, and since 2007 the legal blend is around 25 % ethanol and 75 % gasoline (E25). By December 2011 Brazil had a fleet of 14.8 million flex-fuel automobiles and light trucks and 1.5 million flex-fuel motorcycles that regularly use neat ethanol fuel (known as E100).

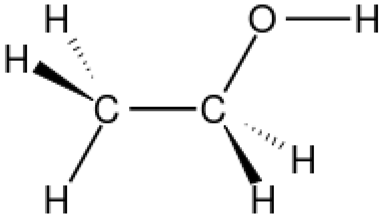
Bioethanol is a form of renewable energy that can be produced from agricultural feed stocks. It can be made from very common crops such as sugar cane, potato, manioc and corn. There has been considerable debate about how useful bioethanol will be in replacing gasoline. Concerns about its production and use relate to increased food prices due to the large amount of arable land required for crops,[11] as well as the energy and pollution balance of the whole cycle of ethanol production, especially from corn.. Recent developments with cellulosic ethanol production and commercialization may allay some of these concerns.

Cellulosic ethanol offers promise because cellulose fibers, a major and universal component in plant cells walls, can be used to produce ethanol. According to the International Energy

Agency, cellulosic ethanol could allow ethanol fuels to play a much bigger role in the future than previously thought.

Saab 9 - 3 Sport Combi BioPower. The second E85 flexifuel model introduced by Saab in the Swedish market.

2 - Chemistry



Structure of ethanol molecule. All bonds are single bonds

During ethanol fermentation, glucose and other sugars in the corn (or sugarcane or other crops) are converted into ethanol and carbon dioxide.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 + \text{heat}$$

Like any fermentation reaction, the fermentation is not 100% selective and other side products such a acetic acid, glycols and many other products are formed to a considerable extent and need to be removed during the purification of the ethanol. The fermentation takes place in aqueous solution and the resulting solution after fermentation has an ethanol content of around 15%. The ethanol is subsequently isolated and purified by a combination of adsorption and distillation techniques. The purification is very energy intensive.

During combustion ethanol reacts with oxygen to produce carbon dioxide, water, and heat:

$$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O + \text{heat}$$

Starch and cellulose are molecules that are strings of glucose molecules. It is also possible to generate ethanol out of cellulosic materials. However, a pretreatment is necessary that splits the cellulose into glycose molecules and other sugars which subsequently can be fermented. The resulting product is called cellulosic ethanol, indicating its source.

Ethanol may also be produced industrially from ethene (ethylene), by hydrolysis of the double bond in the presence of catalysts and high temperature.

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

The by far largest fraction of the global ethanol production, however, is produced by fermentation

3 – Sources

	
Sugar cane harvest	*Corn field in South Africa*
	
Switch grass	

Ethanol is a renewable energy source because the energy is generated by using a resource, sunlight, which cannot be depleted. Creation of ethanol starts with photosynthesis causing a feedstock, such as sugar cane or a grain such as maize (corn), to grow. These feed stocks are processed into ethanol.

About 5 % of the ethanol produced in the world in 2003 was actually a petroleum product. It is made by the catalytic hydration of ethylene with sulfuric acid as the catalyst. It can also be obtained via ethylene or acetylene, from calcium carbide, coal, oil gas, and other sources. Two million tons of petroleum - derived ethanol are produced annually. The principal suppliers are plants in the United States, Europe, and South Africa. Petroleum derived ethanol (synthetic ethanol) is chemically identical to bio - ethanol and can be differentiated only by radiocarbon dating.

Bio - ethanol is usually obtained from the conversion of carbon based feedstock. Agricultural feedstocks are considered renewable because they get energy from the sun using photosynthesis, provided that all minerals required for growth (such as nitrogen and phosphorus) are returned to the land. Ethanol can be produced from a variety of feedstocks such as sugar cane, bagasse, miscanthus, sugar beet, sorghum, grain, switch grass , barley, hemp, kenaf, potatoes, sweet potatoes, cassava, sunflower, fruit, molasses, corn, stover , grain, wheat, straw, cotton, other biomass , as well as many types of cellulose waste and harvestings, whichever has the best well-to-wheel assessment.

An alternative process to produce bio-ethanol from algae is being developed by the company Algenol. Rather than grow algae and then harvest and ferment it the algae grow in sunlight and produce ethanol directly which is removed without killing the algae. It is claimed the process can produce 6,000 US gallons per acre (56,000 litres per ha) per year compared with 400 US gallons per acre (3,750 l/ha) for corn production.

Currently, the first generation processes for the production of ethanol from corn use only a small part of the corn plant: the corn kernels are taken from the corn plant and only the starch, which represents about 50 % of the dry kernel mass, is transformed into ethanol. Two types of second generation processes are under development. The first type uses enzymes and yeast fermentation to convert the plant cellulose into ethanol while the second type uses pyrolysis to convert the whole plant to either a liquid bio - oil or a syngas. Second generation processes can also be used with plants such as grasses, wood or agricultural waste material such as straw.

3 – 1 - Production process

The basic steps for large scale production of ethanol are: microbial (yeast) fermentation of sugars, distillation, dehydration (requirements vary, see Ethanol fuel mixtures, below), and denaturing (optional). Prior to fermentation, some crops require saccharification or hydrolysis of carbohydrates such as cellulose and starch into sugars. Saccharification of cellulose is called cellulolysis (see cellulosic ethanol). Enzymes are used to convert starch into sugar.

3 – 2 - Fermentation

Ethanol is produced by microbial fermentation of the sugar. Microbial fermentation will currently only work directly with sugars. Two major components of plants, starch and cellulose, are both made up of sugars, and can in principle be converted to sugars for fermentation. Currently, only the sugar (e.g. sugar cane) and starch (e.g. corn) portions can be economically converted. There is much activity in the area of cellulosic ethanol, where the cellulose part of a plant is broken down to sugars and subsequently converted to ethanol.

3 – 3 – Distillation

Ethanol plant in Sertãozinho, Brazil.

Ethanol plant in West Burlington, Iowa

For the ethanol to be usable as a fuel, the majority of the water must be removed. Most of the water is removed by distillation, but the purity is limited to 95 – 96 % due to the formation of a low- boiling water-ethanol azeotrope with maximum (95.6 % m / m (96.5 % v/v) ethanol and 4.4 % m/m (3.5 % v/v) water). This mixture is called hydrous ethanol and can be used as a fuel alone, but unlike anhydrous ethanol, hydrous ethanol is not miscible in all ratios with gasoline, so the water fraction is typically removed in further treatment in order to burn in combination with gasoline in gasoline engines.

3 – 4 - Dehydration

There are basically three dehydration processes to remove the water from an azeotropic ethanol / water mixture.

I * The first process, used in many early fuel ethanol plants, is called azeotropic distillation and consists of adding benzene or cyclo hexane to the mixture. When these components are added to the mixture, it forms a heterogeneous azeotropic mixture in vapor-liquid-liquid equilibrium, which when distilled produces anhydrous ethanol in the column bottom, and a vapor mixture of water, ethanol, and cyclo hexane / benzene. When condensed, this becomes a two-phase liquid mixture. The heavier phase, poor in the entrainer (benzene or cyclo hexane), is stripped of the entrainer and recycled to the feed, while the lighter phase together with condensate from the stripping is recycled to the second column.

II * Another early method, called extractive distillation, consists of adding a ternary component which will increase ethanol's relative volatility. When the ternary mixture is distilled, it will produce anhydrous ethanol on the top stream of the column.

With increasing attention being paid to saving energy, many methods have been proposed that avoid distillation altogether for dehydration. Of these methods,

III * A third method has emerged and has been adopted by the majority of modern ethanol plants. This new process uses molecular sieves to remove water from fuel ethanol. In this process, ethanol vapor under pressure passes through a bed of molecular sieve beads. The bead's pores are sized to allow absorption of water while excluding ethanol. After a period of time, the bed is regenerated under vacuum or in the flow of inert atmosphere (e.g. N_2) to remove the absorbed water. Two beds are often used so that one is available to absorb water while the other is being regenerated. This dehydration technology can account for energy saving of 3,000 btus/gallon (840 kJ/L) compared to earlier azeotropic distillation.

4 - Technology

4 -1 – Ethanol - based engines

Ethanol is most commonly used to power automobiles, though it may be used to power other vehicles, such as farm tractors, boats and airplanes. Ethanol (E100) consumption in an engine is approximately 51 % higher than for gasoline since the energy per unit volume of ethanol is 34 % lower than for gasoline. The higher compression ratios in an ethanol - only engine allow for increased power output and better fuel economy than could be obtained with lower compression ratios. In general, ethanol - only engines are tuned to give slightly better power and torque output than gasoline - powered engines. In flexible fuel vehicles , the lower compression ratio requires tunings that give the same output when using either gasoline or hydrated ethanol. For maximum use of ethanol's benefits, a much higher compression ratio should be used. Current high compression neat ethanol engine designs are approximately 20 to 30 % less fuel efficient than their gasoline - only counterparts.

Ethanol contains soluble and insoluble contaminants . These soluble contaminants, halide ions such as chloride ions, have a large effect on the corrosivity of alcohol fuels. Halide ions increase corrosion in two ways; they chemically attack passivating oxide films on several metals causing pitting corrosion, and they increase the conductivity of the fuel. Increased electrical conductivity promotes electric, galvanic, and ordinary corrosion in the fuel system. Soluble contaminants, such as aluminum hydroxide, itself a product of corrosion by halide ions, clog the fuel system over time.

Ethanol is hygroscopic, meaning it will absorb water vapor directly from the atmosphere. Because absorbed water dilutes the fuel value of the ethanol (although it suppresses engine knock) and may cause phase separation of ethanol-gasoline blends, containers of ethanol fuels must be kept tightly sealed. This high miscibility with water means that ethanol cannot be efficiently shipped through modern pipelines, like liquid hydrocarbons, over long distances.[32] Mechanics also have seen increased cases of damage to small engines, in particular, the carburetor, attributable to the increased water retention by ethanol in fuel.

A 2004 MIT study and an earlier paper published by the Society of Automotive Engineers identify a method to exploit the characteristics of fuel ethanol substantially better than mixing it with gasoline. The method presents the possibility of leveraging the use of alcohol to achieve definite improvement over the cost-effectiveness of hybrid electric. The improvement consists of using dual-fuel direct-injection of pure alcohol (or the azeotrope or E85) and gasoline, in any ratio up to 100% of either, in a turbocharged, high compression-ratio, small-displacement engine having performance similar to an engine having twice the displacement. Each fuel is carried separately, with a much smaller tank for alcohol. The high-compression (which increases efficiency) engine will run on ordinary gasoline under low-power cruise conditions. Alcohol is directly injected into the cylinders (and the gasoline injection simultaneously reduced) only when necessary to suppress ‘knock’ such as when significantly accelerating. Direct cylinder injection raises the already high octane rating of ethanol up to an effective 130. The calculated over-all reduction of gasoline use and CO_2 emission is 30 %. The consumer cost payback time shows a 4:1 improvement over turbo-diesel and a 5:1 improvement over hybrid. The problems of water absorption into pre-mixed gasoline (causing phase separation), supply issues of multiple mix ratios and cold-weather starting are also avoided.

Ethanol's higher octane rating allows an increase of an engine's compression ratio for increased thermal efficiency. In one study, complex engine controls and increased exhaust gas recirculation allowed a compression ratio of 19.5 with fuels ranging from neat ethanol to E50. Thermal efficiency up to approximately that for a diesel was achieved. This would result in the fuel economy of a neat ethanol vehicle to be about the same as one burning gasoline.

Since 1989 there have also been ethanol engines based on the diesel principle operating in Sweden . They are used primarily in city buses, but also in distribution trucks and waste collectors. The engines, made by Scania, have a modified compression ratio, and the fuel (known as ED95) used is a mix of 93.6 % ethanol and 3.6% ignition improver, and 2.8 % denaturants . The ignition improver makes it possible for the fuel to ignite in the diesel combustion cycle. It is then also possible to use the energy efficiency of the diesel principle with ethanol. These engines have been used in the United Kingdom by Reading Transport but the use of bioethanol fuel is now being phased out.

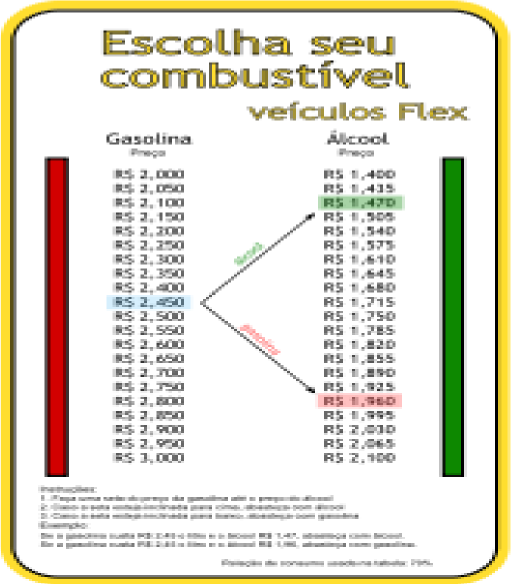
4 - 2 - Engine cold start during the winter

The Brazilian 2008 Honda Civic flex-fuel has outside direct access to the secondary reservoir gasoline tank in the front right side, the corresponding fuel filler door is shown by the arrow.

High ethanol blends present a problem to achieve enough vapor pressure for the fuel to evaporate and spark the ignition during cold weather (since ethanol tends to increase fuel enthalpy of vaporization) . When vapor pressure is below 45 kPa starting a cold engine becomes difficult. In order to avoid this problem at temperatures below 11 °C), and to reduce ethanol higher emissions during cold weather, both the US and the European markets adopted E85 as the maximum blend to be used in their flexible fuel vehicles, and they are optimized to run at such a blend. At places with harsh cold weather, the ethanol blend in the US has a seasonal reduction to E70 for these very cold regions, though it is still sold as E85. At places where temperatures fall below −12 °C during the winter, it is recommended to install an engine heater system, both for gasoline and E85 vehicles. Sweden has a similar seasonal reduction, but the ethanol content in the blend is reduced to E75 during the winter months.

Brazilian flex fuel vehicles can operate with ethanol mixtures up to E100, which is hydrous ethanol (with up to 4% water), which causes vapor pressure to drop faster as compared to E85 vehicles. As a result, Brazilian flex vehicles are built with a small secondary gasoline reservoir located near the engine. During a cold start pure gasoline is injected to avoid starting problems at low temperatures. This provision is particularly necessary for users of Brazil's southern and central regions, where temperatures normally drop below 15 °C during the winter. An improved flex engine generation was launched in 2009 that eliminates the need for the secondary gas storage tank. In March 2009 Volkswagen do Brasil launched the Polo E-Flex, the first Brazilian flex fuel model without an auxiliary tank for cold start.

4 - 3 - Ethanol fuel mixtures



Escolha seu combustível

veículos Flex

Gasolina Preço	Álcool Preço
R$ 2,000	R$ 1,400
R$ 2,050	R$ 1,435
R$ 2,100	R$ 1,470
R$ 2,150	R$ 1,505
R$ 2,200	R$ 1,540
R$ 2,250	R$ 1,575
R$ 2,300	R$ 1,610
R$ 2,350	R$ 1,645
R$ 2,400	R$ 1,680
R$ 2,450	R$ 1,715
R$ 2,500	R$ 1,750
R$ 2,550	R$ 1,785
R$ 2,600	R$ 1,820
R$ 2,650	R$ 1,855
R$ 2,700	R$ 1,890
R$ 2,750	R$ 1,925
R$ 2,800	R$ 1,960
R$ 2,850	R$ 1,995
R$ 2,900	R$ 2,030
R$ 2,950	R$ 2,065
R$ 3,000	R$ 2,100

Hydrated ethanol × gasoline type C price table for use in Brazil

To avoid engine stall due to "slugs" of water in the fuel lines interrupting fuel flow, the fuel must exist as a single phase. The fraction of water that an ethanol-gasoline fuel can contain without phase separation increases with the percentage of ethanol. This shows, for example, that E30 can have up to about 2 % water. If there is more than about 71% ethanol, the remainder can be any proportion of water or gasoline and phase separation will not occur. The fuel mileage declines with increased water content. The increased solubility of water with higher ethanol content permits E30 and hydrated ethanol to be put in the same tank since any combination of them always results in a single phase. Somewhat less water is tolerated at lower temperatures. For E10 it is about 0.5 % v / v at 70 F and decreases to about 0.23 % v / v at −30 F.

ATTENTION

E15

Up to 15% ethanol

Use only in

- 2001 and newer passenger vehicles
- Flex-fuel vehicles

Don't use in other vehicles, boats, or gasoline-powered equipment. It may cause damage and is ***prohibited*** by federal law.

EPA's E15 label required to be displayed in all E15 fuel dispensers in the U.S.

In many countries cars are mandated to run on mixtures of ethanol. All Brazilian light-duty vehicles are built to operate for an ethanol blend of up to 25 % (E25), and since 1993 a federal law requires mixtures between 22 % and 25 % ethanol, with 25% required as of mid July 2011. In the United States all light - duty vehicles are built to operate normally with an ethanol blend of 10 % (E10). At the end of 2010 over 90 percent of all gasoline sold in the U.S. was blended with ethanol . In January 2011 the U.S. Environmental Protection Agency (EPA) issued a waiver to authorize up to 15% of ethanol blended with gasoline (E15) to be sold only for cars and light pickup trucks with a model year of 2001 or newer. Other countries have adopted their own requirements.

Beginning with the model year 1999, an increasing number of vehicles in the world are manufactured with engines which can run on any fuel from 0 % ethanol up to 100 % ethanol without modification. Many cars and light trucks (a class containing minivans, SUVs and pickup trucks) are designed to be flexible-fuel vehicles using ethanol blends up to 85 % (E85) in North America and Europe, and up to 100 % (E100) in Brazil. In older model years, their engine systems contained alcohol sensors in the fuel and/or oxygen sensors in the exhaust that provide input to the engine control computer to adjust the fuel injection to achieve stoichiometric (no residual fuel or free oxygen in the exhaust) air - to - fuel ratio for any fuel mix. In newer models, the alcohol sensors have been removed, with the computer using only oxygen and airflow sensor feed back to estimate alcohol content. The engine control computer can also adjust (advance) the ignition timing to achieve a higher output without pre - ignition when it predicts that higher alcohol percentages are present in the fuel being burned. This method is backed up by advanced knock sensors – used in most high performance gasoline engines regardless of whether they are designed to use ethanol or not – that detect pre-ignition and detonation.

4 - 4 - Hydrous ethanol corrosion

High alcohol fuel blends are reputed to cause corrosion of aluminum fuel system components. However, studies indicate that the addition of water to the high alcohol fuel blends helps prevent corrosion. This is shown in SAE paper 2005-01-3708 Appendix 1.2 where gasoline / alcohol blends of E50 , nP50 ,IP50 nB50, IB50 were tested on steel, copper, nickel, zinc, tin and three types of aluminum. The tests showed that when the water content was increased from 2000 ppm to 1 %, corrosion was no longer evident except some materials showed discolouration.

4 - 5 - Fuel economy

In theory, all fuel - driven vehicles have a fuel economy (measured as miles per US gallon, or liters per 100 km) that is directly proportional to the fuel's energy content . In reality, there are many other variables that come into play that affect the performance of a particular fuel in a particular engine. Ethanol contains approx. 34 % less energy per unit volume than gasoline, and therefore in theory, burning pure ethanol in a vehicle will result in a 34 % reduction in miles per US gallon, given the same fuel economy, compared to burning pure gasoline. Since ethanol has a higher octane rating, the engine can be made more efficient by raising its compression ratio. In fact using a variable turbocharger, the compression ratio can be optimized for the fuel being used, making fuel economy almost constant for any blend. For E10 (10 % ethanol and 90 %

gasoline), the effect is small (~ 3 %) when compared to conventional gasoline , and even smaller (1–2 %) when compared to oxygenated and reformulated blends. For E85 (85 % ethanol), the effect becomes significant. E85 will produce lower mileage than gasoline, and will require more frequent refueling. Actual performance may vary depending on the vehicle. Based on EPA tests for all 2006 E85 models, the average fuel economy for E85 vehicles resulted 25.56 % lower than unleaded gasoline. The EPA-rated mileage of current USA flex-fuel vehicles[58] should be considered when making price comparisons, but E85 is a high performance fuel, with an octane rating of about 94 – 96, and should be compared to premium . In one estimate the US retail price for E85 ethanol is 2.62 US dollar per gallon or 3.71-dollar corrected for energy equivalency compared to a gallon of gasoline priced at 3.03 - dollar. Brazilian cane ethanol (100 %) is priced at 3.88 - dollar against 4.91- dollar for E25 (as July 2007).

4 - 6 - Consumer production systems

While biodiesel production systems have been marketed to home and business users for many years, commercialized ethanol production systems designed for end-consumer use have lagged in the marketplace. In 2008, two different companies announced home-scale ethanol production systems. The AFS125 Advanced Fuel System[61] from Allard Research and Development is capable of producing both ethanol and biodiesel in one machine, while the E-100 Micro Fueler from E - Fuel Corporation is dedicated to ethanol only.

5 - Experience by country

The world's top ethanol fuel producers in 2011 were the United States with 13.9 billion U.S. liquid gallons (bg) (52.6 billion liters) and Brazil with 5.6 bg (21.1 billion liters), accounting together for 87.1% of world production of 22.36 billion US gallons (84.6 billion liters). Strong incentives, coupled with other industry development initiatives, are giving rise to fledgling ethanol industries in countries such as

Germany, Spain, France, Sweden, China, Thailand, Canada, Colombia, India, Australia, and some Central American countries.

World rank	Country/Region	2011	2009	2007
1	United States	13,900	10,938	6,485
2	Brazil	5,573.24	6,577.89	5,019.2
3	European Union	1,199.31	1,039.52	570.30
4	China	554.76	541.55	486.00
5	Thailand		435.20	79.20
6	Canada	462.3	290.59	211.30
7	India		91.67	52.80
8	Colombia		83.21	74.90
9	Australia	87.2	56.80	26.40
10	Other		247.27	
	World Total	22,356.09	19,534.993	13,101.7

6 - Environment

6 - 1 - Energy balance

Energy balance		
Country	**Type**	**Energy balance**
United States	Corn ethanol	1.3
Brazil	Sugarcane ethanol	8
Germany	Biodiesel	2.5
United States	Cellulosic ethanol †	2 – 36 ††

† experimental, not in commercial production

†† depending on production method

All biomass goes through at least some of these steps: it needs to be grown, collected, dried, fermented, and burned. All of these steps require resources and an infrastructure. The total amount of energy input into the process compared to the energy released by burning the resulting ethanol fuel is known as the **energy balance** (or "energy returned on energy invested"). Figures compiled in a 2007 by *National Geographic Magazine* point to modest results for corn ethanol produced in the US: one unit of fossil-fuel energy is required to create 1.3 energy units from the resulting ethanol. The energy balance for sugarcane ethanol produced in Brazil is more favorable, with one unit of fossil-fuel energy required to create 8 from the ethanol. Energy balance estimates are not easily produced, thus numerous such reports have been generated that are contradictory. For instance, a separate survey reports that production of ethanol from sugarcane, which requires a tropical climate to grow productively, returns from 8 to 9 units of energy for each unit expended, as compared to corn which only returns about 1.34 units of fuel energy for each unit of energy expended . A 2006 University of California Berkley study, after analyzing six separate studies , concluded that producing ethanol from corn uses much less petroleum than producing gasoline.

Carbon dioxide, a green house gas, is emitted during fermentation and combustion. This is canceled out by the greater uptake of carbon dioxide by the plants as they grow to produce the biomass. When compared to gasoline, depending on the production method, ethanol releases less greenhouse gases.

6 - 2 - Air pollution

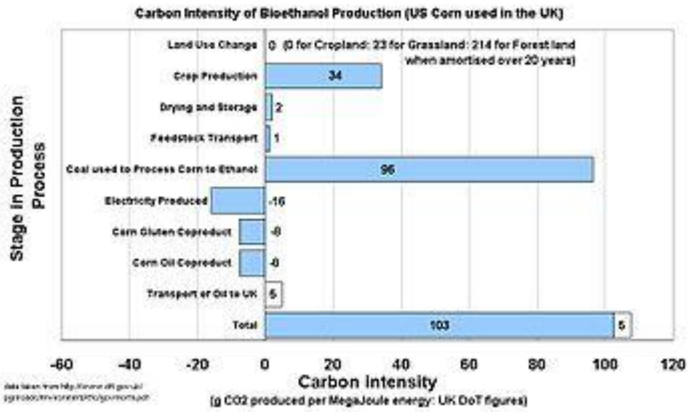
Compared with conventional unleaded gasoline, ethanol is a particulate-free burning fuel source that combusts with oxygen to form carbon dioxide, water and aldehydes. Gasoline produces 2.44 CO_2 equivalent kg/l and ethanol 1.94 . Since ethanol contains 2/3 of the energy per volume as gasoline, ethanol produces 19% more CO_2 than gasoline for the same energy. The Clean Air Act requires the addition of oxygenates to reduce carbon monoxide emissions in the United States. The additive MTBE is currently being phased out due to ground water contamination, hence ethanol becomes an attractive alternative additive. Current production methods include air pollution from the manufacturer of macronutrient fertilizers such as ammonia.

A study by atmospheric scientists at Stanford University found that E85 fuel would increase the risk of air pollution deaths relative to gasoline by 9% in Los Angeles, USA: a very large, urban, car-based metropolis that is a worst case scenario. Ozone levels are significantly increased, thereby increasing photochemical smog and aggravating medical problems such as asthma.

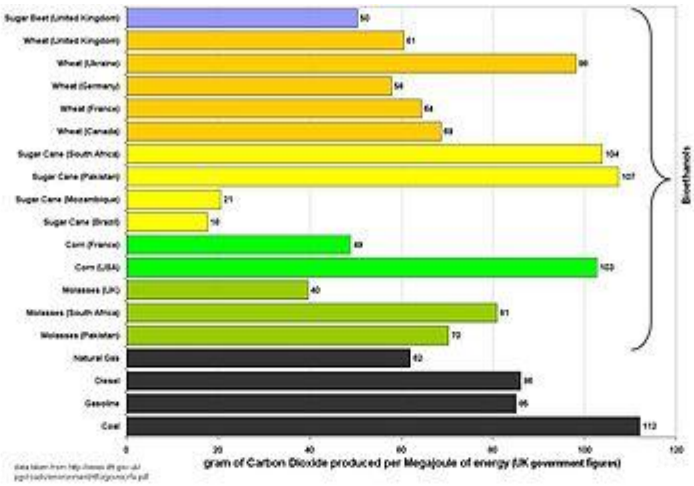
6 - 3 - Manufacture

In 2002, monitoring the process of ethanol production from corn revealed that they released VOCs (volatile organic compounds) at a higher rate than had previously been disclosed . The Environmental Protection Agency (EPA) subsequently reached settlement with Archer Daniels Midland and Cargill , two of the largest producers of ethanol, to reduce emission of these VOCs. VOCs are produced when fermented corn mash is dried for sale as a supplement for livestock feed. Devices known as thermal oxidizers or catalytic oxidizers can be attached to the plants to burn off the hazardous gases.

6 - 4 - Carbon dioxide



UK government calculation of carbon intensity of corn bioethanol grown in the US and burnt in the UK.



Graph of UK figures for the carbon intensity of bioethanol and fossil fuels. This graph assumes that all bioethanols are burnt in their country of origin and that previously existing cropland is used to grow the feedstock.

The calculation of exactly how much carbon dioxide is produced in the manufacture of bioethanol is a complex and inexact process, and is highly dependent on the method by which the ethanol is produced and the assumptions made in the calculation.

A calculation should include :

The cost of growing the feedstock
The cost of transporting the feedstock to the factory
The cost of processing the feedstock into bioethanol

Such a calculation may or may not consider the following effects:

The cost of the change in land use of the area where the fuel feedstock is grown.

The cost of transportation of the bioethanol from the factory to its point of use

The efficiency of the bioethanol compared with standard gasoline

The amount of Carbon Dioxide produced at the tail pipe.

The benefits due to the production of useful bi-products, such as cattle feed or electricity.

The graph on the right shows figures calculated by the UK government for the purposes of the Renewable transport fuel obligation.

The January 2006 Science article from UC Berkeley's ERG, estimated reduction from corn ethanol in GHG to be 13% after reviewing a large number of studies. In a correction to that article released shortly after publication, they reduce the estimated value to 7.4%. A National Geographic Magazine overview article (2007) puts the figures at 22 % less CO_2 emissions in production and use for corn ethanol compared to gasoline and a 56% reduction for cane ethanol. Carmaker Ford reports a 70% reduction in CO_2 emissions with bioethanol compared to petrol for one of their flexible-fuel vehicles.

An additional complication is that production requires tilling new soil which produces a one-off release of GHG that it can take decades or centuries of production reductions in GHG emissions to equalize . As an example, converting grass lands to corn production for ethanol takes about a century of annual savings to make up for the GHG released from the initial tilling.

6 - 5 - Change in land use

Large-scale farming is necessary to produce agricultural alcohol and this requires substantial amounts of cultivated land. University of Minnesota researchers report that if all corn grown in the U.S. were used to make ethanol it would displace 12 % of current U.S. gasoline consumption . There are claims that land for ethanol production is acquired through deforestation, while others have observed that areas currently supporting forests are usually not suitable for growing crops. In any case, farming may involve a decline in soil fertility due to reduction of organic matter , a decrease in water availability and quality , an increase in the use of pesticides and fertilizers, and potential dislocation of local communities. New technology enables farmers and processors to increasingly produce the same output using less inputs.

Cellulosic ethanol production is a new approach which may alleviate land use and related concerns. Cellulosic ethanol can be produced from any plant material, potentially doubling yields, in an effort to minimize conflict between food needs vs. fuel needs. Instead of utilizing only the starch by-products from grinding wheat and other crops, cellulosic ethanol production maximizes the use of all plant materials, including gluten. This approach would have a smaller carbon footprint because the amount of energy-intensive fertilisers and fungicides remain the same for higher output of usable material. The technology for producing cellulosic ethanol is currently in the commercialization stage.

6 – 5 - 1 - Using biomass for electricity instead of ethanol

Converting biomass to electricity for charging electric vehicles may be a more "climate-friendly" transportation option than using biomass to produce ethanol fuel, according to an analysis published in Science in May 2009 "You make more efficient use of the land and more efficient use of the plant biomass by making electricity rather than ethanol," said Elliott Campbell, an environmental scientist at the University of California at Merced , who led the research. "It's another reason that, rather than race to liquid biofuels, we should consider other uses of bio-resources".

For bioenergy to become a widespread climate solution, technological breakthroughs are necessary, analysts say . Researchers continue to search for more cost-effective developments in both cellulosic ethanol and advanced vehicle batteries.

6 – 5 - 2 - Health costs of ethanol emissions

For each billion ethanol - equivalent gallons of fuel produced and combusted in the US, the combined climate-change and health costs are $ 469 million for gasoline, $ 472 – 952 million for corn ethanol depending on biorefinery heat source (natural gas, corn stover, or coal) and technology, but only $ 123 – 208 million for cellulosic ethanol depending on feedstock (prairie biomass, Miscanthus, corn stover, or switchgrass).

7 - Efficiency of common crops

As ethanol yields improve or different feedstocks are introduced, ethanol production may become more economically feasible in the US. Currently, research on improving ethanol yields from each unit of corn is underway using biotechnology. Also, as long as oil prices remain high, the economical use of other feed stocks, such as cellulose, become viable. By - products such as straw or wood chips can be converted to ethanol. Fast growing species like switch grass can be grown on land not suitable for other cash crops and yield high levels of ethanol per unit area.

Crop	Annual yield (Liters/hectare, US gal/acre)	Greenhouse-gas savings vs. petrol[a]	Comments
Miscanthus	7300 L/ha, 780 g/acre	37 % – 73 %	Low-input perennial grass. Ethanol production depends on development of cellulosic technology.
Switchgrass	3100 – 7600 L/ha, 330 – 810 g/acre	37 % – 73 %	Low-input perennial grass. Ethanol production depends on development of cellulosic technology. Breeding efforts underway to increase yields. Higher biomass production possible with mixed species of perennial grasses.
Poplar	3700 – 6000	51 % – 100 %	Fast-growing tree.

	L/ha, 400 – 640 g/acre		Ethanol production depends on development of cellulosic technology. Completion of genomic sequencing project will aid breeding efforts to increase yields.
Sugar cane	6800 – 8000 L/ha, 727 – 870 g/acre	87 % – 96 %	Long-season annual grass. Used as feedstock for most bioethanol produced in Brazil. Newer processing plants burn residues not used for ethanol to generate electricity. Grows only in tropical and subtropical climates.
Sweet sorghum	2500 – 7000 L/ha, 270 – 750 g/acre	No data	Low-input annual grass. Ethanol production possible using existing technology. Grows in tropical and temperate climates, but highest ethanol yield estimates assume multiple crops per year (possible only in tropical climates). Does not store well.
Corn	3100 – 4000 L/ha, 330 – 424 g/acre	10 % – 20 %	High-input annual grass. Used as feedstock for most bioethanol produced in USA. Only kernels can be processed using available technology; development of

	commercial cellulosic technology would allow stover to be used and increase ethanol yield by 1,100 – 2,000 litres/ha.

8 - Reduced petroleum imports and costs

One rationale given for extensive ethanol production in the U.S. is its benefit to energy security, by shifting the need for some foreign-produced oil to domestically produced energy sources. Production of ethanol requires significant energy, but current U.S. production derives most of that energy from coal, natural gas and other sources, rather than oil. Because 66 % of oil consumed in the U.S. is imported, compared to a net surplus of coal and just 16 % of natural gas (2006 figures) , the displacement of oil - based fuels to ethanol produces a net shift from foreign to domestic U.S. energy sources.

According to a 2008 analysis by Iowa State University, the growth in US ethanol production has caused retail gasoline prices to be US $0.29 to US $0.40 per gallon lower than would otherwise have been the case.

9 - Criticism

There are various social, economic, environmental and technical issues with biofuel production and use, which have been discussed in the popular media and scientific journals. These include: the effect of moderating oil prices, the "food vs fuel" debate, poverty reduction potential, carbon emissions levels, sustainable biofuel production, deforestation and soil erosion, loss of biodiversity, impact on water resources, as well as energy balance and efficiency.

10 - Other uses

Ethanol fuel may also be utilized as a rocket fuel. As of 2010 , small quantities of ethanol are used in lightweight rocket-racing aircraft

There is still extensive use of kerosene for lighting and cooking in less developed countries, and ethanol can have a role in reducing petroleum dependency in this use too. A non-profit named Project Gaia seeks to spread the use of ethanol stoves to replace wood, charcoal and kerosene. There is also potential for bio ethanol replacing some kerosene use in domestic lighting from feed stocks grown locally. A 50 % ethanol water mixture has been tested in specially designed stoves and lanterns for rural areas .

Alcohol Fuel

A dish of ethanol aflame

Contents

1 - Introduction

Throughout history, **alcohol** has been used as a **fuel**. The first four aliphatic alcohols (methanol, ethanol, propanol, and butanol) are of interest as fuels because they can be synthesized chemically or biologically, and they have characteristics which allow them to be used in internal combustion engines. The general chemical formula for alcohol fuel is $\mathbf{C_nH_{2n+1}OH}$.

Most methanol is produced from natural gas, although it can be produced from biomass using very similar chemical processes. Ethanol is commonly produced from biological material through fermentation processes. However, "ethanol" that is derived from petroleum should not be considered safe for consumption as this alcohol contains about 5 % methanol and may cause blindness or death. This mixture may also not be purified by simple distillation, as it forms an azeotropic mixture. Biobutanol has the advantage in combustion engines in that its energy density is closer to gasoline than the simpler alcohols (while still retaining over 25% higher octane rating); however, biobutanol is currently more difficult to produce than ethanol or methanol. When obtained from biological materials and/or biological processes, they are known as **bioalcohols** (e.g. "bioethanol"). There is no chemical difference between biologically produced and chemically produced alcohols.

One advantage shared by the four major alcohol fuels is their high octane rating. This tends to increase their fuel efficiency and largely offsets the lower energy density of vehicular alcohol fuels (as compared to petrol/gasoline and diesel fuels), thus resulting in comparable "fuel economy" in terms of distance per volume metrics, such as kilometers per liter, or miles per gallon.

2 - Methanol and ethanol

Methanol and ethanol can both be derived from fossil fuels, biomass, or perhaps most simply, from carbon dioxide and water. Ethanol has most commonly been produced through fermentation of sugars, and methanol has most commonly been produced from synthesis gas, but there are more modern ways to obtain these fuels. Enzymes can be used instead of fermentation. Methanol is the simpler molecule, and ethanol can be made from methanol. Methanol can be produced industrially from nearly any biomass, including animal waste, or from carbon dioxide and water or steam by first converting the biomass to synthesis gas in a gasifier. It can also be produced in a laboratory using electrolysis or enzymes.

As a fuel, methanol and ethanol both have advantages and disadvantages over fuels such as petrol (gasoline) and diesel fuel. In spark ignition engines, both alcohols can run at a much higher exhaust gas recirculation rates and with higher compression ratios. Both alcohols have a high octane rating, with ethanol at 109 RON (Research Octane Number), 90 MON (Motor Octane Number), (which equates to 99.5 AKI) and methanol at 109 RON, 89 MON (which equates to 99 AKI). Note that AKI refers to 'Anti-Knock Index' which averages the RON and MON ratings (RON + MON) / 2, and is used on U.S. gas station pumps. Ordinary European petrol is typically 95 RON, 85 MON, equal to 90 AKI. As a compression ignition engine fuel, both alcohols create very little particulates, but their low cetane number means that an ignition improver like glycol must be mixed into the fuel with approx. 5 %.

When used in spark ignition engines alcohols have the potential to reduce NOx, CO, HC and particulates. A test with E85 fueled Chevrolet Luminas showed that NMHC went down by 20 - 22 %, NO_x by 25 - 32 % and CO by 12 - 24 % compared to reformulated gasoline. Toxic emissions of benzene and 1,3 Butadiene also decreased while aldehyde emissions increased (acetaldehyde in particular).

Tailpipe emissions of CO_2 also decrease due to the lower carbon- to - hydrogen ratio of these alcohols, and the improved engine efficiency.

Methanol and ethanol fuels contain soluble and insoluble contaminants. Halide ions, which are soluble contaminants, such as chloride ions, have a large effect on the corrosivity of alcohol fuels. Halide ions increase corrosion in two ways: they chemically attack passivating oxide films on several metals causing pitting corrosion, and they increase the conductivity of the fuel. Increased electrical conductivity promotes electrical, galvanic and ordinary corrosion in the fuel system. Soluble contaminants such as aluminum hydroxide, itself a product of corrosion by halide ions, clogs the fuel system over time. To prevent corrosion the fuel system must be made of suitable materials, electrical wires must be properly insulated and the fuel level sensor must be of pulse and hold type, magneto resistive or other similar non-contact type. In addition, high quality alcohol should have a low concentration of contaminants and have a suitable corrosion inhibitor added. Japanese scientific evidence reveals that also water is an inhibitor for corrosion by ethanol. The experiments are done with E50, which is more aggressive & speeds up the corrosion effect. It is very clear that by increasing the amount of water in fuel ethanol one can reduce the corrosion. At 2 % or 20,000 ppm water in the fuel ethanol the corrosion stopped. The observations in Japan are in line with the fact that hydrous ethanol is known for being less corrosive than anhydrous ethanol. The reaction mechanism is :

$$3Et\,OH + Al \text{ -------->} Al\,(\,OEt\,)_3 + 3/2\,H_2$$

will be the same at lower-mid blends. When enough water is present in the fuel, the aluminum will react preferably with water to produce Al_2O_2 , repairing the protective aluminum oxide layer which is why the corrosion stops. The aluminum alkoxide does not make a tight oxide layer, which is why the corrosion continues. In other words water is essential to repair the holes in the oxide layer.

Methanol and ethanol are also incompatible with some polymers. The alcohol reacts with the polymers causing swelling, and over time the oxygen breaks down the carbon-carbon bonds in the polymer causing a reduction in tensile strength. For the past few decades though, most cars have been designed to tolerate up to 10 % ethanol (E10) without problem. This include both fuel system compatibility and lambda compensation of fuel delivery with fuel injection engines featuring closed loop lambda control. In some engines ethanol may degrade some compositions of plastic or rubber fuel delivery components designed for conventional petrol, and also be unable to lambda compensate the fuel properly.

"FlexFuel" vehicles have upgraded fuel system and engine components which are designed for long life using E85 or M85, and the ECU can adapt to any fuel blend between gasoline and E85 or M85. Typical upgrades include modifications to: fuel tanks, fuel tank electrical wiring, fuel pumps, fuel filters, fuel lines, filler tubes, fuel level sensors, fuel injectors, seals, fuel rails, fuel pressure regulators, valve seats and inlet valves. "Total Flex" Autos destined for the Brazilian market can use E100 (100 % Ethanol) .

One liter of ethanol contain 21.1 MJ, a liter of methanol 15.8 MJ and a liter of gasoline approximately 32.6 MJ. In other words, for the same energy content as one liter or one gallon of gasoline, one needs 1.6 liters/gallons of ethanol and 2.1 liters/gallons of methanol. The raw energy-per-volume numbers produce misleading fuel consumption numbers however, because alcohol - fueled engines can be made substantially more energy-efficient. A larger percentage of the energy available in a liter of alcohol fuel can be converted to useful work. This difference in efficiency can partially or totally balance out the energy density difference, depending on the particular engines being compared.

Methanol fuel has been proposed as a future biofuel, often as an alternative to the hydrogen economy. Methanol has a long history as a racing fuel. Early Grand Prix Racing used blended mixtures as well as pure methanol. The use of the fuel was primarily used in North America after the war. However, methanol for racing purposes has largely been based on methanol produced from syngas derived from natural gas and therefore this methanol would not be considered a biofuel. Methanol is a possible biofuel, however when the syngas is derived from biomass. In theory, methanol can also be produced from carbon dioxide and hydrogen using nuclear power or any renewable energy source, although this is not likely to be economically viable on an industrial scale (see methanol economy). Compared to bioethanol, the primary advantage of methanol biofuel is its much greater well-to-wheel efficiency. This is particularly relevant in temperate climates where fertilizers are needed to grow sugar or starch crops to make ethanol, whereas methanol can be produced from ligno cellulose (woody) biomass.

Ethanol is already being used extensively as a fuel additive, and the use of ethanol fuel alone or as part of a mix with gasoline is increasing. Compared to methanol its primary advantage is that it is less corrosive and additionally the fuel is non-toxic, although the fuel will produce some toxic exhaust emissions. From 2007, the Indy Racing League will use ethanol as its exclusive fuel, after 40 years of using methanol. Since September 2007 petrol stations in NSW, Australia are mandated to supply all their petrol with 2% Ethanol content

Methanol combustion is :

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O + \text{heat}$$

Ethanol combustion is :

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + \text{heat}$$

3 - Butanol and propanol

Propanol and butanol are considerably less toxic and less volatile than methanol. In particular, butanol has a high flash point of 35 °C, which is a benefit for fire safety, but may be a difficulty for starting engines in cold weather. The concept of flash point is however not directly applicable to engines as the compression of the air in the cylinder means that the temperature is several hundred degrees Celsius before ignition takes place.

The fermentation processes to produce propanol and butanol from cellulose are fairly tricky to execute, and the Weizmann organism (Clostridium acetobutylicum) currently used to perform these conversions produces an extremely unpleasant smell, and this must be taken into consideration when designing and locating a fermentation plant. This organism also dies when the butanol content of whatever it is fermenting rises to 7 %. For comparison, yeast dies when the ethanol content of its feedstock hits 14 %. Specialized strains can tolerate even greater ethanol concentrations - so-called turbo yeast can withstand up to 16 % ethanol . However, if ordinary Saccharomyces yeast can be modified to improve its ethanol resistance, scientists may yet one day produce a strain of the Weizmann organism with a butanol resistance higher than the natural boundary of 7 %. This would be useful because butanol has a higher energy density than ethanol, and because waste fibre left over from sugar crops used to make ethanol could be made into butanol, raising the alcohol yield of fuel crops without there being a need for more crops to be planted.

Despite these drawbacks, DuPont and BP have recently announced that they are jointly to build a small scale butanol fuel demonstration plant alongside the large bioethanol plant they are jointly developing with Associated British Foods.

Energy Environment International developed a method for producing butanol from biomass, which involves the use of two separate micro-organisms in sequence to minimize production of acetone and ethanol byproducts.

The Swiss company Butalco GmbH uses a special technology to modify yeasts in order to produce butanol instead of ethanol. Yeasts as production organisms for butanol have decisive advantages compared to bacteria.

Butanol combustion is:

$$C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O + \text{heat}$$

The 3-carbon alcohol, propanol (C_3H_7OH), is not often used as a direct fuel source for petrol engines(unlike ethanol, methanol and butanol), with most being directed into use as a solvent. However, it is used as a source of hydrogen in some types of fuel cell; it can generate a higher voltage than methanol, which is the fuel of choice for most alcohol-based fuel cells.

However, since propanol is harder to produce than methanol (biologically OR from oil), methanol-utilising fuel cells are preferred over those that utilise propanol.

4 - By country

4 – 1 - Alcohol in Brazil

Brazil was until recently the largest producer of alcohol fuel in the world, typically fermenting ethanol from sugarcane. The country produces a total of 18 billion litres (4.8 billion gallons) annually, of which 3.5 billion liters are exported, 2 billion of them to the U.S. . Alcohol cars debuted in the Brazilian market in 1979 and became quite popular because of heavy subsidy, but in the 80's prices rose and gasoline regained the leading market share.

However, from 2003 on, alcohol is rapidly rising its market share once again because of new technologies involving flexible-fuel engines,[15] called "Flex" or "Total Flex" by all major car manufacturers (Volkswagen, General Motors, Fiat, etc.). "Flex" engines work with gasoline, alcohol or any mixture of both fuels. As of May 2009, more than 88% of new vehicles sold in Brazil are flex fuel

Because of the Brazilian leading production and technology, many countries became very interested in importing alcohol fuel and adopting the "Flex" vehicle concept . On March 7 of 2007, US president George W. Bush visited the city of São Paulo to sign agreements with Brazilian president Lula on importing alcohol and its technology as an alternative fuel.

4 – 2 - Alcohol in China

China has reported with a 70 % methanol use to conventional gasoline an independence from crude oil.

National Committee of Planning and Action Coordination for Clean Automobile had listed key technologies related to alcohol/ether fuel and accelerated industrialization into its main agenda. Alcohol fuels had become part of five main alternative fuels: Two of which were alcohols; methanol and ethanol

4 – 3 - Alcohol in the United States

The United States at the end of 2007 was producing 7 billion gallons (26.9 billion liters) per year. E10 or Gasohol is commonly marketed in Delaware and E85 is found in many states, particularly in the Mid West where ethanol from corn is produced locally. Due to government subsidies, many new vehicles are sold each year that can use E85, although the majority are run solely on gasoline due to the limited availability of E85.

Many states and municipalities have mandated that all gasoline fuel be blended with 10 percent alcohol (usually ethanol) during some or all of the year. This is to reduce pollution and allows these areas to comply with federal pollution limits. Because alcohol is partially oxygenated, it produces less overall pollution, including ozone. In some areas (California in particular) the regulations may also require other formulations or added chemicals that reduce pollution, but add complexity to the fuel distribution and increase the cost of the fuel.

4 – 4 - Alcohol in the European Union

#	Country	2005	2008
1	France	871	4,693
2	Germany	1,682	4,675
3	Sweden	1,681	2,488
4	Netherlands	0	1,512
5	Spain	1,314	1,454
6	Poland	329	1,382
7	United Kingdom	502	1,223
8	Finland	0	858
9	Austria	0	633
10	Hungary	28	454

11	Czech Republic	0	378
12	Ireland	0	207
13	Lithuania	10	182
14	Belgium	0	145
15	Slovakia	0	76
16	Bulgaria	-	72
17	Denmark	0	50
18	Slovenia	0	28
19	Estonia	0	17
20	Latvia	5	0
21	Luxembourg	0	11
22	Portugal	0	0
23	Italy	59	0
24	Greece	0	0
25	Romania	-	0
26	Malta	0	0
27	Cyprus	0	0
27	European Union	6,481	20,538

4 – 5 - Alcohol in Japan

The first alcohol fuel in Japan began with **GAIAX** in 1999. GAIAX was developed in South Korea, and imported by Japan. The principal ingredient was methanol.

Because GAIAX was not gasoline, it was a tax-free object of the gas tax of Japan. However, as a result, the use of GAIAX came to be considered an act of smuggling in Japan by the government and the petroleum industry. Retailing of GAIAX was done to avoid the tax evasion criticism by independently paying the diesel fuel tax in the legal system regulations.

Accidental vehicle fires where GAIAX was being refueled began to be reported in around 2000 when the tax evasion discussion had almost ended. The car industry in Japan criticized

GAIAX, saying that "fires broke out because high density alcohol had corroded the fuel pipes". GAIAX was named a **"High density alcohol fuel"**, and a campaign was executed to exclude it from the market long term. Finally, the Ministry of Economy, Trade and Industry also joined this campaign.

The gasoline quality method was revised under the pretext of safety concerns in 2003. This prohibited the manufacturing and sale of "High density alcohol fuel", and added a substantial GAIAX sales ban. By revising the law, fuel manufacturers are prohibited from adding 3 % or more alcohol to gasoline. This revision to the law is grounds not to be able to sell alcohol fuel greater than E3 in Japan.

Such efforts excluded GAIAX from the market. Consumers also came to widely acknowledge that alcohol fuel was dangerous due to the negative campaign with cooperation from the industrial-government complex.

The petroleum industry in Japan is now proceeding with research and development of an original alcohol fuel that differs from GAIAX. However, the commercial manufacture and sale of any new fuel may be barred by existing laws that currently exclude GAIAX from the market. Moreover, the strong aversion by the Japanese consumer to a high density alcohol fuel of any type may prevent commercial success of any new fuel.

Gasoline Gallon Equivalent

Contents

1 - Introduction

Gasoline gallon equivalent (GGE) or gasoline-equivalent gallon (GEG) is the amount of alternative fuel it takes to equal the energy content of one liquid gallon of gasoline. In 1994, the U.S. National Institute of Standards and Technology or NIST defined "gasoline gallon equivalent (GGE) means 5.660 pounds of natural gas."

GGE allows consumers to compare the energy content of competing fuels against a commonly known fuel—gasoline. Compressed natural gas (CNG), for example, is a gas rather than a liquid. It can be measured by its volume in Standard cubic feet (ft^3) (volume at atmospheric conditions), by its weight in pounds (lb) or by its energy content in joules (J) or British thermal units (BTU) or kilowatt-hours (kW·h). It is difficult to compare the cost of gasoline with other fuels if they are sold in different units. GGE solves this. A GGE of CNG and a GGE of electricity all have the same energy content as one gallon of gasoline. CNG sold at filling stations is priced in dollars per GGE.

One important point that somewhat clouds the practical utility of a GGE for comparing different fuels to each other is that machines which run on them produce usable energy from different fuels at different efficiencies. For example a 2012 Nissan Leaf has a battery capacity of 24 kWh, or a GGE size of 0.72 gallons. A standard small gasoline-powered car with 25 MPG efficiency can go 18 miles on this much fuel. But the higher efficiency Nissan Leaf can go 80-100 miles on this much battery charge.

2 - GGE - Gasoline Gallon Equivalent (US Gallons) tables

GGE Calculated for Gasoline in US Gallons at 114000 BTU per Gallon, or 7594 kilogram calories per litre

Fuel - Liquid, US Gallons	GGE	GGE %	BTU/Gal	kWh/Gal	Cal/litre
Gasoline (base)	1.0000	100.00%	114,000	33.41	7594
Gasoline (conventional, summer)	0.9960	100.40%	114,500	33.56	7624.5
Gasoline (conventional, winter)	1.0130	98.72%	112,500	32.97	7496.5
Gasoline (reformulated gasoline, ethanol)	1.0190	98.14%	111,836	32.78	7452.4
Gasoline (reformulated gasoline, ETBE)	1.0190	98.14%	111,811	32.77	7452.4
Gasoline (reformulated gasoline, MTBE)	1.0200	98.04%	111,745	32.75	7445.1
Gasoline (10% MTBE)	1.0200	98.04%	112,000	32.83	7445.1
Gasoline (regular unleaded)	1.0000	100.00%	114,100	33.44	7594
Diesel #2	0.8800	113.64%	129,500	37.95	8629.8
Biodiesel (B100)	0.9600	104.17%	118,300	34.80	8629.5
Bio Diesel (B20)	0.9000	111.11%	127,250	37.12	8437.7
Liquid natural gas (LNG)	1.5362	65.10%	75,000	21.75	4943.3
Liquefied petroleum	1.3500	74.04%	84,300	24.75	5625.2

GGE Calculated for Gasoline in US Gallons at 114000 BTU per Gallon, or 7594 kilogram calories per litre

Fuel - Liquid, US Gallons	GGE	GGE %	BTU/Gal	kWh/Gal	Cal/litre
gas (propane) (LPG)					
Methanol fuel (M100)	2.0100	49.75%	56,800	16.62	3778.1
Ethanol fuel (E100)	1.5000	66.67%	76,100	22.27	5062.7
Ethanol (E85)	1.3900	71.94%	81,800	24.04	5463.3
Jet fuel (naphtha)	0.9700	103.09%	118,700	34.44	7828.9
Jet fuel (kerosene)	0.9000	111.11%	128,100	37.12	8437.7

Fuel - Non Liquid	GGE	GGE %	BTU/unit
Gasoline (base)	1.0000	100.00%	114,000 BTU/gal
Compressed natural gas (CNG)	126.67 cu ft (3.587 m3)		900 BTU/cu ft
Hydrogen at 101.325 kPa	357.37 cu ft		319 BTU/cu ft
Hydrogen by weight	0.997 kg (2.198 lb)[8]		119.9 MJ/kg (51,500 BTU/lb)
Nitromethane	~2.3	41.23%	~47,000 BTU/gal
Electricity	33.40 kilowatt-hours		3,413 BTU/(kW·h)

3 - Compressed natural gas

One GGE of natural gas is 126.67 cubic feet (3.587 m^3) at standard conditions. This volume of natural gas has the same energy content as one US gallon of gasoline (based on lower heating values: 900 BTU / cu ft of natural gas and 115,000 BTU / gal of gasoline).

One GGE of CNG pressurized at 2,400 psi (17 MPa) is 0.77 cubic foot (21.8 liters). This volume of CNG at 2,400 psi has the same energy content as one US gallon of gasoline (based on lower heating values: 148,144 BTU/cu ft of CNG and

115,000 BTU/gal of gasoline. Using Boyle's Law, the equivalent GGE at 3,600 psi (25 MPa) is 0.51 cubic foot (14.4 L or 3.82 actual US gal).

The National Conference of Weights & Measurements (NCWM) has developed a standard unit of measurement for compressed natural gas, defined in the NIST Handbook 44 Appendix D as follows: "1 Gasoline [US] gallon equivalent (GGE) means 2.567 kg of natural gas."

When consumers refuel their CNG vehicles in the USA, the CNG is usually measured and sold in GGE units. This is fairly helpful as a comparison to gallons of gasoline.

4 - Ethanol and Fuels Like E85

1.5 gallons of ethanol has the same energy content as 1.0 gallon of gasoline.

The energy content of 1.0 US gallon of ethanol is 76,100 BTU, compared to 114,100 BTU for gasoline. (see chart above)

A flex-fuel vehicle may experience as much as 25% lower MPG when using E85 (85% ethanol) products. This is in part because the engine's compression ratio is fixed mechanically and electronic sensors can only modify the timing of the spark and/or instruct the fuel injection system to provide more of the reduced energy-content fuel .

A 2006 University of California Berkley study, after analyzing six separate studies, concluded that producing ethanol from corn uses much less petroleum than producing gasoline.

5 - Efficiency

A concept closely related to the BTU or KWH potential of a given fuel is Engine Efficiency often called Thermal Efficiency in the case of internal combustion engines.

Generally speaking, an electrical motor is more efficient than an internal combustion engine at converting potential energy into work - turning the wheels that may move a car down the road .

A diesel cycle engine can be as high as 40 % to 50 % efficient at converting fuel into work, where a standard automotive gasoline engine will be about 25 % to 30 %.

The efficiency of converting a unit of fuel to rotation of the driving wheels, includes many points of friction (loss): Heat that goes out the exhaust pipe or through the engine block to the radiator. Friction inside the engine, happens along the cylinder walls, crank, cam and main bearings; plus drive chains or gears. Friction outside the engine, includes loads from the generator, power steering pump, power brake pump, A/C pump, transmission, differential and universal joints; plus rolling resistance of the pneumatic tires.

The MPG of a given vehicle starts with the thermal efficiency of the fuel and engine, less all of the above elements of friction.

5 - Miles per gallon of gasoline equivalent (MPGe)

Plug-in electric vehicles (and plug-in-hybrids) present a paradigm shift in articulating the monetary costs of moving a passenger vehicle down the road.

Charts on this page show variable costs of electricity for the BTU equivalent of a Gallon of Gasoline at select local retail prices. That does not address the relative thermal efficiency of an electric traction motor (80% to 99%) vs the thermal efficiency of an internal combustion engine (15% to 25%). This is a significant difference.

The US EPA has addressed this difference with a new standard for electric vehicles. In simple terms, it compares the work delivered by a gallon of gasoline in a passenger vehicle, to the work done by a quantity of electrical Kilowatt Hours, that costs the same as that gallon of regular. The standard is called Miles Per Gallon of gasoline Equivalent or MPGe.

If a gallon of unleaded regular costs $3.499 (Q4, 2012) and electricity $ 0.119 per KWh (national average,) MPGe is the distance you'll travel on $3.499 worth of electricity.

Under this standard, a 2012 Nissan Leaf delivers an MPGe of 92-106.

The methodology of this calculation is evolving, but it's a good start. Depending on contract rate, the cost of electricity may vary significantly, as in the case of off-peak electricity. The cost of gasoline also shifts constantly, but this type of standard needs to stay fixed for about a year, so weekly cost shifts need to be addressed at some point. At the time you read these words calculations may or may not include losses from converting "grid" power to "battery charging" energy, or energy losses during battery charging and storage.

Glow Fuel

Contents

1 - Introduction

Glow fuel is a fuel source used in model engines -- generally the same or similar fuels can be used in model airplanes, helicopters, cars and boats.

Glow fuel can be burned by very simple two stroke engines or by more complicated four stroke engines and these engines can provide impressive amounts of power for their very small size. Glow fuel is primarily for two stroke engines with the need for oil mixed in the fuel and limited exhaust and fuel/air between cycles. Top Fuel race cars with 4 - cycle engines also use methanol nitro methane mixtures but do not contain appreciable oil.

2 - Name

Other commonly used names are **nitro** or just **model fuel**. Note that the **nitro** name is generally inaccurate, as nitro methane is usually not the primary ingredient, and in fact many glow fuels, especially the so-called "FAI" type, named for the Fédération Aéronautique Internationale, which requires such fuel in some forms of aero modeling competition, contain no nitro methane at all.

3 - Ingredients

Glow fuel is a mixture of methanol , nitro methane , and oil.

Methanol is the primary ingredient as it provides the bulk of the fuel, and is needed as a solvent for the other ingredients.

The presence of methanol causes the glow plug found in model engines to heat via a catalytic reaction with the platinum metal wire element which glows in the presence of methanol vapor.

Nitro methane is added to the methanol to increase power and to make the engine easier to tune. Typically glow fuel is about 0 - 30 % nitro methane. While higher concentrations can result in better engine performance, usage of highly concentrated nitro methane is rare due to its cost. Although a given amount of nitro methane contains less energy than the same amount of methanol, it increases the amount of available oxygen in the combustion chamber per every intake stroke, which allows the engine to draw in more fuel while still maintaining a favorable mixture setting. The increased amount of fuel entering the engine increases power output, and also aids in cooling. For racing use, the nitromethane content can be increased to the range of 30 % - 65 % .

Nitro methane is often difficult to obtain in many countries, so in these countries glow fuel typically has no nitro methane at all.

4 - Lubrication

Most model engines require oil to be included with the fuel as a lubricant since the engine has no independent oiling capability. Model engine fuel is typically 8 - 22 % oil, with the higher percentages run in older design two-stroke glow engines that use bushings for the crankshaft bearings. The most commonly used lubricants are castor oil and synthetic oils, and many glow fuels include a mixture of the two. The oils included in glow fuel generally are not burned by the engine, and are expelled out the exhaust of the engine. This also helps the engine dissipate heat, as the oil emitted is generally hot.

Four stroke model engines, since they are generally designed to be simple powerplants while still incorporating the usual camshaft, rocker arms and poppet valves of larger sized four stroke engines, are generally meant to use glow ignition and their fuel. Often, the oil percentage for four stroke glow fuel can be lowered from the 18 -20 % figure used for some two-stroke engines, down to as low as a 12-15 % percentage per unit of blended glow fuel, but use of such low-percentage lubricant fuel can also mandate the need for a small percentage of castor oil in the mix to avoid having too little oil in the mix, and also mandates setting the high-speed fuel mixture carefully by using a handheld digital tachometer to check engine speed to avoid over-leaning of the fuel mixture.

Glow engines generally have to be run slightly rich with a higher fuel/air ratio than is ideal to keep the engine cool as the fuel going out the exhaust also takes heat with it, and so vehicles with glow engines generally get coated with lots of oil. Almost all the oil comes out the exhaust, and some nitromethane and methanol as well (as it's not all burned) requiring some cleaning when one is done using the model.

The nitro methane that exists in many glow fuel blends can cause corrosion of metal parts in model engines, especially four-stroke designs, due to the nitric acid residue formed from combustion of nitro methane - content glow fuel, making the use of a so-called "after - run oil" a common practice after a model flying session with a four - stroke glow engine-powered model.

Glow fuel is not difficult to make, and so many modelers mix their own to save money, but some of the ingredients are flammable and / or explosive and so can be dangerous, especially in large quantities. Most modelers buy their glow fuel premixed from such manufacturers such as Byron, Blue Thunder, FHS Supply, Model Technics, Morgan, Powermaster, Tornado, Wildcat, and many others.

5 -Alternatives

Nitro methane is some times replaced or supplemented by nitro ethane. Propylene oxide is some times added in small percentages.

Another form of model fuel, for small compression ignition engines, is called "Diesel Fuel", which generally consists of kerosene, ether, oil and some sort of ignition improver, usually amyl nitrate or isopropyl nitrate, it is in no way related to the automotive fuel of the same name

P - Series Fuels

1 - Introduction

P - Series fuels are a family of renewable, non-petroleum, liquid fuels that can substitute for gasoline. It is a mixture of ethanol, methyl tetra hydrofuran (MeTHF), "pentanes - plus", and butane. The formulas can be adjusted for cold weather and for 'premium' blends. Approximately 35 % of the blend is or can be created from waste products of other industrial processes. It was originally developed by brothers Scott and Doug Dunlop, the co - founders of the Pure Energy Corporation and optimized by Dr. Stephen F. Paul of Princeton University. It was patented in 1997 (US 5,697,987) by Dr. Paul and assigned to Princeton University. Simultaneously, the Pure Energy Corporation was granted an exclusive license to commercialize P-Series fuels. Responding to a petition submitted by the Pure Energy Corporation, the DOE proposed in 1998 that P-Series be recognized as an alternative fuel in accordance with the Energy Policy Act of 1992 (see the Federal Register/Vol. 63, No. 144/Tuesday, July 28, 1998/Proposed Rules, page 40202.) The final rule designating P-Series as an EPACT alternative fuel was published in the following year,

In addition to the patent, the other publication detailing the P-Series fuels was Dr. Paul's 1998 paper entitled: An Optimized Alternative Motor Fuel Formulation: Natural Gas Liquids Ethanol And A Biomass-Derived Ether, which appeared in the Proceedings of the American Chemical Society Division of Fuel Chemistry, Fuels for the Year 2000 and Beyond, 216th ACS National Meeting & Exposition, August 23–27, Boston, 1998 43(3), p. 373-377.

2 - Overview

A multi-component, liquid, non-petroleum, alternative motor fuel for spark ignition engines has been developed. The fuel is composed of approximately equal volumes of ;

(1) medium-molecular weight alkanes, iso alkanes, and cyclo alkanes (C5 - C8) which are extracted in the course of coal bed gas or natural gas production and / or processing ,

(2) anhydrous fermentation ethanol, and

(3) 2 – methyl THF, a biomass-derived heterocyclic ether. The ether serves as a co-solvent that reduces the volatility of the ethanol/hydrocarbon blend. The formulation can be adjusted to vary the fuel characteristics over a range to formulate winter / summer and regular/premium grades:87-94 octane; 0.74 - 0.78 specific gravity; and 6.5 - 13.5 psi Reid vapor pressure. P-Series fuels contain little or no sulfur, phosphorus, aromatics, olefins, or high- boiling - point hydrocarbons, but does contain 11 - 19% oxygen (by weight), with a corresponding reduction in heat content (100,000 - 106,000 BTU / gal) . This fuel has been tested in unmodified 1996 and 1997 Ford Taurus ethanol-Flexible Fuel Vehicles. They vehicles come equipped with a fuel sensor that automatically adjust the air/fuel ratio to optimize running on a particular fuel. Emissions testing (USEPA's FTP protocol) show the following differences in the tailpipe exhaust characteristics (compared to conventional gasoline): 40 - 50% less unburned hydrocarbons, 20% less CO, no significant change in NOx , 4% less COz, 40 % less ozone-forming potential, and 2 - 3 times less toxicity.

Most flexible fuel vehicles capable of running on E85 should also be able to handle P-Series fuel.

The projected retail price will be about 10 % less than gasoline. As of June 2012 it is not available to the ge

Bioconversion of Biomass to Mixed Alcohol Fuels

Contents

1 - Introduction

The bioconversion of biomass to mixed alcohol fuels can be accomplished using the MixAlco process. Through bioconversion of biomass to a mixed alcohol fuel, more energy from the biomass will end up as liquid fuels than in converting biomass to ethanol by yeast fermentation.

The process involves a biological/chemical method for converting any biodegradable material (e.g., urban wastes, such as municipal solid waste, biodegradable waste, and sewage sludge, agricultural residues such as corn stover, sugarcane bagasse, cotton gin trash, manure) into useful chemicals, such as carboxylic acids (e.g., acetic, propionic, butyric acid), ketones (e.g., acetone, methyl ethyl ketone, diethyl ketone) and biofuels, such as a mixture of primary alcohols (e.g., ethanol, propanol, *n*-butanol) and/or a mixture of secondary alcohols (e.g., isopropanol, 2-butanol, 3-pentanol). Because of the many products that can be economically produced, this process is a true bio refinery.

The process uses a mixed culture of naturally occurring microorganisms found in natural habitats such as the rumen of cattle, termite guts, and marine and terrestrial swamps to anaerobically digest biomass into a mixture of carboxylic acids produced during the acidogenic and acetogenic stages of anaerobic digestion, however with the inhibition of the methanogenic final stage. The more popular methods for production of ethanol and cellulosic ethanol use enzymes that must be isolated first to be added to the biomass and thus convert the starch or cellulose into simple sugars, followed then by yeast fermentation into ethanol. This process does not need the addition of such enzymes as these microorganisms make their own.

Pilot Plant (College Station, Texas)

As the micro oganisms an aerobically digest the biomass and convert it into a mixture of carboxylic acids, the pH must be controlled. This is done by the addition of a buffering agent (e.g., ammonium bicarbonate, calcium carbonate), thus yielding a mixture of carboxylate salts. Methanogenesis, being the natural final stage of anaerobic digestion, is inhibited by the presence of the ammonium ions or by the addition of an inhibitor (e.g., iodoform). The resulting fermentation broth contains the produced carboxylate salts that must be dewatered. This is achieved efficiently by vapor-compression evaporation. Further chemical refining of the dewatered fermentation broth may then take place depending on the final chemical or biofuel product desired.

The condensed distilled water from the vapor-compression evaporation system is recycled back to the fermentation. On the other hand, if raw sewage or other waste water with high BOD in need of treatment is used as the water for the fermentation, the condensed distilled water from the evaporation can be recycled back to the city or to the original source of the high-BOD waste water. Thus, this process can also serve as a water treatment facility, while producing valuable chemicals or biofuels.

Because the system uses a mixed culture of microorganisms, besides not needing any enzyme addition, the fermentation requires no sterility or aseptic conditions, making this front step in the process more economical than in more popular methods for the production of cellulosic ethanol. These savings in the front end of the process, where volumes are large, allows flexibility for further chemical transformations after dewatering, where volumes are small.

2 - Carboxylic acids

Carboxylic acids can be regenerated from the carboxylate salts using a process known as "acid springing". This process makes use of a high-molecular-weight tertiary amine (e.g., tri octyl amine), which is switched with the cation (e.g., ammonium or calcium). The resulting amine carboxylate can then be thermally decomposed into the amine itself, which is recycled, and the corresponding carboxylic acid. In this way, theoretically, no chemicals are consumed or wastes produced during this step.

3 - Ketones

There are two methods for making ketones. The first one consists on thermally converting calcium carboxylate salts into the corresponding ketones. This was a common method for making acetone from calcium acetate during World War I.[6] The other method for making ketones consists on converting the vaporized carboxylic acids on a catalytic bed of zirconium oxide.

4 - Alcohols

4 – 1 - Primary alcohols

The undigested residue from the fermentation may be used in gasification to make hydrogen (H_2). This H_2 can then be used to hydrogenolyze the esters over a catalyst (e.g., copper chromite), which are produced by esterifying either the ammonium carboxylate salts (e.g., ammonium acetate, propionate, butyrate) or the carboxylic acids (e.g., acetic, propionic , butyric acid) with a high-molecular-weight alcohol (e.g., hexanol, heptanol) . From the hydrogenolysis, the final products are the high-molecular-weight alcohol, which is recycled back to the esterification, and the corresponding primary alcohols (e.g., ethanol, propanol, butanol).

4 – 2 - Secondary alcohols

The secondary alcohols (e.g., iso propanol, 2-butanol, 3-pentanol) are obtained by hydrogenating over a catalyst (e.g., Raney nickel) the corresponding ketones (e.g., acetone, methyl ethyl ketone, diethyl ketone).[

5 – Drop - in biofuels

The primary or secondary alcohols obtained as described above may undergo conversion to drop-in biofuels, fuels which are compatible with current fossil fuel infrastructure such as biogasoline, green diesel and bio-jet fuel. Such is done by subjecting the alcohols to dehydration followed by oligomerization using zeolite catalysts in a manner similar to the methanex process, which used to produce gasoline from methanol in New Zealand.

6 - Acetic acid versus ethanol

Cellulosic-ethanol - manufacturing plants are bound to be net exporters of electricity because a large portion of the lignocellulosic biomass, namely lignin, remains undigested and it must be burned, thus producing electricity for the plant and excess electricity for the grid. As the market grows and this technology becomes more widespread, coupling the liquid fuel and the electricity markets will become more and more difficult.

Acetic acid, unlike ethanol, is biologically produced from simple sugars without the production of carbon dioxide :

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

(Biological production of ethanol)

$$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$$

(Biological production of acetic acid)

Because of this, on a mass basis, the yields will be higher than in ethanol fermentation. If then, the undigested residue (mostly lignin) is used to produce hydrogen by gasification, it is ensured that more energy from the biomass will end up as liquid fuels rather than excess heat/electricity.

$$3\ CH_3COOH + 6\ H_2 \rightarrow 3\ CH_3CH_2OH + 3\ H_2O$$

(Hydrogenation of acetic acid)

$$C_6H_{12}O_6 \text{ (from cellulose)} + 6\ H_2 \text{ (from lignin)} \rightarrow 3\ CH_3CH_2OH + 3\ H_2O$$

(Overall reaction)

A more comprehensive description of the economics of each of the fuels is given on the pages alcohol fuel and ethanol fuel, more information about the economics of various systems can be found on the central page biofuel.

7 - Stage of development

The system has been in development since 1991, moving from the laboratory scale (10 g/day) to the pilot scale (200 lb/day) in 2001. A small demonstration-scale plant (5 ton/day) has been constructed and is under operation and a 220 ton/day demonstration plant is expected in 2012.

Biodiesel

Contents

1 - Introduction

Biodiesel refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat (tallow)) with an alcohol producing fatty acid esters.

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel *converted* diesel engines. Biodiesel can be used alone, or blended with petro diesel. Biodiesel can also be used as a low carbon alternative to heating oil.

The National Biodiesel Board (USA) also has a technical definition of "biodiesel" as a mono-alkyl ester.

Bus run by biodiesel

2 - Blends

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix:

100 % biodiesel is referred to as B100, while
20 % biodiesel, 80 % petro diesel is labeled B20
5 % biodiesel, 95 % petro diesel is labeled B5
2 % biodiesel, 98 % petro diesel is labeled B2.

Blends of 20 % biodiesel and lower can be used in diesel equipment with no, or only minor modifications , although certain manufacturers do not extend warranty coverage if equipment is damaged by these blends. The B6 to B20 blends are covered by the ASTM D7467 specification. Biodiesel can also be used in its pure form (B100) , but may require certain engine modifications to avoid maintenance and performance problems. Blending B100 with petroleum diesel may be accomplished by:

Mixing in tanks at manufacturing point prior to delivery to tanker truck

Splash mixing in the tanker truck (adding specific percentages of biodiesel and petroleum diesel)

In-line mixing, two components arrive at tanker truck simultaneously.

Metered pump mixing, petroleum diesel and biodiesel meters are set to X total volume, transfer pump pulls from two points and mix is complete on leaving pump.

3 - Applications

Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. New extreme high-pressure (29,000 psi) common rail engines have strict factory limits of B5 or B20, depending on manufacturer . Biodiesel has different solvent properties than petro diesel, and will degrade natural rubber gaskets and hoses in vehicles (mostly vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced with FKM, which is nonreactive to biodiesel. Biodiesel has been known to break down deposits of residue in the fuel lines where petrodiesel has been used.[8] As a result, fuel filters may become clogged with particulates if a quick transition to pure biodiesel is made. Therefore, it is recommended to change the fuel filters on engines and heaters shortly after first switching to a biodiesel blend.

3 – 1 - Distribution

Since the passage of the Energy Policy Act of 2005, biodiesel use has been increasing in the United States . In the UK, the Renewable Transport Fuel Obligation obliges suppliers to include 5%

renewable fuel in all transport fuel sold in the UK by 2010. For road diesel, this effectively means 5% biodiesel (B5).

3 – 2 - Vehicular use and manufacturer acceptance

In 2005, Chrysler (then part of DaimlerChrysler) released the Jeep Liberty CRD diesels from the factory into the American market with 5 % biodiesel blends, indicating at least partial acceptance of biodiesel as an acceptable diesel fuel additive . In 2007, DaimlerChrysler indicated its intention to increase warranty coverage to 20 % biodiesel blends if biofuel quality in the United States can be standardized.

The Volkswagen Group has released a statement indicating that several of its vehicles are compatible with B5 and B100 made from rape seed oil and compatible with the EN 14214 standard. The use of the specified biodiesel type in its cars will not void any warranty.

Mercedes Benz does not allow diesel fuels containing greater than 5 % biodiesel (B5) due to concerns about "production shortcomings". Any damages caused by the use of such non-approved fuels will not be covered by the Mercedes-Benz Limited Warranty.

Starting in 2004, the city of Halifax, Nova Scotia decided to update its bus system to allow the fleet of city buses to run entirely on a fish-oil based biodiesel. This caused the city some initial mechanical issues, but after several years of refining, the entire fleet had successfully been converted.

In 2007, McDonalds of UK announced it would start producing biodiesel from the waste oil byproduct of its restaurants. This fuel would be used to run its fleet.

3 – 3 - Railway usage

British train operating company Virgin Trains claimed to have run the UK's first "biodiesel train", which was converted to run on 80 % petro diesel and 20 % biodiesel.

The Royal Train on 15 September 2007 completed its first ever journey run on 100 % biodiesel fuel supplied by Green Fuels Ltd. His

Royal Highness, The Prince of Wales, and Green Fuels managing director, James Hygate, were the first passengers on a train fueled entirely by biodiesel fuel. Since 2007, the Royal Train has operated successfully on B100 (100% biodiesel).

Similarly, a state-owned short-line railroad in eastern Washington ran a test of a 25% biodiesel / 75% petrodiesel blend during the summer of 2008, purchasing fuel from a biodiesel producer sited along the railroad tracks. The train will be powered by biodiesel made in part from canola grown in agricultural regions through which the short line runs.

Also in 2007, Disneyland began running the park trains on B98 (98% biodiesel). The program was discontinued in 2008 due to storage issues, but in January 2009, it was announced that the park would then be running all trains on biodiesel manufactured from its own used cooking oils. This is a change from running the trains on soy-based biodiesel.

3 – 4 - Aircraft use

A test flight has been performed by a Czech jet aircraft completely powered on biodiesel.[22] Other recent jet flights using biofuel, however, have been using other types of renewable fuels.

On November 7, 2011 United Airlines flew the world's first commercial aviation flight on a microbially derived biofuel using Solajet™, Solazyme's algae-derived renewable jet fuel. The Eco-skies Boeing 737-800 plane was fueled with 40 percent Solajet and 60 percent petroleum-derived jet fuel. The commercial Eco-skies flight 1403 departed from Houston's IAH airport at 10:30 and landed at Chicago's ORD airport at 13:03.

3 – 5 - As a heating oil

Biodiesel can also be used as a heating fuel in domestic and commercial boilers, a mix of heating oil and biofuel which is standardized and taxed slightly differently than diesel fuel used for transportation. It is sometimes known as "bioheat" (which is a registered trademark of the National Biodiesel Board [NBB] and the

National Oilheat Research Alliance [NORA] in the U.S., and Columbia Fuels in Canada). Heating biodiesel is available in various blends. ASTM 396 recognizes blends of up to 5 percent biodiesel as equivalent to pure petroleum heating oil. Blends of higher levels of up to 20 % biofuel are used by many consumers. Research is underway to determine whether such blends affect performance.

Older furnaces may contain rubber parts that would be affected by biodiesel's solvent properties, but can otherwise burn biodiesel without any conversion required. Care must be taken, however, given that varnishes left behind by petrodiesel will be released and can clog pipes- fuel filtering and prompt filter replacement is required. Another approach is to start using biodiesel as a blend, and decreasing the petroleum proportion over time can allow the varnishes to come off more gradually and be less likely to clog. Thanks to its strong solvent properties, however, the furnace is cleaned out and generally becomes more efficient . A technical research paper describes laboratory research and field trials project using pure biodiesel and biodiesel blends as a heating fuel in oil - fired boilers. During the Biodiesel Expo 2006 in the UK, Andrew J. Robertson presented his biodiesel heating oil research from his technical paper and suggested B20 biodiesel could reduce UK household CO_2 emissions by 1.5 million tons per year.

A law passed under Massachusetts Governor Deval Patrick requires all home heating diesel in that state to be 2 % biofuel by July 1, 2010, and 5% biofuel by 2013. New York City has passed a similar law.

4 - Historical background

Trans esterification of a vegetable oil was conducted as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional . Rudolf Diesel's prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany, on 10 August 1893 running on nothing but peanut oil. In remembrance of this event, 10 August has been declared "International Biodiesel Day".

It is often reported that Diesel designed his engine to run on peanut oil, but this is not the case. Diesel stated in his published papers, "at the Paris Exhibition in 1900 (*Exposition Universelle*) there was shown by the Otto Company a small Diesel engine, which, at the request of the French government ran on arachide (earth-nut or pea-nut) oil (see biodiesel), and worked so smoothly that only a few people were aware of it. The engine was constructed for using mineral oil, and was then worked on vegetable oil without any alterations being made. The French Government at the time thought of testing the applicability to power production of the Arachide, or earth-nut, which grows in considerable quantities in their African colonies, and can easily be cultivated there." Diesel himself later conducted related tests and appeared supportive of the idea . In a 1912 speech Diesel said, "the use of vegetable oils for engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time."

Despite the widespread use of petroleum-derived diesel fuels, interest in vegetable oils as fuels for internal combustion engines was reported in several countries during the 1920s and 1930s and later during World War II. Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan and China were reported to have tested and used vegetable oils as diesel fuels during this time. Some operational problems were reported due to the high viscosity of vegetable oils compared to petroleum diesel fuel, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves. Attempts to overcome these problems included heating of the vegetable oil, blending it with petroleum-derived diesel fuel or ethanol, pyrolysis and cracking of the oils.

On 31 August 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a "Procedure for the transformation of vegetable oils for their uses as fuels" (fr. "*Procédé de Transformation d'Huiles Végétales en Vue de Leur Utilisation comme Carburants*") Belgian Patent 422,877. This patent described the alcoholysis (often referred to as trans esterification) of vegetable oils using ethanol (and mentions methanol) in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. This appears to be the first account of the production of what is known as "biodiesel" today.

More recently, in 1977, Brazilian scientist Expedito Parente invented and submitted for patent, the first industrial process for the production of biodiesel . This process is classified as biodiesel by international norms, conferring a "standardized identity and quality. No other proposed biofuel has been validated by the motor industry." As of 2010, Parente's company Tecbio is working with Boeing and NASA to certify bio querosene (bio-kerosene), another product produced and patented by the Brazilian scientist.

Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa in 1979. By 1983, the process for producing fuel-quality, engine-tested biodiesel was completed and published internationally.[33] An Austrian company, Gaskoks, obtained the technology from the South African Agricultural Engineers; the company erected the first biodiesel pilot plant in November 1987, and the first industrial-scale plant in April 1989 (with a capacity of 30,000 tons of rapeseed per annum).

Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany and Sweden. France launched local production of biodiesel fuel (referred to as *diester*) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g. public transportation) at a level of 30%. Renault, Peugeot and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiments with 50% biodiesel are underway. During the same period, nations in other parts of the world also saw local production of biodiesel starting up: by 1998, the Austrian Biofuels Institute had identified 21 countries with commercial biodiesel projects. 100% biodiesel is now available at many normal service stations across Europe.

5 - Properties

Biodiesel has better lubricating properties and much higher cetane ratings than today's lower sulfur diesel fuels. Biodiesel addition reduces fuel system wear, and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called *unit injectors*) and fuel injectors.

Older diesel Mercedes are popular for running on biodiesel.

The calorific value of biodiesel is about 37.27 MJ/kg.[35] This is 9% lower than regular Number 2 petro diesel. Variations in biodiesel energy density is more dependent on the feedstock used than the production process. Still, these variations are less than for petro diesel. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petro diesel.

Biodiesel is a liquid which varies in color — between golden and dark brown —depending on the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. *The flash point of biodiesel (>130 °C, >266 °F)[38] is significantly higher than that of petroleum diesel (64 °C) or gasoline (− 45 °C). Biodiesel has a density of ~ 0.88 g / cm^3, higher than petro diesel (~ 0.85 g/cm^3).

Biodiesel has virtually no sulfur content,[39] and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petrodiesel provide much of the lubricity.

5 – 1 - Material compatibility

Plastics: High density polyethylene (HDPE) is compatible but polyvinyl chloride (PVC) is slowly degraded . Polystyrene is dissolved on contact with biodiesel.

Metals: Biodiesel has an effect on copper-based materials (e.g. brass), and it also affects zinc, tin, lead, and cast iron . Stainless steels (316 and 304) and aluminum are unaffected.

Rubber: Biodiesel also affects types of natural rubbers found in some older engine components. Studies have also found that fluorinated elastomers (FKM) cured with peroxide and base-metal oxides can be degraded when biodiesel loses its stability caused by oxidation. Commonly used synthetic rubbers FKM- GBL-S and FKM- GF-S found in modern vehicles were found to handle biodiesel in all conditions.

6 - Technical standards

Biodiesel has a number of standards for its quality including European standard EN 14214, ASTM International D6751, and others.

7 - Low temperature gelling

When biodiesel is cooled below a certain point, some of the molecules aggregate and form crystals. The fuel starts to appear cloudy once the crystals become larger than one quarter of the wavelengths of visible light - this is the cloud point (CP). As the fuel is cooled further these crystals become larger. The lowest temperature at which fuel can pass through a 45 micro meter filter is the cold filter plugging point (CFPP). As biodiesel is cooled further it will gel and then solidify. Within Europe, there are differences in the CFPP requirements between countries. This is reflected in the different national standards of those countries. The temperature at which pure (B100) biodiesel starts to gel varies significantly and depends upon the mix of esters and therefore the feedstock oil used to produce the biodiesel. For example, biodiesel produced from low erucic acid varieties of canola seed (RME) starts to gel at approximately −10 °C (14 °F). Biodiesel produced from tallow tends to gel at around +16 °C

(61 °F). There are a number of commercially available additives that will significantly lower the pour point and cold filter plugging point of pure biodiesel. Winter operation is also possible by blending biodiesel with other fuel oils including #2 low sulfur diesel fuel and #1 diesel / kerosene.

Another approach to facilitate the use of biodiesel in cold conditions is by employing a second fuel tank for biodiesel in addition to the standard diesel fuel tank. The second fuel tank can be insulated and a heating coil using engine coolant is run through the tank. The fuel tanks can be switched over when the fuel is sufficiently warm. A similar method can be used to operate diesel vehicles using straight vegetable oil.

8 - Contamination by water

Biodiesel may contain small but problematic quantities of water. Although it is not miscible with water, it is, like ethanol, hygroscopic (absorbs water at a molecular level) . One of the reasons biodiesel can absorb water is the persistence of mono and diglycerides left over from an incomplete reaction. These molecules can act as an emulsifier, allowing water to mix with the biodiesel . In addition, there may be water that is residual to processing or resulting from storage tank condensation. The presence of water is a problem because :

Water reduces the heat of fuel combustion, causing smoke, harder starting, and reduced power.

Water causes corrosion of fuel system components (pumps, fuel lines, etc.)

Microbes in water cause the paper-element filters in the system to rot and fail, causing failure of the fuel pump due to ingestion of large particles.

Water freezes to form ice crystals that provide sites for nucleation, accelerating gelling of the fuel.

Water causes pitting in pistons.

Previously, the amount of water contaminating biodiesel has been difficult to measure by taking samples, since water and oil separate. However, it is now possible to measure the water content using water-in-oil sensors .

Water contamination is also a potential problem when using certain chemical catalysts involved in the production process, substantially reducing catalytic efficiency of base (high pH) catalysts such as potassium hydroxide. However, the super-critical methanol production methodology, whereby the trans esterification process of oil feedstock and methanol is effectuated under high temperature and pressure, has been shown to be largely unaffected by the presence of water contamination during the production phase.

9 - Availability and prices

In some countries biodiesel is less expensive than conventional diesel

Global biodiesel production reached 3.8 million tons in 2005. Approximately 85 % of biodiesel production came from the European Union.

In 2007, in the United States, average retail (at the pump) prices, including federal and state fuel taxes, of B2/B5 were lower than petroleum diesel by about 12 cents, and B20 blends were the same as petro diesel. However, as part as a dramatic shift in diesel pricing, by July 2009, the US DOE was reporting average costs of B20 15 cents per gallon higher than petroleum diesel ($ 2.69 / gal vs. $2.54 / gal). B99 and B100 generally cost more than petro diesel except where local governments provide a tax incentive or subsidy.

10 - Production

Biodiesel is commonly produced by the trans esterification of the vegetable oil or animal fat feedstock. There are several methods for carrying out this transesterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods.

Chemically, trans esterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol (converted to sodium methoxide) to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester - FAME) as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester (commonly referred to as Fatty Acid Ethyl Ester - FAEE) biodiesel and higher alcohols such as iso propanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient trans esterification reaction. A lipid transesterification production process is used to convert the base oil to the desired esters. Any free fatty acids (FFAs) in the base oil are either converted to soap and removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst. After this processing, unlike straight vegetable oil, biodiesel has combustion properties very similar to those of petroleum diesel, and can replace it in most current uses.

The methanol used in most biodiesel production processes is made using fossil fuel inputs. However, there are sources of renewable methanol made using carbon dioxide or biomass as feedstock, making their production processes free of fossil fuels.

A by-product of the transesterification process is the production of glycerol. For every 1 tonne of biodiesel that is manufactured, 100 kg of glycerol are produced. Originally, there was a valuable market for the glycerol, which assisted the economics of the process as a whole. However, with the increase in global biodiesel production, the market price for this crude glycerol (containing 20% water and catalyst residues) has crashed. Research is being conducted globally to use this glycerol as a chemical building block. One initiative in the UK is The Glycerol Challenge.

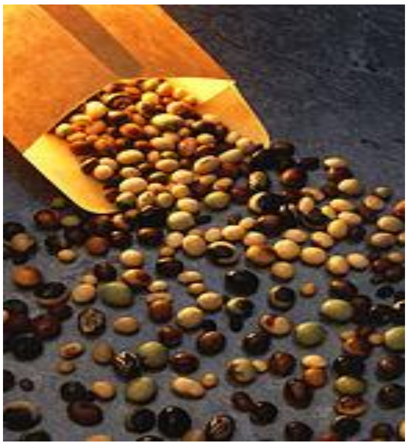
Usually this crude glycerol has to be purified, typically by performing vacuum distillation. This is rather energy intensive. The refined glycerol (98 % + purity) can then be utilized directly, or converted into other products. The following announcements were made in 2007: A joint venture of Ashland Inc. and Cargill announced plans to make propylene glycol in Europe from glycerol and Dow Chemical announced similar plans for North America. Dow also plans to build a plant in China to make epichlorhydrin from glycerol. Epichlorhydrin is a raw material for epoxy resins.

10 – 1 - Production levels

In 2007, biodiesel production capacity was growing rapidly, with an average annual growth rate from 2002 - 06 of over 40%.[49] For the year 2006, the latest for which actual production figures could be obtained, total world biodiesel production was about 5-6 million tonnes, with 4.9 million tonnes processed in Europe (of which 2.7 million tones was from Germany) and most of the rest from the USA. In 2008 production in Europe alone had risen to 7.8 million tonnes.[50] In July 2009, a duty was added to American imported biodiesel in the European Union in order to balance the competition from European, especially German producers . The capacity for 2008 in Europe totaled 16 million tones. This compares with a total demand for diesel in the US and Europe of approximately 490 million tonnes (147 billion gallons).[53] Total world production of vegetable oil for all purposes in 2005/06 was about 110 million tones, with about 34 million tones each of palm oil and soybean oil.

US biodiesel production in 2011 brought the industry to a new milestone. Under the EPA Renewable Fuel Standard, targets have been implemented for the biodiesel production plants in order to monitor and document production levels in comparison to total demand. According to the year-end data released by the EPA, biodiesel production in 2011 reached more than 1 billion gallons. This production number far exceeded the 800 million gallon target set by the EPA. The projected production for 2020 is nearly 12 billion gallons.

10 – 2 - Biodiesel feed stocks



Soybeans are used as a source of biodiesel

A variety of oils can be used to produce biodiesel. These include :

* Virgin oil feed stock – rapeseed and soybean oils are most commonly used, soybean oil accounting for about half of U.S. production . It also can be obtained from Pongamia, field pennycress and jatropha and other crops such as mustard, jojoba, flax, sunflower, palm oil, coconut, hemp (see list of vegetable oils for biofuel for more information);

* Waste vegetable oil (WVO) ;

* Animal fats including tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil.

* Algae, which can be grown using waste materials such as sewage and without displacing land currently used for food production.

* Oil from halophytes such as *Salicornia bigelovii*, which can be grown using saltwater in coastal areas where conventional crops cannot be grown, with yields equal to the yields of soybeans and other oilseeds grown using freshwater irrigation]

* Sewage Sludge - The sewage – to - biofuel field is attracting interest from major companies like Waste Management and startups

like InfoSpi, which are betting that renewable sewage biodiesel can become competitive with petroleum diesel on price.

* Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating in the world, this local solution could not scale to the current rate of consumption.

* Animal fats are a by-product of meat production and cooking. Although it would not be efficient to raise animals (or catch fish) simply for their fat, use of the by-product adds value to the livestock industry (hogs, cattle, poultry). Today, multi-feedstock biodiesel facilities are producing high quality animal-fat based biodiesel. Currently, a 5-million dollar plant is being built in the USA, with the intent of producing 11.4 million litres (3 million gallons) biodiesel from some of the estimated 1 billion kg (2.2 billion pounds) of chicken fat produced annually at the local Tyson poultry plant.[57] Similarly, some small-scale biodiesel factories use waste fish oil as feedstock. An EU- funded project (ENERFISH) suggests that at a Vietnamese plant to produce biodiesel from catfish (basa, also known as pangasius), an output of 13 tons/day of biodiesel can be produced from 81 tons of fish waste (in turn resulting from 130 tons of fish). This project utilizes the biodiesel to fuel a CHP unit in the fish processing plant, mainly to power the fish freezing plant.

10 – 2 - 1 - Quantity of feed stocks required

Current worldwide production of vegetable oil and animal fat is not sufficient to replace liquid fossil fuel use. Furthermore, some object to the vast amount of farming and the resulting fertilization, pesticide use, and land use conversion that would be needed to produce the additional vegetable oil. The estimated transportation diesel fuel and home heating oil used in the United States is about 160 million tons (350 billion pounds) according to the Energy Information Administration, US Department of Energy.[65] In the United States, estimated production of vegetable oil for all uses is about 11 million tons (24 billion pounds) and estimated production of animal fat is 5.3 million tonnes (12 billion pounds).

If the entire arable land area of the USA (470 million acres, or 1.9 million square kilometers) were devoted to biodiesel production from soy, this would just about provide the 160 million tonnes required (assuming an optimistic 98 US gal/acre of biodiesel). This land area could in principle be reduced significantly using algae, if the obstacles can be overcome. The US DOE estimates that if algae fuel replaced all the petroleum fuel in the United States, it would require 15,000 square miles (38,849 square kilometers), which is a few thousand square miles larger than Maryland, or 30 % greater than the area of Belgium , assuming a yield of 140 tones / hectare (15,000 US gal/acre). Given a more realistic yield of 36 tones / hectare the area required is about 152,000 square kilometers, or roughly equal to that of the state of Georgia or of England and Wales. The advantages of algae are that it can be grown on non-arable land such as deserts or in marine environments, and the potential oil yields are much higher than from plants.

10 - 3 - Yield

Feed stock yield efficiency per unit area affects the feasibility of ramping up production to the huge industrial levels required to power a significant percentage of vehicles.

Crop	**Yield L / ha**
Chinese tallow	907
Palm oil	4752
Coconut	2151
Rape seed	954
Soy (Indiana)	554 - 922
Peanut	842
Sun flower	767
Hemp	242

Algae fuel yields have not yet been accurately determined, but DOE is reported as saying that algae yield 30 times more energy per acre than land crops such as soybeans . Yields of 36 tones/hectare are considered practical by Ami Ben-Amotz of the Institute of

Oceanography in Haifa, who has been farming Algae commercially for over 20 years.

Jatropha has been cited as a high-yield source of biodiesel but yields are highly dependent on climatic and soil conditions. The estimates at the low end put the yield at about 200 US gal/acre (1.5-2 tonnes per hectare) per crop; in more favorable climates two or more crops per year have been achieved. It is grown in the Philippines, Mali and India, is drought-resistant, and can share space with other cash crops such as coffee, sugar, fruits and vegetables.[73] It is well-suited to semi-arid lands and can contribute to slow down desertification, according to its advocates.

10 - 4 - Efficiency and economic arguments

According to a study by Drs. Van Dyne and Raymer for the Tennessee Valley Authority, the average US farm consumes fuel at the rate of 82 liters per hectare of land to produce one crop. However, average crops of rapeseed produce oil at an average rate of 1,029 L / ha . and high-yield rapeseed fields produce about 1,356 L / ha . The ratio of input to output in these cases is roughly 1:12.5 and 1:16.5. Photosynthesis is known to have an efficiency rate of about 3-6% of total solar radiation and if the entire mass of a crop is utilized for energy production, the overall efficiency of this chain is currently about 1 % While this may compare unfavorably to solar cells combined with an electric drive train, biodiesel is less costly to deploy (solar cells cost approximately US $ 250 per square meter) and transport (electric vehicles require batteries which currently have a much lower energy density than liquid fuels). A 2005 study found that biodiesel production using soybeans required 27 % more fossil energy than the biodiesel produced and 118 % more energy using sunflowers.

However, these statistics by themselves are not enough to show whether such a change makes economic sense. Additional factors must be taken into account, such as: the fuel equivalent of the energy required for processing, the yield of fuel from raw oil, the return on cultivating food, the effect biodiesel will have on food prices and the relative cost of biodiesel versus petrodiesel, water pollution from farm run-off, soil depletion' ' and the externalized costs of political and military interference in oil - producing countries intended to control the price of petro diesel.

The debate over the energy balance of biodiesel is ongoing. Transitioning fully to biofuels could require immense tracts of land if traditional food crops are used (although non food crops can be utilized). The problem would be especially severe for nations with large economies, since energy consumption scales with economic output.

If using only traditional food plants, most such nations do not have sufficient arable land to produce biofuel for the nation's vehicles. Nations with smaller economies (hence less energy consumption) and more arable land may be in better situations, although many regions cannot afford to divert land away from food production.

For third world countries, biodiesel sources that use marginal land could make more sense; e.g., honge oil nuts grown along roads or jatropha grown along rail lines.

In tropical regions, such as Malaysia and Indonesia, plants that produce palm oil are being planted at a rapid pace to supply growing biodiesel demand in Europe and other markets. Scientists have shown that the removal of rainforest for palm plantations is not ecologically sound since the expansion of oil palm plantations poses a threat to natural rainforest and biodiversity.

It has been estimated in Germany that palm oil biodiesel has less than one third of the production costs of rapeseed biodiesel.[81] The direct source of the energy content of biodiesel is solar energy captured by plants during photosynthesis. Regarding the positive energy balance of biodiesel

When straw was left in the field, biodiesel production was strongly energy positive, yielding 1 GJ biodiesel for every 0.561 GJ of energy input (a yield/cost ratio of 1.78).

When straw was burned as fuel and oilseed rapemeal was used as a fertilizer, the yield/cost ratio for biodiesel production was even better (3.71). In other words, for every unit of energy input to produce biodiesel, the output was 3.71 units (the difference of 2.71 units would be from solar energy).

11 - Economic impact

Multiple economic studies have been performed regarding the economic impact of biodiesel production. One study, commissioned by the National Biodiesel Board, reported the 2011 production of biodiesel supported 39,027 jobs and more than 2.1 billion dollars in household income . The growth in biodiesel also helps significantly increase GDP. In 2011, biodiesel created more than 3 billion dollars in GDP. Judging by the continued growth in the Renewable Fuel Standard and the extension of the biodiesel tax incentive, the number of jobs can increase to 50,725, 2.7 billion dollars in income, and reaching 5 billion dollars in GDP by 2012 and 2013.

12 - Energy security

One of the main drivers for adoption of biodiesel is energy security. This means that a nation's dependence on oil is reduced, and substituted with use of locally available sources, such as coal, gas, or renewable sources. Thus a country can benefit from adoption of biofuels, without a reduction in greenhouse gas emissions. While the total energy balance is debated, it is clear that the dependence on oil is reduced. One example is the energy used to manufacture fertilizers, which could come from a variety of sources other than petroleum. The US National Renewable Energy Laboratory (NREL) states that energy security is the number one driving force behind the US biofuels programme,[83] and a White House "Energy Security for the 21st Century" paper makes it clear that energy security is a major reason for promoting biodiesel.[84] The EU commission president, Jose Manuel Barroso, speaking at a recent EU biofuels conference, stressed that properly managed biofuels have the potential to reinforce the EU's security of supply through diversification of energy sources.

13 - Environmental effects

The surge of interest in biodiesels has highlighted a number of environmental effects associated with its use. These potentially include reductions in greenhouse gas emissions , deforestation, pollution and the rate of biodegradation.

According to the EPA's Renewable Fuel Standards Program Regulatory Impact Analysis, released in February 2010, biodiesel from soy oil results, on average, in a 57 % reduction in greenhouse gases compared to petroleum diesel, and biodiesel produced from waste grease results in an 86 % reduction. See chapter 2.6 of the EPA report for more detailed information.

However, environmental organizations, for example, Rainforest Rescue and Greenpeace,[88] criticize the cultivation of plants used for biodiesel production, e.g., oil palms, soybeans and sugar cane. They say the deforestation of rainforests exacerbates climate change and that sensitive ecosystems are destroyed to clear land for oil palm, soybean and sugar cane plantations. Moreover, that biofuels contribute to world hunger, seeing as arable land is no longer used for growing foods. The Environmental Protection Agency(EPA) published data in January 2012, showing that biofuels made from palm oil won’t count towards the nation’s renewable fuels mandate as they are not climate - friendly . Environmentalists welcome the conclusion because the growth of oil palm plantations has driven tropical deforestation, for example, in Indonesia and Malaysia.

14 - Food , land and water vs. fuel

In some poor countries the rising price of vegetable oil is causing problems. Some propose that fuel only be made from non-edible vegetable oils such as camelina , jatropha or seashore mallow which can thrive on marginal agricultural land where many trees and crops will not grow, or would produce only low yields.

Others argue that the problem is more fundamental. Farmers may switch from producing food crops to producing biofuel crops to make more money, even if the new crops are not edible. The law of supply and demand predicts that if fewer farmers are producing food the price of food will rise. It may take some time, as farmers can take some time to change which things they are growing, but increasing demand for first generation biofuels is likely to result in price increases for many kinds of food. Some have pointed out that there are poor farmers and poor countries who are making more money because of the higher price of vegetable oil.

Biodiesel from sea algae would not necessarily displace terrestrial land currently used for food production and new algaculture jobs could be created.

15 - Current research

There is ongoing research into finding more suitable crops and improving oil yield. Other sources are possible including human fecal matter, with Ghana building its first "fecal sludge-fed biodiesel plant." [97] Using the current yields, vast amounts of land and fresh water would be needed to produce enough oil to completely replace fossil fuel usage. It would require twice the land area of the US to be devoted to soybean production, or two-thirds to be devoted to rapeseed production, to meet current US heating and transportation needs .

Specially bred mustard varieties can produce reasonably high oil yields and are very useful in crop rotation with cereals, and have the added benefit that the meal leftover after the oil has been pressed out can act as an effective and biodegradable pesticide.

The NFESC, with Santa Barbara - based Biodiesel Industries is working to develop biodiesel technologies for the US navy and military, one of the largest diesel fuel users in the world.

A group of Spanish developers working for a company called Ecofasa announced a new biofuel made from trash. The fuel is created from general urban waste which is treated by bacteria to produce fatty acids, which can be used to make biodiesel.

Another approach that does not require the use of chemical for the production involves the use of genetically modified microbes.

15 – 1 - Algal biodiesel

From 1978 to 1996, the U.S. NREL experimented with using algae as a biodiesel source in the "Aquatic Species Program".[83] A self-published article by Michael Briggs, at the UNH Biodiesel Group, offers estimates for the realistic replacement of all vehicular fuel with biodiesel by utilizing algae that have a natural oil content greater than 50 %, which Briggs suggests can be grown on algae ponds at waste water treatment plants . This oil - rich algae can then be extracted from the system and processed into biodiesel, with the dried remainder further reprocessed to create ethanol.

The production of algae to harvest oil for biodiesel has not yet been undertaken on a commercial scale, but feasibility studies have been conducted to arrive at the above yield estimate. In addition to its projected high yield, alga culture — unlike crop-based biofuels — does not entail a decrease in food production, since it requires neither farmland nor fresh water. Many companies are pursuing algae bio-reactors for various purposes, including scaling up biodiesel production to commercial levels.

15 – 2 - Pongamia

Pongamia pinnata is a leguminous, oil seed - bearing tree that has been identified as a candidate for non-edible vegetable oil production.

15 – 3 - Jatropha

Several groups in various sectors are conducting research on Jatropha curcas, a poisonous shrub-like tree that produces seeds considered by many to be a viable source of biodiesel feedstock oil. Much of this research focuses on improving the overall per acre oil yield of Jatropha through advancements in genetics, soil science, and horticultural practices.

SG Biofuels, a San Diego-based Jatropha developer, has used molecular breeding and biotechnology to produce elite hybrid seeds of Jatropha that show significant yield improvements over first generation varieties. SG Biofuels also claims that additional benefits have arisen from such strains, including improved flowering synchronicity, higher resistance to pests and disease, and increased cold weather tolerance.

Plant Research International, a department of the Wageningen University and Research Centre in the Netherlands, maintains an ongoing Jatropha Evaluation Project (JEP) that examines the feasibility of large scale Jatropha cultivation through field and laboratory experiments.

The Center for Sustainable Energy Farming (CfSEF) is a Los Angeles - based non - profit research organization dedicated to Jatropha research in the areas of plant science, agronomy, and horticulture. Successful exploration of these disciplines is projected to increase Jatropha farm production yields by 200 – 300 % in the next ten years.

15 – 4 - Fungi

A group at the Russian Academy of Sciences in Moscow published a paper in September 2008, stating that they had isolated large amounts of lipids from single-celled fungi and turned it into biodiesel in an economically efficient manner. More research on this fungal species; *Cunninghamella japonica*, and others, is likely to appear in the near future.

The recent discovery of a variant of the fungus *Gliocladium roseum* points toward the production of so - called myco - diesel from cellulose. This organism was recently discovered in the rainforests of northern Patagonia and has the unique capability of converting cellulose into medium length hydrocarbons typically found in diesel fuel.

15 – 6 - Biodiesel from used coffee grounds

Researchers at the University of Nevada, Reno, have successfully produced biodiesel from oil derived from used coffee grounds. Their analysis of the used grounds showed a 10 % to 15 % oil content (by weight). Once the oil was extracted, it underwent conventional processing into biodiesel. It is estimated that finished biodiesel could be produced for about one US dollar per gallon. Further, it was reported that "the technique is not difficult" and that "there is so much coffee around that several hundred million gallons of biodiesel could potentially be made annually." However, even if all the coffee grounds in the world were used to make fuel, the amount produced would be less than 1 percent of the diesel used in the United States annually. “It won’t solve the world’s energy problem,” Dr. Misra said of his work.

15 – 6 - Exotic sources

Recently, alligator fat was identified as a source to produce biodiesel. Every year, about 15 million pounds of alligator fat are disposed of in landfills as a waste byproduct of the alligator meat and skin industry. Studies have shown that biodiesel produced from alligator fat is similar in composition to biodiesel created from soybeans, and is cheaper to refine since it is primarily a waste product.

Bio Fuel

Information on pump regarding
ethanol fuel blend up to 10 %, California

Contents

1 – Introduction

A **biofuel** is a type of fuel whose energy is derived from bio logical carbon fixation. Bio fuels include fuels derived from bio mass conversion, as well as solid bio mass , liquid fuel sand various biogases. Bio fuels are gaining increased public and scientific attention, driven by factors such as oil price hikes and the need for increased energy security. However, according to the European Environment Agency, biofuels address global warming concerns only in specific cases.

Bioethanol is an alcohol made by fermentation, mostly from carbohydrates produced in sugar or starch crops such as corn or sugarcane . Cellulosic biomass, derived from non-food sources, such as trees and grasses, is also being developed as a feedstock for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil. Current plant design does not provide for converting the lignin portion of plant raw materials to fuel components by fermentation.

Biodiesel is made from vegetable oils and animal fats. Biodiesel can be used as a fuel for vehicles in its pure form, but it is usually used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. Biodiesel is produced from oils or fats using trans esterification and is the most common biofuel in Europe.

In 2010, worldwide biofuel production reached 105 billion liters (28 billion gallons US), up 17 % from 2009, and biofuels provided 2.7% of the world's fuels for road transport, a contribution largely made up of ethanol and biodiesel . Global ethanol fuel production reached 86 billion liters (23 billion gallons US) in 2010, with the United States and Brazil as the world's top producers, accounting together for 90 % of global production. The world's largest biodiesel producer is the European Union, accounting for 53 % of all biodiesel production in 2010.[3] As of 2011, mandates for blending biofuels exist in 31 countries at the national level and in 29 states or provinces. The International Energy Agencyhas a goal for biofuels to meet more than a quarter of world demand for transportation fuels by 2050 to reduce dependence on petroleum and coal.

2 - Liquid fuels for transportation

Most transportation fuels are liquids, because vehicles usually require high energy density, as occurs in liquids and solids. High power density can be provided most inexpensively by an internal combustion engine; these engines require clean-burning fuels, to keep the engine clean and minimize air pollution.

The fuels that are easiest to burn cleanly are typically liquids and gases. Thus, liquids (and gases that can be stored in liquid form) meet the requirements of being both portable and clean-burning. Also, liquids and gases can be pumped, which means handling is easily mechanized, and thus less laborious.

2 – 1 - First-generation biofuels

'First-generation' or conventional biofuels are made from sugar, starch, or vegetable oil.

2 – 1 – 1 - Bioalcohols

Biologically produced alcohols , most commonly ethanol , and less commonly propanol and butanol, are produced by the action of micro organisms and enzymes through the fermentation of sugars or starches (easiest), or cellulose (which is more difficult) . Biobutanol (also called bio gasoline) is often claimed to provide a direct replacement for gasoline, because it can be used directly in a gasoline engine (in a similar way to biodiesel in diesel engines).

Ethanol fuel is the most common biofuel worldwide, particularly in Brazil. Alcohol fuels are produced by fermentation of sugars derived from wheat, corn, sugar beets, sugar cane, molasses and any sugar or starch from which alcoholic beverages can be made (such as potato and fruit waste, etc.). The ethanol production methods used are enzyme digestion (to release sugars from stored starches), fermentation of the sugars, distillation and drying. The distillation process requires significant energy input for heat (often unsustainable natural gas fossil fuel, but cellulosic biomass such as bagasse, the waste left after sugar cane is pressed to extract its juice, can also be used more sustainably).

Ethanol can be used in petrol engines as a replacement for gasoline; it can be mixed with gasoline to any percentage. Most existing car petrol engines can run on blends of up to 15% bioethanol with petroleum/gasoline. Ethanol has a smaller energy density than that of gasoline; this means it takes more fuel (volume and mass) to produce the same amount of work. An advantage of ethanol (CH_3CH_2OH) is that it has a higher octane rating than ethanol-free gasoline available at roadside gas stations, which allows an increase of an engine's compression ratio for increasedthermal efficiency. In high-altitude (thin air) locations, some states mandate a mix of gasoline and ethanol as a winter oxidizer to reduce atmospheric pollution emissions.

Ethanol is also used to fuel bioethanol fireplaces. As they do not require a chimney and are "flueless", bioethanol fires are extremely useful for newly built homes and apartments without a flue. The downside to these fireplaces is their heat output is slightly less than electric heat or gas fires.

In the current corn-to-ethanol production model in the United States, considering the total energy consumed by farm equipment, cultivation, planting , fertilizers , pesticides , herbicides , and fungicides made from petroleum, irrigation systems, harvesting, transport of feed stock to processing plants, fermentation, distillation, drying, transport to fuel terminals and retail pumps, and lower ethanol fuel energy content, the net energy content value added and delivered to consumers is very small. And, the net benefit (all things considered) does little to reduce imported oil and fossil fuels required to produce the ethanol.

Although corn - to - ethanol and other food stocks have implications both in terms of world food prices and limited, yet positive, energy yield (in terms of energy delivered to customer/fossil fuels used), the technology has led to the development of cellulosic ethanol. According to a joint research agenda conducted through the US Department of Energy,[8] the fossil energy ratios (FER) for cellulosic ethanol, corn ethanol, and gasoline are 10.3, 1.36, and 0.81, respectively.

Even dry ethanol has roughly one-third lower energy content per unit of volume compared to gasoline, so larger (therefore heavier) fuel tanks are required to travel the same distance, or more fuel stops are required. With large current unsustainable, un scalable subsidies, ethanol fuel still costs more per distance traveled than current high gasoline prices in the United States.

Methanol is currently produced from natural gas, a non renew able fossil fuel. It can also be produced from biomass as biomethanol. The methanol economy is an alternative to the hydrogen economy, compared to day's hydrogen production from natural gas.

Butanol (C_4H_9OH) is formed by ABE fermentation(acetone, butanol, ethanol) and experimental modifications of the process show potentially high net energy gains with butanol as the only liquid product. Butanol will produce more energy and allegedly can be burned "straight" in existing gasoline engines (without modification to the engine or car), and is less corrosive and less water-soluble than ethanol, and could be distributed via existing infrastructures . DuPont and BP are working together to help develop butanol. *E. coli* strains have also been successfully engineered to produce butanol by hijacking their amino acid metabolism.

2 – 1 – 2 – Biodiesel

Biodiesel is the most common biofuel in Europe. It is produced from oils or fats using trans esterification and is a liquid similar in composition to fossil/mineral diesel. Chemically, it consists mostly of fatty acid methyl (or ethyl) esters (FAMEs). Feed stocks for biodiesel include animal fats, vegetable oils , soy ,rapeseed , jatropha , mahua , mustard, flax, sunflower, palm oil , hemp, field pennycress , *Pongamia pinnata* and algae. Pure biodiesel (B100) is the lowest-emission diesel fuel. Although liquefied petroleum gas and hydrogen have cleaner combustion, they are used to fuel much less efficient petrol engines and are not as widely available.

Biodiesel can be used in any diesel engine when mixed with mineral diesel. In some countries, manufacturers cover their diesel engines under warranty for B100 use, although Volkswagen of Germany , for example, asks drivers to check by telephone with the VW environmental services department before switching to B100. B100 may become more viscous at lower temperatures, depending on the feedstock used. In most cases, biodiesel is compatible with diesel engines from 1994 onwards, which use 'Viton' (by DuPont) synthetic rubber in their mechanical fuel injection systems.

Electronically controlled 'common rail' and 'unit injector' type systems from the late 1990s onwards may only use biodiesel blended with conventional diesel fuel. These engines have finely metered and atomized multiple-stage injection systems that are very sensitive to the viscosity of the fuel. Many current-generation diesel engines are made so that they can run on B100 without altering the engine itself, although this depends on the fuel rail design. Since biodiesel is an effective solvent and cleans residues deposited by mineral diesel, engine filters may need to be replaced more often, as the biofuel dissolves old deposits in the fuel tank and pipes. It also effectively cleans the engine combustion chamber of carbon deposits, helping to maintain efficiency. In many European countries, a 5% biodiesel blend is widely used and is available at thousands of gas stations.[15][16] Biodiesel is also an oxygenated fuel, meaning it contains a reduced amount of carbon and higher hydrogen and oxygen content than fossil diesel. This improves the combustion of biodiesel and reduces the particulate emissions from un burnt carbon.

Biodiesel is also safe to handle and transport because it is as biodegradable as sugar, one-tenth as toxic as table salt, and has a high flash point of about 148°C compared to petroleum diesel fuel, which has a flash point of 52°C .

In the USA, more than 80 % of commercial trucks and city buses run on diesel. The emerging US biodiesel market is estimated to have grown 200 % from 2004 to 2005.

2 – 1 – 3 - Green diesel

Green diesel is produced through hydro cracking biological oil feed stocks, such as vegetable oils and animal fats. Hydro cracking is a refinery method that uses elevated temperatures and pressure in the presence of a catalyst to break down larger molecules, such as those found in vegetable oils, into shorter hydrocarbon chains used in diesel engines. It may also be called renewable diesel, hydro treated vegetable oil or hydrogen - derived renewable diesel. Green diesel has the same chemical properties as petroleum-based diesel. It does not require new engines, pipelines or infrastructure to distribute and use, but has not been produced at a cost that is competitive with petroleum. Gasoline versions are also being developed. Green diesel is being developed in Louisiana and Singapore by Conoco Phillips ,Neste Oil , Valero, Dynamic Fuels, and Honey well UOP.

2 – 1 – 4 - Vegetable oil

Straight un modified edible vegetable oil is generally not used as fuel, but lower-quality oil can and has been used for this purpose. Used vegetable oil is increasingly being processed into biodiesel, or (more rarely) cleaned of water and particulates and used as a fuel.

Also here, as with 100% biodiesel (B100), to ensure the fuel injectors atomize the vegetable oil in the correct pattern for efficient combustion , vegetable oil fuel must be heated to reduce its viscosity to that of diesel, either by electric coils or heat exchangers. This is easier in warm or temperate climates. Big corporations like MAN B&W Diesel, Wärtsilä , and Deutz AG, as well as a number of smaller companies, such as Elsbett, offer engines that are compatible with straight vegetable oil, without the need for after-market modifications.

Vegetable oil can also be used in many older diesel engines that do not use common rail or unit injection electronic diesel injection systems. Due to the design of the combustion chambers in indirect injection engines, these are the best engines for use with vegetable oil. This system allows the relatively larger oil molecules more time to burn. Some older engines, especially Mercedes, are driven experimentally by enthusiasts without any conversion, a handful of drivers have experienced limited success with earlier pre-"Pumpe Duse" VW TDI engines and other similar engines with direct injection. Several companies, such as Elsbett or Wolf, have developed professional conversion kits and successfully installed hundreds of them over the last decades.

Oils and fats can be hydrogenated to give a diesel substitute. The resulting product is a straight - chain hydrocarbon with a high cetane number, low in aromatics and sulfur and does not contain oxygen. Hydrogenated oilscan be blended with diesel in all proportions. They have several advantages over biodiesel, including good performance at low temperatures, no storage stability problems and no susceptibility to microbial attack.

2 – 1 – 5 - Bioethers

Bioethers (also referred to as fuel ethers or oxygenated fuels) are cost-effective compounds that act as octane rating enhancers. They also enhance engine performance, whilst significantly reducing engine wear and toxic exhaust emissions. Greatly reducing the amount of ground – level ozone , they contribute to air quality.

2 – 1 – 6 - Biogas

Biogas is methane produced by the process of anaerobic digestion of organic material by anaerobes. It can be produced either from biodegradable waste materials or by the use of energy crops fed into anaerobic digesters to supplement gas yields. The solid by product , dig estate , can be used as a biofuel or a fertilizer.

Biogas can be recovered from mechanical biological treatment waste processing systems.

Note :Land fill gas, a less clean form of biogas, is produced in land fills through naturally occurring anaerobic digestion. If it escapes into the atmosphere, it is a potential green house gas.

Farmers can produce biogas from manure from their cattle by using anaerobic digesters.

2 – 1 – 7 - Syngas

Syngas, a mixture of carbon monoxide, hydrogen and other hydrocarbons, is produced by partial combustion of biomass, that is, combustion with an amount of oxygen that is not sufficient to convert the biomass completely to carbon dioxide and water. Before partial combustion, the biomass is dried, and sometimes pyrolysed. The resulting gas mixture, syngas, is more efficient than direct combustion of the original biofuel; more of the energy contained in the fuel is extracted.

Syngas may be burned directly in internal combustion engines, turbines or high-temperature fuel cells.[29]The wood gas generator, a wood-fueled gasification reactor, can be connected to an internal combustion engine.

Syngas can be used to produce methanol, DME and hydrogen , or converted via the Fischer-Tropsch process to produce a diesel substitute, or a mixture of alcohols that can be blended into gasoline. Gasification normally relies on temperatures greater than 700°C.

Lower - temperature gasification is desirable when co - producing biochar , but results in syngas polluted with tar .

2 – 1 – 8 - Solid biofuels

Examples include wood, sawdust, grass trimmings , domestic refuse , charcoal, agricultural waste, non food energy crops, and dried manure.

When raw biomass is already in a suitable form (such as fire wood), it can burn directly in a stove or furnace to provide heat or raise steam. When raw biomass is in an inconvenient form (such as sawdust, wood chips, grass, urban waste wood, agricultural residues), the typical process is to densify the biomass. This process includes grinding the raw biomass to an appropriate particulate size (known as hogfuel), which, depending on the densification type, can be from 1 to 3 cm (0 to 1 in), which is then concentrated into a fuel product. The current processes produce wood pellets, cubes, or pucks. The pellet process is most common in Europe, and is typically a pure wood product. The other types of densification are larger in size compared to a pellet, and are compatible with a broad range of input feed stocks. The resulting densified fuel is easier to transport and feed into thermal generation systems, such as boilers.

One of the advantages of solid biomass fuel is that it is often a byproduct, residue or waste-product of other processes, such as farming, animal husbandry and forestry.[30] In theory, this means fuel and food production do not compete for resources, although this is not always the case.

A problem with the combustion of raw biomass is that it emits considerable amounts of pollutants, such as particulates and polycyclic aromatic hydrocarbons. Even modern pellet boilers generate much more pollutants than oil or natural gas boilers. Pellets made from agricultural residues are usually worse than wood pellets, producing much larger emissions of dioxins and chloro phenols.

Not with standing the above noted study, numerous studies have shown biomass fuels have significantly less impact on the environment than fossil based fuels. Of note is the US Department of Energy Laboratory, operated by Midwest Research Institute Biomass Power and Conventional Fossil Systems with and without CO2 Sequestration – Comparing the Energy Balance ,Green house Gas Emissions and Economics Study. Power generation emits significant amounts of greenhouse gases (GHGs), mainly carbon dioxide (CO_2). Sequestering CO_2 from the power plant flue gas can significantly reduce the GHGs from the power plant itself, but this is not the total picture. CO_2 capture and sequestration consumes additional energy, thus lowering the plant's fuel-to-electricity efficiency. To compensate for this, more fossil fuel must be procured and consumed to make up for lost capacity.

Taking this into consideration, the global warming potential (GWP) , which is a combination of CO_2, methane (CH_4), and nitrous oxide (N_2O) emissions, and energy balance of the system need to be examined using a life cycle assessment. This takes into account the upstream processes which remain constant after CO_2 sequestration, as well as the steps required for additional power generation. Firing biomass instead of coal led to a 148 % reduction in GWP.

A derivative of solid biofuel is biochar, which is produced by biomass pyrolysis. Biochar made from agricultural waste can substitute for wood charcoal. As wood stock becomes scarce, this alternative is gaining ground. In eastern Democratic Republic of Congo, for example, biomass briquettes are being marketed as an alternative to charcoal to protect Virunga National Park from de fore station associated with charcoal production.

2 – 2 – Second - generation (advanced) biofuels

Second - generation biofuels are produced from sustainable feed stock. Sustainability of a feed stock is defined, among others, by availability of the feedstock, impact on GHGe missions, and impact on biodiversity and land use. Many second-generation biofuels are under development such as Cellulosic ethanol , Algae fuel ., Bio hydrogen , biomethanol , DMF, BioDME, Fischer-Tropsch diesel, Bio hydrogen diesel, mixed alcohols and wood diesel.

Cellulosic ethanol production uses nonfood crops or inedible waste products and does not divert food away from the animal or human food chain. Ligno cellulose is the "woody" structural material of plants. This feedstock is abundant and diverse, and in some cases (like citrus peels or sawdust) it is in itself a significant disposal problem.

Producing ethanol from cellulose is a difficult technical problem to solve. In nature, ruminant livestock (such ascattle) eat grass and then use slow enzymatic digestive processes to break it into glucose (sugar). In cellulosic ethanol laboratories, various experimental processes are being developed to do the same thing, and then the sugars released can be fermented to make ethanol fuel. In 2009, scientists reported developing, using "synthetic biology", "15 new highly stable fungal enzyme catalysts that efficiently break down cellulose into sugars at high temperatures", adding to the 10 previously known.[35] The use of high temperatures has been identified as an important factor in improving the overall economic feasibility of the biofuel industry and the identification of enzymes that are stable and can operate efficiently at extreme temperatures is an area of active research. In addition, research conducted at Delft University of Technology by Jack Pronk has shown that elephant yeast, when slightly modified, can also produce ethanol from inedible ground sources (e.g. straw).

The recent discovery of the fungus *Gliocladium roseum*points toward the production of so-called my co-diesel from cellulose. This organism (recently discovered in rainforests of northern Patagonia) has the unique capability of converting cellulose into medium-length hydrocarbons typically found in diesel fuel. Scientists also work on experimental recombinant DNA genetic engineering organisms that could increase biofuel potential.

Scientists working with the New Zealand company Lanzatech have developed a technology to use industrial waste gases, such as carbon monoxide from steel mills, as a feedstock for a microbial fermentation process to produce ethanol. In October 2011, Virgin Atlantic announced it was joining with Lanzatech to commission a demonstration plant in Shanghai that would produce an aviation fuel from waste gases from steel production.

Scientists working in Minnesota have developed co-cultures of *Shewanella* and *Synechococcus* that produce long - chain hydrocarbons directly from water, carbon dioxide, and sunlight. The technology has receivedARPA-E funding.

3 - Biofuels by region

There are international organizations such as IEA Bioenergy , established in 1978 by the OECD International Energy Agency (IEA), with the aim of improving cooperation and information exchange between countries that have national programs in bioenergy research, development and deployment. The UN International Biofuels Forum is formed by Brazil , China , India , Pakistan , South Africa, the United States and theEuropean Commission.[45] The world leaders in biofuel development and use are Brazil, the United States, France, Sweden and Germany. Russia also has 22% of world's forest,[46] and is a big biomass (solid biofuels) supplier. In 2010, Russian pulp and paper maker, Vyborgskaya Cellulose, said they would be producing pellets that can be used in heat and electricity generation from its plant in Vyborg by the end of the year. The plant will eventually produce about 900,000 tons of pellets per year, making it the largest in the world once operational.

Biofuels currently make up 3.1 % of the total road transport fuel in the UK or 1,440 million litres. By 2020, 10 % of the energy used in UK road and rail transport must come from renewable sources – this is the equivalent of replacing 4.3 million tones of fossil oil each year. Conventional biofuels are likely to produce between 3.7 and 6.6% of the energy needed in road and rail transport, while advanced biofuels could meet up to 4.3 % of the UK's renewable transport fuel target by 2020.

4 - Issues with biofuel production and use

There are various social, economic, environmental and technical issues with biofuel production and use, which have been discussed in the popular media and scientific journals. These include: the effect of moderating oil prices, the "food vs fuel" debate, poverty reduction potential , carbon emissions levels, sustainable biofuel production , de fore station and soil erosion, loss of biodiversity, and impact on water resources, as well as energy balance and efficiency. The International Resource Panel, which provides independent scientific assessments and expert advice on a variety of resource-related themes, assessed the issues relating to biofuel use in its first report, *Towards sustainable production and use of resources: Assessing Biofuels* . The report outlined the wider and interrelated factors that need to be considered when deciding on the relative merits of pursuing one biofuel over another. It concluded not all biofuels perform equally in terms of their impact on climate, energy security, and ecosystems, and suggested environmental and social impacts need to be assessed throughout the entire life-cycle.

Although many current issues are noted with biofuel production and use, the development of new biofuel crops and second - generation biofuels attempts to circumvent these issues. Many scientists and researchers are working to develop biofuel crops that require less land and use fewer resources, such as water, than current biofuel crops do. According to the journal *Renewable fuels from algae: An answer to debatable land based fuels*, algae are a source for biofuels that could use currently unprofitable land and wastewater from different industries. Algae are able to grow in wastewater, which does not affect the land or freshwater needed to produce current food and fuel crops. Furthermore, algae are not part of the human food chain, so do not take away food resources from humans.

The effects of the biofuel industry on food are still being debated. According to a recent study, biofuel production accounted for 3 - 30 % of the increase in food prices in 2008. A recent study for the International Centre for Trade and Sustainable Development shows market-driven expansion of ethanol in the US increased corn prices by 21 % in 2009, in comparison with what prices would have been had ethanol production been frozen at 2004 levels. This has prompted researchers to develop biofuel crops and technologies that will reduce the impact of the growing biofuel industry on food production and cost.

One step to overcoming these issues is developing biofuel crops best suited to each region of the world. If each region used a specific biofuel crop, the need to use fossil fuels to transport the fuel to other places for processing and consumption will be diminished. Furthermore, certain areas of the globe are unsuitable for producing crops that require large amounts of water and nutrient-rich soil. Therefore, current biofuel crops, such as corn, are unpractical in different environments and regions of the globe.

In 2012, the United States House Committee on Armed Services put language into the 2013 National Defense Authorization Act that would prevent the Pentagon from purchasing biofuels that offered improved performance for combat aircraft.

5 - Current research

Research is ongoing into finding more suitable biofuel crops and improving the oil yields of these crops. Using the current yields, vast amounts of land and fresh water would be needed to produce enough oil to completely replace fossil fuel usage. It would require twice the land area of the US to be devoted to soybean production, or two-thirds to be devoted to rapeseed production, to meet current US heating and transportation needs .

Specially bred mustard varieties can produce reasonably high oil yields and are very useful in crop rotation with cereals, and have the added benefit that the meal leftover after the oil has been pressed out can act as an effective and biodegradable pesticide.

The NFESC, with Santa Barbara - based Biodiesel Industries, is working to develop biofuels technologies for the US navy and military, one of the largest diesel fuel users in the world . A group of Spanish developers working for a company called Ecofasa announced a new biofuel made from trash. The fuel is created from general urban waste which is treated by bacteria to produce fatty acids, which can be used to make biofuels.

5 – 1 – Ethanol biofuels

As the primary source of biofuels in North America, many organizations are conducting research in the area of ethanol production. The National Corn - to - Ethanol Research Center (NCERC) is a research division of Southern Illinois University Edwardsville dedicated solely to ethanol - based biofuel research projects . On the federal level, the USDA conducts a large amount of research regarding ethanol production in the United States. Much of this research is targeted toward the effect of ethanol production on domestic food markets. A division of the U.S. Department of Energy, the National Renewable Energy Laboratory (NREL), has also conducted various ethanol research projects, mainly in the area of cellulosic ethanol.

5 – 2 – Algal biofuels

From 1978 to 1996, the US NREL experimented with using algae as a biofuels source in the "Aquatic Species Program".[61] A self-published article by Michael Briggs, at the UNH Biofuels Group, offers estimates for the realistic replacement of all vehicular fuel with biofuels by using algae that have a natural oil content greater than

50%, which Briggs suggests can be grown on algae ponds atwaste water treatment plants. This oil-rich algae can then be extracted from the system and processed into biofuels, with the dried remainder further reprocessed to create ethanol. The production of algae to harvest oil for biofuels has not yet been undertaken on a commercial scale, but feasibility studies have been conducted to arrive at the above yield estimate. In addition to its projected high yield, alga culture — unlike crop - based biofuels — does not entail a decrease in food production, since it requires neither farmland nor fresh water. Many companies are pursuing algae bioreactors for various purposes, including scaling up biofuels production to commercial levels. Prof. Rodrigo E. Teixeira from the University of Alabama in Huntsville demonstrated the extraction of biofuels lipids from wet algae using a simple and economical reaction in ionic liquids.

5 – 3 – Jatropha

Several groups in various sectors are conducting research on *Jatropha curcas*, a poisonous shrub-like tree that produces seeds considered by many to be a viable source of biofuels feedstock oil. Much of this research focuses on improving the overall per acre oil yield of Jatropha through advancements in genetics, soil science, and horticultural practices.

SG Biofuels, a San Diego - based jatropha developer, has used molecular breeding and biotechnology to produce elite hybrid seeds that show significant yield improvements over first-generation varieties. SG Biofuels also claims additional benefits have arisen from such strains, including improved flowering synchronicity, higher resistance to pests and diseases, and increased cold-weather tolerance.

Plant Research International, a department of theWageningen University and Research Centre in the Netherlands, maintains an ongoing Jatropha Evaluation Project that examines the feasibility of large - scale jatropha cultivation through field and laboratory experiments. The Center for Sustainable Energy Farming (CfSEF) is a Los Angeles-based nonprofit research organization dedicated to jatropha research in the areas of plant science, agronomy, and horticulture. Successful exploration of these disciplines is projected to increase jatropha farm production yields by 200 - 300 % in the next 10 years.

5 – 3 – Fungi

A group at the Russian Academy of Sciences in Moscow, in a 2008 paper, stated they had isolated large amounts of lipids from single - celled fungi and turned it into biofuels in an economically efficient manner. More research on this fungal species, *Cunninghamella japonica*, and others, is likely to appear in the near future. The recent discovery of a variant of the fungus *Gliocladium roseum* points toward the production of so-called myco - diesel from cellulose. This organism was recently discovered in the rainforests of northern Patagonia, and has the unique capability of converting cellulose into medium-length hydrocarbons typically found in diesel fuel.

6 - Green house gas emissions

According to Britain's National Non - Food Crops Centre, total net savings from using first-generation biodiesel as a transport fuel range from 25 - 82 % (depending on the feedstock used), compared to diesel derived from crude oil . Nobel Laureate Paul Crutzen, however, finds that the emissions of nitrous oxide due to nitrate fertilisers is seriously underestimated, and tips the balance such that most biofuels produce more greenhouse gases than the fossil fuels they replace. Producing ligno cellulosic biofuels offers potentially greater greenhouse gas emissions savings than those obtained by first-generation biofuels. Ligno cellulosic biofuels are predicted by oil industry body CONCAWE [1] to reduce greenhouse gas emissions by around 90 % when compared with fossil petroleum, in contrast first generation biofuels were found to offer savings of 20 – 70 %

Some scientists have expressed concerns about land-use change in response to greater demand for crops to use for biofuel and the subsequent carbon emissions . The payback period, that is, the time it will take biofuels to pay back the carbon debt they acquire due to land-use change, has been estimated to be between 100 and 1000 years, depending on the specific instance and location of land-use change. However, no-till practices combined with cover-crop practices can reduce the payback period to three years for grassland conversion and 14 years for forest conversion.[76] Biofuels made from waste biomass or from biomass grown on abandoned agricultural lands incur little to no carbon debt.

Biomass planting mandated by law (as in European Union) is causing concerns over raising food prices[78] and actual emissions reductions, as large quantities of biomass are being transported to the EU from Africa, Asia, and the Americas (Canada, USA, Brazil). For example in Poland, as much as 85% of biomass used is imported from outside of the EU, with a single electric plant in Łódź importing over 7000 tons of wood biomass from the Republic of Komi (Russia) over distance of 7000 kilometers on monthly basis.

Biogas

Contents

1 - Introduction

Biogas typically refers to a gas produced by the breakdown of organic matter in the absence of oxygen. It is a renewable energy source, like solar and wind energy. Furthermore, biogas can be produced from regionally available raw materials and recycled waste and is environmentally friendly and CO_2 neutral.

Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials such as manure, sewage, municipal waste, green waste, plant material, and crops.[1] Biogas comprises primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulphide (H_2S), moisture and siloxanes.

The gases methane, hydrogen, and carbon monoxide (CO) can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel. Biogas can be used as a fuel in any country for any heating purpose, such as cooking. It can also be used in anaerobic digesters where it is typically used in a gas engine to convert the energy in the gas into electricity and heat. Biogas can be compressed, much like natural gas, and used to power motor vehicles. In the UK, for example, biogas is estimated to have the potential to replace around 17 % of vehicle fuel.[3] Biogas is a renewable fuel so it qualifies for renewable energy subsidies in some parts of the world. Biogas can also be cleaned and upgraded to natural gas standards when it becomes bio methane.

2 - Production

Biogas production in rural Germany

Bio gas is practically produced as landfill gas (LFG) or digested gas. A *bio gas plant* is the name often given to an anaerobic digester that treats farm wastes or energy crops. Bio gas can be produced using anaerobic digesters. These plants can be fed with energy crops such as maize silage or biodegradable wastes including sewage sludge and food waste. During the process, as an air-tight tank transforms biomass waste into methane producing renewable energy that can be used for heating, electricity, and many other operations that use any variation of an internal combustion engine, such as GE Jenbacher gas engines. There are two key processes: Mesophilic and Thermophilic digestion. In experimental work at University of Alaska Fairbanks, a 1000 - litre digester using psychrophiles harvested from "mud from a frozen lake in Alaska" has produced 200 – 300 liters of methane per day, about 20–30% of the output from digesters in warmer climates.[6] Landfill gas is produced by wet organic waste decomposing under anaerobic conditions in a landfill. The waste is covered and mechanically compressed by the weight of the material that is deposited from above. This material prevents oxygen exposure thus allowing anaerobic microbes to thrive. This gas builds up and is slowly released into the atmosphere if the landfill site has not been engineered to capture the gas. Landfill gas is hazardous for three key reasons. Landfill gas becomes explosive when it escapes from the landfill and mixes with oxygen. The lower explosive limit is 5% methane and the upper explosive limit is 15% methane.[9] The methane contained within biogas is 20 times more potent as a greenhouse gas than is carbon dioxide. Therefore, uncontained landfill gas, which escapes into the atmosphere may significantly contribute to the effects of global warming. In addition, landfill gas impact in global warming, volatile organic compounds (VOCs) contained within landfill gas contribute to the formation of photochemical smog.

3 - Composition

Typical composition of biogas

Compound	Molecular formula	%
Methane	CH_4	50 – 75
Carbon dioxide	CO_2	25 – 50
Nitrogen	N_2	0 – 10
Hydrogen	H_2	0 – 1
Hydrogen sulphide	H_2S	0 – 3
Oxygen	O_2	0 – 0

The composition of biogas varies depending upon the origin of the anaerobic digestion process. Landfill gas typically has methane concentrations around 50 %. Advanced waste treatment technologies can produce biogas with 55 – 75 % methane, which for reactors with free liquids can be increased to 80 - 90 % methane using in-situ gas purification techniques As - produced, biogas also contains water vapor. The fractional volume of water vapor is a function of biogas temperature; correction of measured gas volume for both water vapor content and thermal expansion is easily done via a simple mathematic algorithm which yields the standardized volume of dry biogas.

In some cases, biogas contains siloxanes. These siloxanes are formed from the anaerobic decomposition of materials commonly found in soaps and detergents. During combustion of biogas containing siloxanes, silicon is released and can combine with free oxygen or various other elements in the combustion gas. Deposits are formed containing mostly silica (SiO_2) or silicates (Si_xO_y) and can also contain calcium, sulfur, zinc, phosphorus. Such white mineral deposits accumulate to a surface thickness of several millimeters and must be removed by chemical or mechanical means.

Practical and cost-effective technologies to remove siloxanes and other biogas contaminants are currently available .

4 - Benefits

When biogas is used, many advantages arise. In North America, utilization of biogas would generate enough electricity to meet up to three percent of the continent's electricity expenditure. In addition, biogas could potentially help reduce global climate change. Normally, manure that is left to decompose releases two main gases that cause global climate change: nitrogen dioxide and methane. Nitrogen dioxide (NO_2) warms the atmosphere 310 times more than carbon dioxide and methane 21 times more than carbon dioxide. By converting cow manure into methane biogas via anaerobic digestion, the millions of cows in the United States would be able to produce one hundred billion kilowatt hours of electricity, enough to power millions of homes across the United States. In fact, one cow can produce enough manure in one day to generate three kilowatt hours of electricity; only 2.4 kilowatt hours of electricity are needed to power a single one hundred watt light bulb for one day.[15] Furthermore, by converting cow manure into methane biogas instead of letting it decompose, global warming gases could be reduced by ninety-nine million metric tons or four percent. In Nepal biogas is being used as a reliable source of rural energy, says Bikash Haddi of Biogas promotion center.

5 - Applications

Biogas can be utilized for electricity production on sewage works, in a CHP gas engine, where the waste heat from the engine is conveniently used for heating the digester; cooking; space heating; water heating; and process heating. If compressed, it can replace compressed natural gas for use in vehicles, where it can fuel an internal combustion engine or fuel cells and is a much more effective displacer of carbon dioxide than the normal use in on-site CHP plants. [18]

Methane within biogas can be concentrated via a biogas upgrader to the same standards as fossil natural gas, which itself has had to go through a cleaning process, and becomes *biomethane*. If the local gas network allows for this, the producer of the biogas may utilize the local gas distribution networks. Gas must be very clean to reach pipeline quality, and must be of the correct composition for the local distribution network to accept. Carbon dioxide, water, hydrogen sulfide, and particulates must be removed if present.

5 – 1 - Biogas up grading

Raw biogas produced from digestion is roughly 60% methane and 29 % CO_2 with trace elements of H_2S, and is not high quality enough to be used as fuel gas for machinery. The corrosive nature of H_2S alone is enough to destroy the internals of a plant. The solution is the use of biogas upgrading or purification processes whereby contaminants in the raw biogas stream are absorbed or scrubbed, leaving more methane per unit volume of gas. There are four main methods of biogas upgrading, these include water washing, pressure swing absorption, selexol absorption, and amine gas treating.[19] The most prevalent method is water washing where high pressure gas flows into a column where the carbon dioxide and other trace elements are scrubbed by cascading water running counter-flow to the gas. This arrangement could deliver 98 % methane with manufacturers guaranteeing maximum 2 % methane loss in the system. It takes roughly between 3 - 6 % of the total energy output in gas to run a biogas upgrading system....

5 – 2 - Biogas gas - grid injection

Gas-grid injection is the injection of biogas into the methane grid (natural gas grid). Injections includes biogas:[20] until the breakthrough of micro combined heat and power two-thirds of all the energy produced by biogas power plants was lost (the heat), using the grid to transport the gas to customers, the electricity and the heat can be used for on-site generation resulting in a reduction of losses in the transportation of energy. Typical energy losses in natural gas transmission systems range from 1 – 2 %. The current energy losses on a large electrical system range from 5 – 8 %.

5 – 3 - Biogas in transport

If concentrated and compressed, it can also be used in vehicle transportation. Compressed biogas is becoming widely used in Sweden, Switzerland, and Germany. A biogas - powered train has been in service in Sweden since 2005. Biogas also powers automobiles and in 1974, a British documentary film entitled *Sweet as a Nut* detailed the biogas production process from pig manure, and how the biogas fueled a custom-adapted combustion engine.[25][26] In 2007, an estimated 12,000 vehicles were being fueled with upgraded biogas worldwide, mostly in Europe.

6 - Legislation

The European Union presently has some of the strictest legislation regarding waste management and landfill sites called the Landfill Directive. The United States legislates against landfill gas as it contains VOCs. The United States Clean Air Act and Title 40 of the Code of Federal Regulations (CFR) requires landfill owners to estimate the quantity of non - methane organic compounds (NMOCs) emitted. If the estimated NMOC emissions exceeds 50 tonnes per year, the landfill owner is required to collect the landfill gas and treat it to remove the entrained NMOCs. Treatment of the landfill gas is usually by combustion. Because of the remoteness of landfill sites, it is sometimes not economically feasible to produce electricity from the gas. However, countries such as the United Kingdom and Germany now have legislation in force that provides farmers with long-term revenue and energy security.

7 - Development around the world

7 – 1 - United States

With the many benefits of biogas, it is starting to become a popular source of energy and is starting to be utilized in the United States more. In 2003, the United States consumed 147 trillion BTU of energy from "landfill gas", about 0.6% of the total U.S. natural gas consumption. Methane biogas derived from cow manure is also being tested in the U.S. According to a 2008 study, collected by the *Science and Children* magazine, methane biogas from cow manure would be sufficient to produce 100 billion kilowatt hours enough to power millions of homes across America. Furthermore, methane biogas has been tested to prove that it can reduce 99 million metric tons of greenhouse gas emissions or about 4 % of the greenhouse gases produced by the United States.

In Vermont, for example, biogas generated on dairy farms around the state is included in the CVPS Cow Power program. The Cow Power program is offered by Central Vermont Public Service Corporation as a voluntary tariff. Customers can elect to pay a premium on their electric bill, and that premium is passed directly to the farms in the program. In Sheldon, Vermont, Green Mountain Dairy has provided renewable energy as part of the Cow Power program. It all started when the brothers who own the farm, Bill and Brian Rowell, wanted to address some of the manure management challenges faced by dairy farms, including manure odor, and nutrient availability for the crops they need to grow to feed the animals. They installed an anaerobic digester to process the cow and milking center waste from their nine hundred and fifty cows to produce renewable energy, a bedding to replace sawdust, and a plant friendly fertilizer. The energy and environmental attributes are sold. On average, the system run by the Rowell brothers produces enough electricity to power three hundred to three hundred fifty other homes. The generator capacity is about 300 kilowatts.

In Hereford, Texas, cow manure is being used to power an ethanol power plant. By switching to methane biogas, the ethanol power plant has saved one thousand barrels of oil a day. Overall, the power plant has reduced transportation costs and will be opening many more jobs for future power plants that will be relying on biogas.

7 – 2 - UK

There are currently around 60 non-sewage biogas plants in the UK, most are on-farm, but some larger facilities exist off-farm, which are taking food and consumer wastes.

On 5 October 2010, biogas was injected into the UK gas grid for the first time. Sewage from over 30,000 Oxfordshire homes is sent to Didcot sewage treatment works, where it is treated in an anaerobic digestor to produce biogas, which is then cleaned to provide gas for approximately 200 homes.

7 – 3 - Germany

Germany is Europe's biggest biogas producer as it is the market leader in biogas technology. In 2010 there were 5,905 biogas plants operating throughout the whole country, in which Lower Saxony, Bavaria and the eastern federal states are the main regions. Most of these plants are employed as power plants. Usually the biogas plants are directly connected with a CHP which produces electric power by burning the bio methane. The electrical power is then fed into the public power grid. In 2010, the total installed electrical capacity of these power plants was 2,291 MW. The electricity supply was approximately 12.8 TWh, which is 12.6 per cent of the total generated renewable electricity. Biogas in Germany is primarily extracted by the co-fermentation of energy crops (called ‘NawaRo’, an abbreviation of ‘nachwachsende Rohstoffe’, which is German for renewable resources) mixed with manure, the main crop utilized is corn. Organic waste and industrial and agricultural residues such as waste from the food industry are also used for biogas generation. In this respect, Biogas production in Germany differs significantly from the UK, where biogas generated from landfill sites is most common.

Biogas production in Germany has developed rapidly over the last 20 years. The main reason for this development is the legally created frameworks. Governmental support of renewable energies started at the beginning of the 1990s with the Law on Electricity Feed (StrEG). This law guaranteed the producers of energy from renewable sources the feed into the public power grid, thus the power companies were forced to take all produced energy from independent private producers of green energy. In 2002 the Law on Electricity Feed was replaced by the Renewable Energy Source Act (EEG). This law even guaranteed a fixed compensation for the produced electric power over 20 years. The amount of ca. 0.08 Euro gave particular farmers the opportunity to become an energy supplier and gaining a further source of income in the same place. The German agricultural biogas production was given a further push in 2004 by implementing the so-called NawaRo-Bonus. This is a special bonus payment given for the usage of renewable resources i.e. energy crops.[41] In 2007 the German government stressed its intention to invest further effort and support in improving the renewable energy supply to provide an answer on growing climate challenges and increasing oil prices by the 'Integrated Climate and Energy Programme'.

This continual trend of renewable energy promotion induces a number of challenges facing the management and organisation of renewable energy supply that has also several impacts on the biogas production. The first challenge to be noticed is the high area-consuming of the biogas electric power supply. In 2011 energy crops for biogas production consumed an area of circa 800,000 ha in Germany. This high demand of agricultural areas generates new competitions with the food industries that did not exist yet. Moreover new industries and markets were created in predominately rural regions entailing different new players with an economic, political and civil background. Their influence and acting has to be governed to gain all advantages this new source of energy is offering. Finally biogas will furthermore play an important role in the German renewable energy supply if good governance is focused.

7 – 4 - Indian subcontinent

In India, Nepal, Pakistan and Bangladesh biogas produced from the anaerobic digestion of manure in small-scale digestion facilities is called gobar gas; it is estimated that such facilities exist in over two million households in India, fifty thousands in Bangladesh and thousands in Pakistan, particularly North Punjab, due to the thriving population of livestock. The digester is an airtight circular pit made of concrete with a pipe connection. The manure is directed to the pit, usually directly from the cattle shed. The pit is then filled with a required quantity of wastewater. The gas pipe is connected to the kitchen fireplace through control valves. The combustion of this biogas has very little odour or smoke. Owing to simplicity in implementation and use of cheap raw materials in villages, it is one of the most environmentally sound energy sources for rural needs. One type of these system is the Sintex Digester. Some designs use vermiculture to further enhance the slurry produced by the biogas plant for use as compost. In order to create awareness and associate the people interested in biogas, an association "Indian Biogas Association" (www.biogas-India.com) is formed. The “Indian Biogas Association” aspires to be a unique blend of; nationwide operators, manufacturers and planners of biogas plants, and representatives from science and research. The association was founded in 2010 and is now ready to start mushrooming. The sole motto of the association is “propagating Biogas in a sustainable way”.

The Deenabandhu Model is a new biogas-production model popular in India. (*Deenabandhu* means "friend of the helpless.") The unit usually has a capacity of 2 to 3 cubic metres. It is constructed using bricks or by a ferrocement mixture. In India, the brick model costs slightly more than the ferro cement model; however, India's Ministry of New and Renewable Energy offers some subsidy per model constructed.

In Pakistan, the Rural Support Programmes Network is running the Pakistan Domestic Biogas Programme which has installed over 1500 biogas plants and has trained in excess of 200 masons on the technology and aims to develop the Biogas Sector in Pakistan.

Also PAK - Energy Solution has taken the most innovative and responsible initiatives in biogas technology. In this regard, the company is also awarded by 1st prize in "Young Entrepreneur Business Plan Challenge" jointly organized by Punjab Govt. & LCCI.

They have designed and developed Uetians Hybrid Model, in which they have combined fixed dome and floating drums and Uetians Triplex Model. Moreover, Pakistan Dairy Development Company has also taken an initiative to develop this kind of alternative source of energy for Pakistani farmers. Biogas is now running diesel engines, gas generators, kitchen ovens, geysers, and other utilities in Pakistan. In Nepal, the government provides subsidies to build biogas plant.

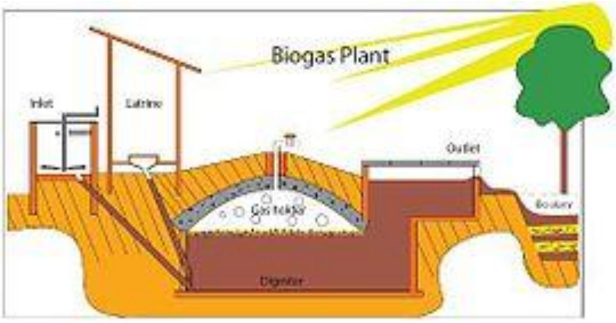
Jain irrigation, Jalgaon is successfully operating a 1.7 MW Biogas based power generation plant with CHP module [63]. It is designed for 100 to 150 MT/day solid waste. Generate 1.7 MW power, 450 TR refrigeration and 10 MT/day compost.

7 – 5 - China

The Chinese had experimented the applications of biogas since 1958. Around 1970, China had installed 6,000,000 digesters in an effort to make agriculture more efficient. During the last years the technology has met high growth rates. This seems to be the earliest developments in generating biogas from agricultural waste.

7 – 6 - In developing nations

Domestic biogas plants convert livestock manure and night soil into biogas and slurry, the fermented manure. This technology is feasible for small holders with livestock producing 50 kg manure per day, an equivalent of about 6 pigs or 3 cows. This manure has to be collectable to mix it with water and feed it into the plant. Toilets can be connected. Another precondition is the temperature that affects the fermentation process. With an optimum at 36 C° the technology especially applies for those living in a (sub) tropical climate. This makes the technology for small holders in developing countries often suitable.



Simple sketch of household biogas plant

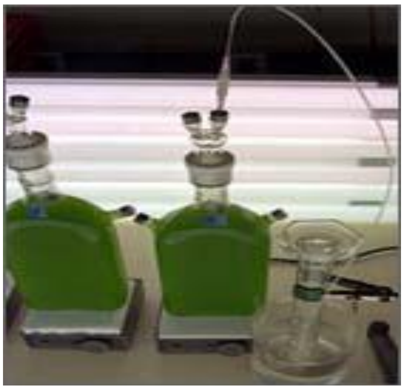
Depending on size and location, a typical brick made fixed dome biogas plant can be installed at the yard of a rural household with the investment between 300 to 500 US $ in Asian countries and up to 1400 US $ in the African context. A high quality biogas plant needs minimum maintenance costs and can produce gas for at least 15–20 years without major problems and re-investments. For the user, biogas provides clean cooking energy, reduces indoor air pollution, and reduces the time needed for traditional biomass collection, especially for women and children. The slurry is a clean organic fertilizer that potentially increases agricultural productivity.

Domestic biogas technology is a proven and established technology in many parts of the world, especially Asia. Several countries in this region have embarked on large- scale programmes on domestic biogas, such as China and India. The Netherlands Development Organisation, SNV, supports national programmes on domestic biogas that aim to establish commercial-viable domestic biogas sectors in which local companies market, install and service biogas plants for households. In Asia, SNV is working in Nepal, Vietnam , Bangladesh, Bhutan, Cambodia, Lao PDR, Pakistan and Indonesia, and in Africa; Rwanda, Senegal, Burkina Faso, Ethiopia, Tanzania, Uganda, Kenya, Benin and Cameroon.

8 - In popular culture

In the 1985 Australian film Mad Max Beyond Thunder dome the post-apocalyptic settlement Barter town is powered by a central biogas system based upon a piggery. As well as providing electricity, methane is used to power Barter town's vehicles.

Bio Hydrogen



Microbial hydrogen production.

Contents

1 - Introduction

Bio hydrogen is defined as hydrogen produced biologically, most commonly by algae, bacteria and archaea. Bio hydrogen is a potential biofuel obtainable from both cultivation and from waste organic materials.

Currently, there is a huge demand of the chemical hydrogen. There is no log of the production volume and use of hydrogen world-wide. However the estimated consumption of hydrogen is expected to reach 900 billion cubic meters in 2011

Refineries are large-volume producers and consumers of hydrogen. Today 96 % of all hydrogen is derived from fossil fuels, with 48% from natural gas, 30 % from hydrocarbons, 18 % from coal and about 4 % from electrolysis. Oil-sands processing, gas-to-liquids and coal gasification projects that are ongoing, require a huge amount of hydrogen and is expected to boost the requirement significantly within the next few years. Environmental regulations implemented in most countries, increase the hydrogen requirement at refineries for gas-line and diesel desulfurization

An important future application of hydrogen could be as an alternative for fossil fuels, once the oil deposits are depleted.[4] This application is however dependent on the development of storage techniques to enable proper storage, distribution and combustion of hydrogen. If the cost of hydrogen production, distribution, and end-user technologies decreases, hydrogen as a fuel could be entering the market in 2020.

Industrial fermentation of hydrogen, or whole-cell catalysis, requires a limited amount of energy, since fission of water is achieved with whole cell catalysis, to lower the activation energy.[6] This allows hydrogen to be produced from any organic material that can be derived through whole cell catalysis since this process does not depend on the energy of substrate.

2 - Algaeic Bio hydrogen

In 1939 a German researcher named Hans Gaffron, while working at the University of Chicago, observed that the algae he was studying, *Chlamydomonas reinhardtii* (a green-algae), would sometimes switch from the production of oxygen to the production of hydrogen.[7] Gaffron never discovered the cause for this change and for many years other scientists failed in their attempts at its discovery. In the late 1990s professor Anastasios Melis a researcher at the University of California at Berkeley discovered that if the algae culture medium is deprived of sulfur it will switch from the production of oxygen (normal photosynthesis), to the production of hydrogen. He found that the enzyme responsible for this reaction is hydrogenase, but that the hydrogenase lost this function in the presence of oxygen. Melis found that depleting the amount of sulfur available to the algae interrupted its internal oxygen flow, allowing the hydrogenase an environment in which it can react, causing the algae to produce hydrogen. *Chlamydomonas moewusii* is also a good strain for the production of hydrogen. Scientists at the U.S. Department of Energy's Argonne National Laboratory are currently trying to find a way to take the part of the hydrogenase enzyme that creates the hydrogen gas and introduce it into the photosynthesis process. The result would be a large amount of hydrogen gas, possibly on par with the amount of oxygen created.

It would take about 25,000 square kilometres to be sufficient to displace gasoline use in the US. To put this in perspective, this area represents approximately 10 % of the area devoted to growing soya in the US. The US Department of Energy has targeted a selling price of $2.60 / kg as a goal for making renewable hydrogen economically viable. 1 kg is approximately the energy equivalent to a gallon of gasoline. To achieve this, the efficiency of light-to-hydrogen conversion must reach 10 % while current efficiency is only 1% and selling price is estimated at $13.53 / kg. According to the DOE cost estimate, for a refueling station to supply 100 cars per day, it would need 300 kg. With current technology, a 300 kg per day stand-alone system will require 110,000 m^2 of pond area, 0.2 g / l cell concentration, a truncated antennae mutant and 10 cm pond depth. Areas of research to increase efficiency include developing oxygen-tolerant Fe Fe - hydrogenases and increased hydrogen production rates through improved electron transfer.

3 - Bacterial Bio hydrogen

3 - 1 - Process requirements

If hydrogen by fermentation is to be introduced as an industry, the fermentation process will be dependent on organic acids as substrate for photo-fermentation. The organic acids are necessary for high hydrogen production rates.

The organic acids can be derived from any organic material source such as sewage waste waters or agricultural wastes. The most important organic acids are acetic acid (HAc), butyric acid (HBc) and propionic acid (HPc). A huge advantage is that production of hydrogen by fermentation does not require glucose as substrate.

The fermentation of hydrogen has to be a continuous fermentation process, in order sustain high production rates, since the amount of time for the fermentation to enter high production rates are in days.

3 – 2 - Fermentation

Several strategies for the production of hydrogen by fermentation in lab-scale have been found in literature. However no strategies for industrial - scale productions have been found. In order to define an industrial - scale production, the information from lab-scale experiments has been scaled to an industrial-size production on a theoretical basis. In general, the method of hydrogen fermentation is referred to in three main categories. The first category is dark-fermentation, which is fermentation which does not involve light. The second category is photo-fermentation, which is fermentation which requires light as the source of energy. The third is combined - fermentation, which refers to the two fermentations combined.

3 – 2 – 1 - Dark fermentation

There are several bacteria with a potential for hydrogen production. The Gram - positive bacteria of the *Clostridium* genus, is promising because it has a natural high hydrogen production rate. In addition, it is fast growing and capable of forming spores, which make the bacteria easy to handle in industrial application.

Species of the *Clostridium* genus allow hydrogen production in mixed cultures, under mesophilic or thermophilic conditions within a pH range of 5.0 to 6.5. Dark - fermentation with mixed cultures seems promising since a mixed bacterial environment within the fermenter, allows cooperation of different species to efficiently degrade and convert organic waste materials into hydrogen, accompanied by the formation of organic acids. The clostridia produce H2 via a reversible hydrogenase (H2ase) enzyme (2H + 2e <=> H2) and this reaction is important in achieving the redox balance of fermentation. The rate of H2 formation is inhibited as H2 production causes the partial pressure of H2 (pH2) to increase. This can limit substrate conversion and growth and the bacteria may respond by switching to a different metabolic pathway in order to achieve redox balance, energy generation and growth - by producing solvents instead of hydrogen and organic acids.

Enteric bacteria such as *Escherichia coli* and *Enterobacter aerogenes* are also interesting for Bio hydrogen fermentation.[20][21] Unlike the clostridia, the enteric bateria produce hydrogen primarily (or exclusively in the case of *E. coli*) by the cleavage of formate (HCOOH --> H2 + CO2), which serves to detoxify the medium by removing formate. Cleavage is not a redox reaction and it has no consequence on the redox balance of fermentation. This detoxification is particularly important for *E. coli* as it cannot protect itself by forming spores. Formate cleavage is an irreversible reaction, hence H2 production is insensitive to the partial pressure of hydrogen (pH2) in the fermenter.

E. coli has been referred to as the workhorse of molecular microbiology and many workers have investigated metabolic engineering approaches to improve Bio hydrogen fermentation in *E. coli*.

Whereas oxygen kills clostridia, the enteric bacteria are facultative anaerobes; they grow very quickly when oxygen is available and transition progressively from aerobic to anaerobic metabolism as oxygen becomes depleted. Growth rate is much slower during anaerobic fermentation than during aerobic respiration because fermentation less metabolic energy from the same substrate. In practical terms, facultative anaerobes are useful because they can be grown quickly to a very high concentration with oxygen and then used to produce hydrogen at a high rate when the oxygen supply is stopped.

For fermentation to be sustainable at industrial-scale, it is necessary to control the bacterial community inside the fermenter. Feed stocks may contain micro - organisms, which could cause changes in the microbial community inside the fermenter. The enteric bacteria and most clostridia are mesophilic; they have an optimum temperature of around 30 degrees C as do many common environmental microorganisms. Therefore, these fermentations are susceptible to changes in the microbial community unless the feedstock is sterilized, for example where a hydrothermal pretreatment is involved, sterilization is a side - effect. A way to prevent harmful micro-organisms from gaining control of the bacterial environment inside the fermenter could be through addition of the desired bacteria . Hyperthermophilic archaea such as *Thermotoga neapolitana* can also be used for hydrogen fermentation. Because they operate at around 70 degrees C, there is little chance of feedstock contaminants becoming established.

Fermentations produce organic acids are toxic to the bacteria. High concentrations inhibit the fermentation process and may trigger changes in metabolism and resistance mechanisms such as sporulation in different species. This fermentation of hydrogen is accompanied production of carbon-dioxide which can be separated from hydrogen with a passive separation process.

The fermentation will convert some of the substrate (e.g. waste) into biomass instead of hydrogen.

The biomass is, however, a carbohydrate-rich by-product which can be fed back into the fermenter, to ensure that the process is sustainable. Fermentation of hydrogen by dark-fermentation is restricted by incomplete degradation of organic material, into organic acids and this is why we need the photo-fermentation.

The separation of organic acids from biomass in the outlet stream can be done with a settler tank in the outlet stream, where the sludge (biomass) is pumped back into the fermenter to increase the rate of hydrogen production .

In traditional fermentation systems, the dilution rate must be carefully controlled as it affects the concentration of bacterial cells and toxic end-products (organic acids and solvents) inside the fermenter. A more complex *electro-fermentation* technique decouples the retention of water and biomass and overcomes inhibition by organic acids.

3 – 2 – 2 - Photo - fermentation

Photo - fermentation refers to the method of fermentation where light is required as the source of energy. This fermentation relies on photosynthesis to maintain the cellular energy levels. Fermentation by photosynthesis compared to other fermentations has the advantage of light as the source of energy instead of sugar. Sugars are usually available in limited quantities.

All plants, algae and some bacteria are capable of photosynthesis: utilizing light as the source of metabolic energy. *Cyanobacteria* are frequently mentioned capable of hydrogen production by oxygenic photosynthesis.[36] However the purple non-sulphur (PNS) bacteria (e.g. genus *Rhodobacter*) hold significant promise for the production of hydrogen by anoxygenic photosynthesis and photo-fermentation.

Studies have shown that *Rhodobacter sphaeroides* is highly capable of hydrogen production while feeding on organic acids, consuming 98% to 99% of the organic acids during hydrogen production.[6] Organic acids may be sourced sustanably from the dark fermentation of waste feedstocks. The resultant system is called *combined fermentation* (see below).

Photo - fermentative bacteria can use light in the wavelength range 400 - 1000 nm (visible and near-infrared) which differs from algae and cyanobacteria (400-700 nm; visible).

Currently there is limited experience with photo-fermentation at industrial-scale. The distribution of light within the industrial scale photo-fermenter has to be designed to minimize self-shading. Therefore any externally illuminated photo bio reactor must have a high ratio of high surface area to volume. As a result, photo bio reactor construction is materials - intensive and expensive.

A method to ensure proper light distribution and limit self-shading within the fermenter, could be to distribute the light with an optic fiber where light is transferred into the fermenter and distributed from within the fermenter. Photo - fermentation with *Rhodobacter sphaeroides* require mesophilic conditions . An advantage of the optical fiber photo bio reactor is that radiant heat-gain can be controlled by dumping excess light and filtering out wavelengths which cannot be used by the organisms.

3 – 2 – 3 - Combined fermentation

Combining dark - and photo - fermentation has shown to be the most efficient method to produce hydrogen through fermentation.[40] The combined fermentation allows the organic acids produced during dark-fermentation of waste materials, to be used as substrate in the photo-fermentation process. Many independent studies show this tehcnique to be effective and practical.

For industrial fermentation of hydrogen to be economical feasible, by-products of the fermentation process has to be minimized. Combined fermentation has the unique advantage of allowing reuse of the otherwise useless chemical, organic acids, through photosynthesis.

Many wastes are suitable for fermentation and this is equivalent the initial stages of anaerobic digestion, now the most important biotechnology for energy from waste. One of the main challenges in combined fermentation is that effluent fermentation contains not only useful organic acids but excess nitrogenous compounds and ammonia, which inhibit nitrogenase activity by wild - type PNS bacteria. The problem can be solved by genetic engineering to interrupt down-regulation of nitrogenase in response to nitrogen excess.[However, genetically engineered bacterial strains may pose containment issues for application. A physical solution to this problem was developed at The University of Birmingham UK, which involves selective electro-separation of organic acids from an active fermentation . The energetic cost of electro - separation of organic acids was found to be acceptable in a combined fermentation. "Electro-fermentation" has the side-effect of a continuous, high-rate dark hydrogen fermentation.

As the method for hydrogen production, combined fermentation currently holds significant promise.

3 – 3 - Metabolic processes

The metabolic process for hydrogen production are dependent on the reduction of the metabolite ferredoxin (except in the enteric bacteria, where an alternative formate pathway operates).

$$4H^+ + \text{ferredoxin (ox)} \rightarrow \text{ferredoxin (red)} + 2\ H_2$$

For this process to run, ferredoxin has to be recycled through oxidation. The recycling process is dependent on the transfer of electrons from nicotinamide adenine dinucleotide (NADH) to ferredoxin.

$$2\ \text{ferredoxin(red)} + 2\ \text{NADH} \rightarrow 2\ \text{ferredoxin(ox)} + H_2$$

The enzymes that catalyze this recycling process are referred to as hydrogen - forming enzymes and have complex metal loclusters in their active site and require several maturation proteins to attain their active form. The hydrogen - forming enzymes are inactivated by molecular oxygen and must be separated from oxygen, to produce hydrogen.

The three main classes of hydrogen-forming enzymes are [FeFe]-hydrogenase, [NiFe] - hydrogenase and nitrogenase.[46] These enzymes behave differently in dark-fermentation with *Clostridium* and photo-fermentation with *Rhodobacter*. The interplay of these enzymes are the key in hydrogen production by fermentation.

3 – 3 - 1 - Clostridium

The interplay of the hydrogen-forming enzymes in *Clostridium* is unique with little or no involvement of nitrogenase. The hydrogen production in this bacteria is mostly due to [FeFe]-hydrogenase, which activity is a hundred times higher than [NiFe]-hydrogenase and a thousand times higher than nitrogenase. [FeFe]-hydrogenase has a Fe-Fe catalytic core with a variety of electron donors and acceptors.

The enzyme [NiFe]-hydrogenase in *Clostridium*, catalyse a reversible oxidation of hydrogen. [NiFe]-hydrogenase is responsible for hydrogen uptake, utilizing the electrons from hydrogen for cellular maintenance.

In Clostridium, glucose is broken down into pyruvate and nicotinamide adenine dicleotide (NADH). The formed pyruvate is then further converted to acetyl-CoA and hydrogen by pyruvate ferredoxin oxidoreductase with the reduction of ferredoxin. Acetyl-CoA is then converted to acetate, butyrate and propionate.

Acetate fermentation processes are well understood and have a maximum yield of 4 mol hydrogen pr. mol glucose. The yield of hydrogen from the conversion of acetyl-CoA to butyrate, has half the yield as the conversion to acetate. In mixed cultures of *Clostridium* the reaction is a combined production of acetate, butyrate and propionate. The organic acids which are the by-product of fermentation with *Clostridium*, can be further processed as substrate for hydrogen production with *Rhodobacter*.

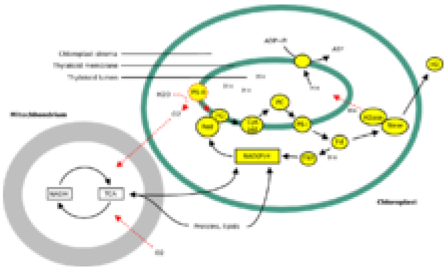
3 – 3 – 2 - Rhodobacter

The purple non - sulphur (PNS) bacteria *Rhodobacter sphaeroides* is able to produce hydrogen from a wide range of organic compounds (chiefly organic acids) and light.

The photo-system required for hydrogen production in *Rhodobacter* (PS-I), differ from its oxygenic photosystem (PS-II) due to the requirement of organic acids and the inability to oxidize water. In the absence of water-splitting photosynthesis is anoxygenic. Therefore, hydrogen production is sustained without inhibition from generated oxygen.

In PNS bacteria, hydrogen production is due to catalysis by nitrogenase. Hydrogenases are also present but the production of hydrogen by [FeFe]-hydrogenase is less than 10 times the hydrogen uptake by [NiFe]-hydrogenase.

Only under nitrogen-deficient conditions is nitrogenase activity sufficient to overcome uptake hydrogenase activity, resulting in net generation of hydrogen.



Rhodobacter hydrogen metabolism

The main photosynthetic membrane complex is PS-I which accounts for most of the light-harvest. The photosynthetic membrane complex PS-II produces oxygen, which inhibit hydrogen production and thus low partial pressures of oxygen most be sustained during fermentation.

The range of photosynthetically active radiation for PNS bacteria is 400-1000 nm. This includes the visible (VIS) and near-infrared (NIR)sections of the spectrum and not (despite erroneous writings) ultraviolet. This range is wider than that of algae and cyano bacteria (400-700 nm; VIS). The response to light (action spectrum) varies dramatically across the active range. Around 80 % of activity is associated with the NIR. VIS is absorbed but much less efficiently utilized.

To attain high production rates of hydrogen, the hydrogen production by nitrogenase has to exceed the hydrogen uptake by hydrogenase. The substrate is oxidized through the tri carboxylic acids circle and the produced electrons are transferred to the nitrogenase catalyzed reduction of protons to hydrogen, through the electron transport chain.

3 – 4 – LED - fermenter

To build an industrial - size photo-fermenter without using large areas of land could achieved using a fermenter with light - emitting diodes (LED) as light source. This design prevents self - shading within the fermenter, require limited energy to maintain photosynthesis and has very low installation costs. This design would also allow cheap models to be built for educational purpose

However, it is impossible for any photobioreactor using artificial lights to generate energy. The maximum light conversion efficiency into hydrogen is about 10 % (by PNS bacteria) and the maximum efficiency of electricity generation from hydrogen about 80% (by PEM fuel cell) and the maximum efficiency of light generation from electricity (via LED) is about 80%. This represents a cycle of diminishing returns. For the purposes of fuel or energy production sunlight is necessary but artificially lit photobioreactors such as the LED - fermenter could be useful for the production of other valuable commodities.

3 – 5 - Metabolic engineering

There is a huge potential for improving hydrogen yield by metabolic engineering. The bacteria *Clostridium* could be improved for hydrogen production by disabling the uptake hydrogenase, or disabling the oxygen system. This will make the hydrogen production robust and increase the hydrogen yield in the dark-fermentation step.

The photo - fermentation step with Rhodobacter, is the step which is likely to gain the most from metabolic engineering. An option could be to disable the uptake - hydrogenase or to disable the photosynthetic membrane system II (PS-II). Another improvement could be to decrease the expression of pigments, which shields of the photo - system.

Bio Mass

Contents

1 - Introduction

Biomass is biological material from living, or recently living organisms, most often referring to plants or plant-derived materials.[1] As a renewable energy source, biomass can either be used directly, or indirectly — once or converted into another type of energy product such as biofuel. Biomass can be converted to energy in three ways: *thermal conversion*, *chemical conversion*, and *biochemical conversion*.

Historically, humans have harnessed biomass derived energy products since the time when people began burning wood to make fire.[2] In modern times, the term can be referred to in two meanings. In the first sense, biomass is plant matter used either to generate electricity (via steam turbines or gasifiers), or to produce heat (via direct combustion). Wood remains the largest biomass energy source today;[2] examples include forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even municipal solid waste. In the second sense, biomass includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuels. Industrial biomass can be grown from numerous types of plants, including miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane, bamboo, and a variety of tree species, ranging from eucalyptus to oil palm (palm oil).

The adoption of biomass-based energy plants has been a slow but steady process. Over the past decade, the production of these plants has increased 14 %. In the United States, alternative electricity-production sources on the whole generate about 13 % of power; of this fraction, biomass contributes approximately 11 % of the alternative production. According to a study conducted in early 2012, of the 107 operating biomass plants in the United States, 85 have been cited by federal or state regulators for the violation of clean air or water standards laws over the past 5 years. This data also includes minor infractions.

Biomass - derived energy also holds the promise of reducing carbon dioxide emissions, a significant contributor to global warming, as carbon dioxide acts as a “green house” gas by trapping heat absorbed by the earth from the sun. Although the burning of biomass releases as much carbon dioxide as the burning of fossil fuels, biomass burning does not release “new carbon” into the atmosphere, which the burning of fossil fuels does. This is because carbon dioxide released from fossil fuels was carbon that was fixated via photosynthesis millions of years ago that had been locked in the hydrocarbons of fossil fuels.

Industry professionals claim that a range of issues can affect a plant’s ability to comply with emissions standards. Some of these challenges, unique to biomass plants, include inconsistent fuel supplies and age. The type and amount of the fuel supply is completely reliant factors; the fuel can be in the form of building debris or agricultural waste (such as deforestation of invasive species or orchard trimmings). Furthermore, many of the biomass plants are old, use outdated technology and were not built to comply with today’s stringent standards. In fact, many are based on technologies developed during the term of President Jimmy Carter, who created the Department of Energy in 1977.

The Energy Information Administration projected that by 2017, biomass is expected to be about twice as expensive as natural gas, slightly more expensive than nuclear power, and much less expensive than solar panels. In another EIA study released, concerning the government’s plan to implement a 25% renewable energy standard by

2025, the agency assumed that 598 million tons of biomass would be available, accounting for 12 % of the renewable energy in the plan .

2 - Biomass sources

Wood is a typical source of biomass

Biomass is all biologically-produced matter based in carbon, hydrogen and oxygen. The estimated biomass production in the world is 146 billion tons a year, consisting of mostly wild plant growth.[9] Biomass energy is derived from six distinct energy sources: garbage, wood, plants, waste, landfill gases, and alcohol fuels.

Wood energy is derived by using ligno cellulosic biomass (second generation biofuels) as fuel. This is either using harvested wood directly as a fuel, or collecting from wood waste streams. The largest source of energy from wood is pulping liquor or “black liquor,” a waste product from processes of the pulp, paper and paperboard industry.

Waste energy is the second-largest source of biomass energy. The main contributors of waste energy are municipal solid waste (MSW), manufacturing waste, and landfill gas. Energy derived from biomass is the largest non-hydroelectric renewable resource of electricity in the U.S., where waste-to-energy power plants generate enough electricity to supply 1.3 million homes.

Sugars and oils (first generation biofuels), such as sugar cane and corn, are used to produce bio ethanol, an alcohol fuel. Alcohol fuels can be used directly, like other fuels, or as an additive to gasoline . Second generation biofuels are less simple to extract or process, while first generation biofuels are more prone to escalating the Food vs. Fuel dilemma.

Plant energy is produced by crops specifically grown for use as fuel that offer high biomass output per hectare with low input energy. Some examples of these plants are wheat, which typically yield 7.5-8 tons of grain per hectare, and straw, which typically yield 3.5-5 tons per hectare. The grain can be used for liquid transportation fuels while the straw can be burned to produce heat or electricity. Plant biomass can also be degraded from cellulose to glucose through a series of chemical treatments, and the resulting sugar can then be used as a first generation biofuel. The use of plants as a biofuel source not only provides sustainability but also a way to reduce a major greenhouse gas, carbon dioxide.

Biomass can be converted to other usable forms of energy like methane gas or transportation fuels like ethanol and biodiesel. Rotting garbage, and agricultural and human waste, all release methane gas—also called "landfill gas" or "biogas." Crops, such as corn and sugar cane, can be fermented to produce the transportation fuel, ethanol. Biodiesel, another transportation fuel, can be produced from left-over food products like vegetable oils and animal fats. Also, biomass to liquids (BTLs) and cellulosic ethanol are still under research.

There is a great deal of research involving algal biomass due to the fact that it's a non-food resource and can be produced at rates 5 to 10 times those of other types of land-based agriculture, mainly corn and soy. Once harvested, it can be fermented to produce biofuels such as ethanol, butanol, and methane, as well as biodiesel and hydrogen. Algal biomass may be produced commercially for this specific purpose or as a byproduct of nutrient removal systems like the Algal Turf Scrubber used to re-oxygenate aquatic dead zones and waste water treatment. Efforts are being made to identify which species of algae are most suitable for energy production. Genetic engineering approaches could also be utilized to improve microalgae as a source of biofuel.

The biomass used for electricity generation varies by region.[22] Forest by-products, such as wood residues, are common in the United States.[22] Agricultural waste is common in Mauritius (sugar cane residue) and Southeast Asia (rice husks). Animal husbandry residues, such as poultry litter, are common in the UK.

3 - Biomass conversion process to useful energy

There are a number of technological options available to make use of a wide variety of biomass types as a renewable energy source. Conversion technologies may release the energy directly, in the form of heat or electricity, or may convert it to another form, such as liquid biofuel or combustible biogas. While for some classes of biomass resource there may be a number of usage options, for others there may be only one appropriate technology.

3 – 1 - Thermal conversion

Biomass briquettes are an example fuel for production of dendrothermal energy

Thermal conversion processes use heat as the dominant mechanism to convert biomass into another chemical form. The basic alternatives of combustion, torrefaction, pyrolysis, and gasification are separated principally by the extent to which the chemical reactions involved are allowed to proceed (mainly controlled by the availability of oxygen and conversion temperature).

Energy created by burning biomass (fuel wood), also known as dendrothermal energy, is particularly suited for countries where the fuel wood grow more rapidly, e.g. tropical countries. There are a number of other less common, more experimental or proprietary thermal processes that may offer benefits such as hydrothermal upgrading (HTU) and hydro processing. Some have been developed for use on high moisture content biomass, including aqueous slurries, and allow them to be converted into more convenient forms. Some of the applications of thermal conversion are combined heat and power (CHP) and co-firing. In a typical dedicated biomass power plant, efficiencies range from 7–27 % (HHV basis). Biomass cofiring with coal, by contrast, typically occurs at efficiencies near those of the coal combustor (30 – 40 %, HHV basis).

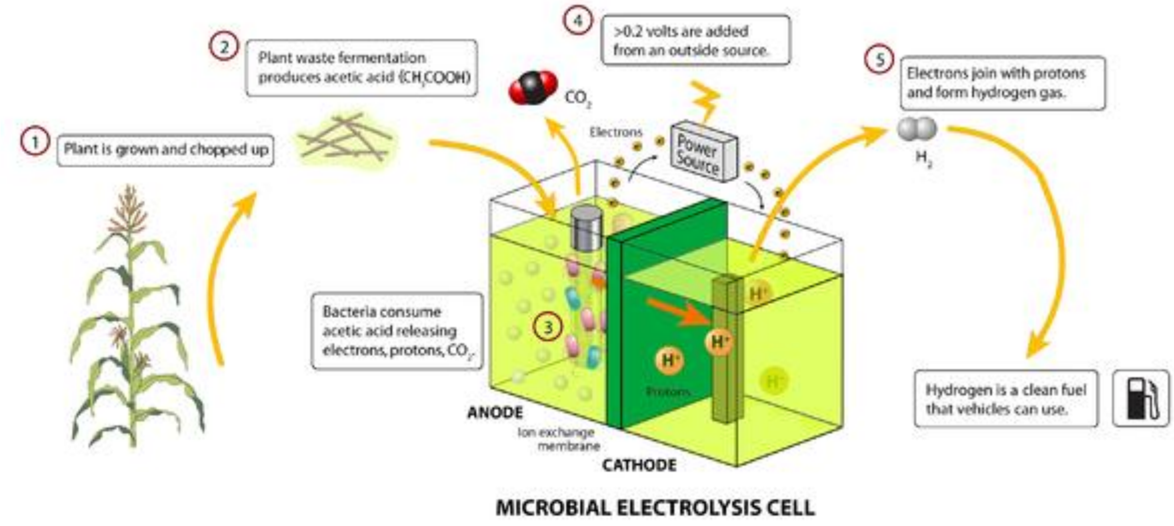
This type of energy is technically called *dendrothermal energy*, when used in power plants as a fuel for production of energy.

3 – 2 - Chemical conversion

A range of chemical processes may be used to convert biomass into other forms, such as to produce a fuel that is more conveniently used, transported or stored, or to exploit some property of the process itself. Many of these processes are based in large part on similar coal-based processes, such as Fischer-Tropsch synthesis, methanol production, olefins (ethylene and propylene), and similar chemical or fuel feed stocks. In most cases, the first step involves gasification, which step generally is the most expensive and involves the greatest technical risk . Biomass is more difficult to feed into a pressure vessel than coal or any liquid. Therefore, biomass gasification is frequently done at atmospheric pressure and causes incomplete combustion of biomass to produce a combustible gas consisting of carbon monoxide, hydrogen, and traces of methane. This gas mixture, called a producer gas, can provide fuel for various vital processes, such as internal combustion engines, as well as substitute for furnace oil in direct heat applications. Because any biomass material can undergo gasification, this process is far more attractive than ethanol or biomass production, where only particular biomass materials can be used to produce a fuel. In addition, biomass gasification is a desirable process due to the ease at which it can convert solid waste (such as wastes available on a farm) into producer gas, which is a very usable fuel.

Biomass also has the potential to be converted to multiple commodity chemicals. Halomethanes have successfully been by produced using a combination of A. fermentans and engineered S. cerevisiae. This method converts NaX salts and unprocessed biomass such as switch grass, sugar cane, corn stover, or poplar into halomethanes. S-adenosylmethionine which is naturally occurring in S. cerevisiae allows a methyl group to be transferred. Production levels of 150 mg L-1H-1 iodomethane were achieved. At these levels roughly 173000L of capacity would need to be operated just to replace the United States' need for iodomethane.[27] However, an advantage of this method is that it uses NaI rather than I2; NaI is significantly less hazardous than I2. This method may be applied to produce ethylene in the future.

3 – 3 - Biochemical conversion



A microbial electrolysis cell can be used to directly make hydrogen gas from plant matter

As biomass is a natural material, many highly efficient biochemical processes have developed in nature to break down the molecules of which biomass is composed, and many of these biochemical conversion processes can be harnessed.

Biochemical conversion makes use of the enzymes of bacteria and other micro-organisms to break down biomass. In most cases micro-organisms are used to perform the conversion process: anaerobic digestion, fermentation and composting. Other chemical processes such as converting straight and waste vegetable oils into biodiesel is trans esterification. Another way of breaking down biomass is by breaking down the carbohydrates and simple sugars to make alcohol. However, this process has not been perfected yet. Scientists are still researching the effects of converting biomass.

4 - Environmental impact

A cogeneration station in Metz, France. The 45MW boiler uses waste wood biomass as energy source.

The biomass power generating industry in the United States, which consists of approximately 11,000 MW of summer operating capacity actively supplying power to the grid, produces about 1.4 percent of the U.S. electricity supply.

Currently, the New Hope Power Partnership is the largest biomass power plant in North America. The 140 MW facility uses sugar cane fiber (bagasse) and recycled urban wood as fuel to generate enough power for its large milling and refining operations as well as to supply renewable electricity for nearly 60,000 homes. The facility reduces dependence on oil by more than one million barrels per year, and by recycling sugar cane and wood waste, preserves landfill space in urban communities in Florida.

Using biomass as a fuel produces air pollution in the form of carbon monoxide, carbon dioxide, NOx (nitrogen oxides), VOCs (volatile organic compounds), particulates and other pollutants, in some cases at levels above those from traditional fuel sources such as coal or natural gas. Black carbon – a pollutant created by incomplete combustion of fossil fuels, biofuels, and biomass – is possibly the second largest contributor to global warming . In 2009 a Swedish study of the giant brown haze that periodically covers large areas in South Asia determined that it had been principally produced by biomass burning, and to a lesser extent by fossil-fuel burning.[36] Researchers measured a significant concentration of ^{14}C , which is associated with recent plant life rather than with fossil fuels.

Biomass systems can reduce waste energy from 66 % to 25 % compared to traditional fossil fuels , meaning a significantly smaller amount of input material (biomass) is used, therefore having a positive effect on the global environment and use of fuel. In addition, modern biomass systems utilize biomass sources such as energy crops with a 1 year lifecycle, meaning that (carbon) emissions are able to be recycled within 1 year following their emission – considerably better than the millions of years needed to recycle coal or nuclear materials. The same modern biomass systems use filters. These filters capture carbon and other pollutants before they enter the atmosphere. Thus in the biomass lifecycle, the pollutants are captured by trees and crops, they are burnt, pollutants are captured and less are released back into the environment . Any pollutants released are then reabsorbed by trees and plants. Consequently, each burning cycle can significantly lower the amount of pollutants in the atmosphere and the biomass unit acts like a large cleaning unit for the planet.

Biomass power plant size is often driven by biomass availability in close proximity as transport costs of the (bulky) fuel play a key factor in the plant's economics. It has to be noted, however, that rail and especially shipping on waterways can reduce transport costs significantly, which has led to a global biomass market.[39] To make small plants of 1 MW_{el} economically profitable those power plants have need to be equipped with technology that is able to convert biomass to useful electricity with high efficiency such as ORC technology, a cycle similar to the water steam power process just with an organic working medium. Such small power plants can be found in Europe.

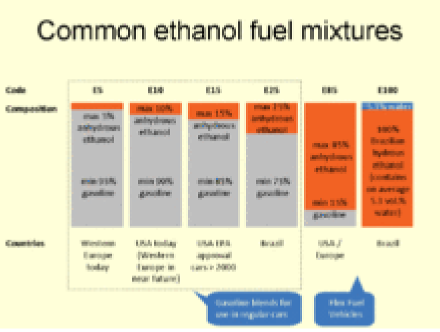
On combustion, the carbon from biomass is released into the atmosphere as carbon dioxide (CO_2). The amount of carbon stored in dry wood is approximately 50 % by weight. However, according to the Food and Agriculture Organization of the United Nations, plant matter used as a fuel can be replaced by planting for new growth. When the biomass is from forests, the time to recapture the carbon stored is generally longer, and the carbon storage capacity of the forest may be reduced overall if destructive forestry techniques are employed.

Despite harvesting, biomass crops may sequester carbon. For example, soil organic carbon has been observed to be greater in switchgrass stands than in cultivated cropland soil, especially at depths below 12 inches. The grass sequesters the carbon in its increased root biomass. Typically, perennial crops sequester much more carbon than annual crops due to much greater non-harvested living biomass, both living and dead, built up over years, and much less soil disruption in cultivation.

The biomass - is – carbon - neutral proposal put forward in the early 1990s has been superseded by more recent science that recognizes that mature, intact forests sequester carbon more effectively than cut-over areas. When a tree’s carbon is released into the atmosphere in a single pulse, it contributes to climate change much more than woodland timber rotting slowly over decades. Current studies indicate that "even after 50 years the forest has not recovered to its initial carbon storage" and "the optimal strategy is likely to be protection of the standing forest".

Forest - based biomass has recently come under fire from a number of environmental organizations, including Greenpeace and the Natural Resources Defense Council, for the harmful impacts it can have on forests and the climate. Greenpeace recently released a report entitled "Fuelling a BioMess" which outlines their concerns around forest-based biomass. Because any part of the tree can be burned, the harvesting of trees for energy production encourages Whole-Tree Harvesting, which removes more nutrients and soil cover than regular harvesting, and can be harmful to the long-term health of the forest. In some jurisdictions, forest biomass is increasingly consisting of elements essential to functioning forest ecosystems, including standing trees, naturally disturbed forests and remains of traditional logging operations that were previously left in the forest. Environmental groups also cite recent scientific research which has found that it can take many decades for the carbon released by burning biomass to be recaptured by regrowing trees, and even longer in low productivity areas; furthermore, logging operations may disturb forest soils and cause them to release stored carbon. In light of the pressing need to reduce greenhouse gas emissions in the short term in order to mitigate the effects of climate change, a number of environmental groups are opposing the large-scale use of forest biomass in energy production.

Common Ethanol Fuel Mixtures



Summary of the main ethanol blends used around the world

Contents

1 - Introduction

Several common ethanol fuel mixtures are in use around the world. The use of pure hydrous or anhydrous ethanol in internal combustion engines (ICEs) is only possible if the engines are designed or modified for that purpose. Anhydrous ethanol can be blended with gasoline (petrol) in various ratios for use in unmodified gasoline engines, and with minor modifications, can also be used with a higher content of ethanol.

Ethanol fuel mixtures have "E" numbers which describe the percentage of ethanol fuel in the mixture by volume, for example, E85 is 85% anhydrous ethanol and 15% gasoline. Low-ethanol blends, from E5 to E25, are also known as gasohol, though internationally the most common use of the term refers to the E10 blend.

Blends of E10 or less are used in more than 20 countries around the world, led by the United States, where ethanol represented 10% percent of the U.S. gasoline fuel supply in 2011 . Blends from E20 to E25 have been used in Brazil since the late 1970s. E85 is commonly used in the U.S. and Europe for flexible-fuel vehicles. Hydrous ethanol or E100 is used in Brazilian neat ethanol vehicles and flex-fuel light vehicles and in hydrous E15 called hE15 for modern petrol cars in the Netherlands.

2 - E10 or less

E10, a fuel mixture of 10 % anhydrous ethanol and 90 % gasoline sometimes called gasohol, can be used in the internal combustion engines of most modern automobiles and light-duty vehicles without need for any modification on the engine or fuel system. E10 blends are typically rated as 2 to 3 octane higher than regular gasoline and are approved for use in all new U.S. automobiles, and are mandated in some areas for emissions and other reasons.[3] The E10 blend and lower ethanol content mixtures have been used in several countries, and its use has been primarily driven by the several world energy crises that have taken place since the 1973 oil crisis.

Other common blends include E5 and E7. These concentrations are generally safe for recent engines that run on pure gasoline. As of 2006, mandates for blending bioethanol into vehicle fuels had been enacted in at least 36 states / provinces and 17 countries at the national level, with most mandates requiring a blend of 10 to 15% ethanol with gasoline.

One way to measure alternative fuels in the U.S. is the "gasoline - equivalent gallons" (GEG). In 2002, the U.S. used as fuel an amount of ethanol equal to 137,000 tera joules (TJ), the energy equivalent of 4.3 billion liters of gasoline. This was less than 1 % of the total fuel used that year.

E10 and other blends of ethanol are considered to be useful in decreasing U.S. dependence on foreign oil, and can reduce carbon monoxide (CO) emissions by 20 to 30% under the right conditions. Although E10 does decrease emissions of CO and greenhouse gases such as CO_2 by an estimated 2% over regular gasoline, it can cause increases in evaporative emissions and some pollutants depending on factors such as the age of the vehicle and weather conditions.[7] According to the Philippine Department of Energy, the use of not more than a 10 % ethanol-gasoline mixture is not harmful to cars' fuel systems. Generally, automobile gasoline containing alcohol (ethanol or methanol) is not allowed to be used in U.S. certificated aircraft.

2 – 1 - Availability

E10 was introduced nationwide in Thailand, and replaced high-octane pure gasoline in that country in 2007.

E10 is also commonly available in the Midwestern United States. It has also been mandated for use in all standard automobile fuel in the state of Florida by the end of 2010. Due to the phasing out of MTBE as a gasoline additive and mainly due to the mandates established in the Energy Policy Act of 2005 and the Energy Independence and Security Act of 2007, ethanol blends have increased throughout the United States, and by 2009, the ethanol market share in the U.S. gasoline supply reached almost 8% by volume.

The Tesco chain of supermarkets in the UK have started selling an E5 brand of gasoline marketed as 99 RON super-unleaded. Its selling price is lower than the other two forms of high-octane unleaded on the market, Shell's V-Power (99 RON) and BP's Ultimate (97 RON).

Many petrol stations throughout Australia now also sell E10, typically at a few cents cheaper per litre than regular unleaded. It is more commonly found throughout the state of Queensland due to its large sugarcane farming regions. The use of E10 is also subsidised by the Queensland government. Some Shell service stations are also selling a 100 RON E5 blend called V-Power Racing (as opposed to the normal ethanol-free 98 RON V-Power). This is typically about 17 cents more expensive than regular unleaded. Many petrol stations no longer offer a "Regular 91" petrol option, instead only offering Regular E10 (91), Premium (95) and Premium (98).

In Sweden, all 95-octane gasoline is E5, while the status of 98-octane fuel is currently unclear. The product data sheets of the major fuel chains do not clearly state ethanol content of their 98-octane gasoline. In the early-mid 1990s, some fuel chains sold E10.

From January 2011, all 95- octane fuel in Finland is E10, and 98E5 octane fuel is also available.

Mandatory blending of ethanol was approved in Mozambique, but the percentage in the blend has not been specified.

South Africa approved a bio fuel strategy in 2007, and mandated an 8% blend of ethanol by 2013.

A 2007 Uruguayan law mandates a minimum of 5% of ethanol blended with gasoline starting in January 2015.[14] The monopolic, state - owned fuel producer ANCAP started blending premium gasoline with 10 % of bioethanol in December 2009, which will be available in all the country by early January 2010.[15] The other two gasolines will follow later in 2010.

The Dominican Republic has a mandate for blending 15% of ethanol by 2015 .

Chile is considering the introduction of E5, and Bolivia and Venezuela of E10.

A 2011 study conducted by VTT Technical Research Centre of Finland found practically no difference in fuel consumption in normal driving conditions between commercial gasoline grades 95E10 and 98E5 sold in Finland, despite the public perception that fuel consumption is significantly higher with 95E10. VTT performed the comparison test under controlled laboratory conditions and their measurements showed the cars tested used an average of 10.30 liters of 95E10 per 100 km , as opposed to 10.23 liters of 98E5 per 100 km . The difference was 0.07 in favor of 98E5 on average, meaning that using 95E10 gasoline, which has a higher ethanol content, increases consumption by 0.7 %. When the measurements are normalized, the difference becomes 1.0%, a result that is highly consistent with an estimation of calorific values based on approximate fuel composition, which came out at 1.1% in favour of E5.

3 - E15

E15 contains 15% ethanol and 85 % gasoline. This is generally the highest ratio of ethanol to gasoline that is possible to use in vehicles recommended by auto manufacturers to run on E10 in the US.

As a result of the Energy Independence and Security Act of 2007, which mandates an increase in renewable fuels for the transport sector, the U.S. Department of Energy began assessments for the feasibility of using intermediate ethanol blends in the existing vehicle fleet as a way to allow higher consumption of ethanol fuel. The National Renewable Energy Laboratory (NREL) conducted tests to evaluate the potential impacts of intermediate ethanol blends on legacy vehicles and other engines. In a preliminary report released in October 2008, the NREL presented the results of the first evaluations of the effects of E10, E15 and E20 gasoline blends on tailpipe and evaporative emissions, catalyst and engine durability, vehicle drive ability , engine operability, and vehicle and engine materials. This preliminary report found none of the vehicles displayed a malfunction indicator light as a result of the ethanol blend used; no fuel filter plugging symptoms were observed; no cold start problems were observed at 24 °C and 10 °C laboratory conditions; and as expected, all test vehicles exhibited a loss in fuel economy proportional with the lower energy density of ethanol, for example, with E20, the average reduction in fuel economy was 7.7% when compared to the miles per gallon achieved by the gasoline only (E0) test vehicles.

In March 2009, a lobbying group from the ethanol industry, Growth Energy, formally requested the U.S. Environmental

Protection Agency (EPA) to allow the ethanol content in gasoline to be increased to 15 % from 10%. Organizations doing such studies included the Energy Department, the State of Minnesota, the Renewable Fuels Association, the Rochester Institute of Technology, the Minnesota Center for Automotive Research, and Stockholm University in Sweden.

In October 2010, the EPA granted a waiver to allow up to 15% of ethanol blended with gasoline to be sold only for cars and light pickup trucks with a model year of 2007 or later, representing about 15% of vehicles on U.S. roads. In January 2011, the waiver was expanded to authorize use of E15 to include model year 2001 through 2006 passenger vehicles. The EPA also decided not to grant any waiver for E15 use in any motorcycles, heavy-duty vehicles, or nonroad engines because current testing data do not support such a waiver. According to the Renewable Fuels Association, the E15 waivers now cover 62% of vehicles on the road in the US, and the ethanol group estimates if all 2001 and newer cars and pickups were to use E15, the theoretical blend wall for ethanol use would be approximately 17.5 billion gallons (66.2 billion liters) per year. The EPA is still studying if older cars can withstand a 15% ethanol blend.

As the EPA waiver authorizes, but does not require stations to offer E15, a practical barrier to the commercialization of the higher blend is the lack of infrastructure, similar to the limitations suffered by sales of E85, as most fuel stations do not have enough pumps to offer the new blend, few existing pumps are certified to dispense E15, and no dedicated tanks are readily available to store E15. Also, some state and federal regulations would have to change before E15 can be legally sold. The National Association of Convenience Stores, which represents most gasoline retailers, considers the potential for actual E15 demand is small, "because the auto industry is not embracing the fuel and is not adjusting their warranties or recommendations for the fuel type." One possible solution to the infrastructure barriers is the introduction of blender pumps that allow consumers to turn a dial to select the level of ethanol, which would also allow owners of flexible - fuel cars to buy E85 fuel.

In June 2011 EPA, in cooperation with the Federal Trade Commission, issued its final ruling regarding the E15 warning label required to be displayed in all E15 fuel dispensers in the U.S. to inform consumers about what vehicles can, and what vehicles and equipment cannot, use the E15 blend. Both the Alliance of Automobile Manufacturers and the National Petrochemical and Refiners Association complained that relying solely on this warning label is not enough to protect consumers from misfueling . In July 2012, a fueling station in Lawrence, Kansas became the first in the U.S. to sell the E15 blend. The fuel is sold through a blender pump that allows customers to choose between E10, E15, E30 or E85, with the latter blends sold only to flexible-fuel vehicles.

In December 2010, several groups, including the Alliance of Automobile Manufacturers, the American Petroleum Institute, the Association of International Automobile Manufacturers, the National Marine Manufacturers Association, the Outdoor Power Equipment Institute, and the Grocery Manufacturers Association, filed suit against the EPA in the United States Court of Appeals for the District of Columbia Circuit. The plaintiffs argued the EPA does not have the authority to issue a “partial waiver” that covers some cars and not others. Among other arguments, the groups argued that the higher ethanol blend is not only a problem for cars, but also for fuel pumps and underground tanks not designed for the E15 mixture. It was also argued that the rise in ethanol has contributed to the big jump in corn prices in recent years . In August 2012, the federal appeals court rejected the suit against the EPA. The case was thrown out on a technical reason, as the court ruled the groups did not have legal standing to challenge EPA's decision to issue the waiver for E15.[63][64] As of November 2012, sales of E15 are not authorized in California, and according to the California Air Resources Board (CARB), the blend is still awaiting approval, and in a public statement the agency said that "*it would take several years to complete the vehicle testing and rule development necessary to introduce a new transportation fuel into California's market*."

4 - hE15

A 15 % hydrous ethanol and 85 % gasoline blend, hE15, has been introduced at public gas stations in the Netherlands since 2008. Ethanol fuel specifications worldwide traditionally dictate use of anhydrous ethanol (less than 1% water) for gasoline blending. This results in additional costs, energy usage and environmental impacts associated with the extra processing step required to dehydrate the hydrous ethanol produced via distillation (3.5- 4.9 vol.% water) to meet the current anhydrous ethanol specifications. A patented discovery reveals hydrous ethanol can be effectively used in most ethanol/gasoline blending applications.

According to the Brazilian ANP specification, hydrous ethanol contains up to 4.9 vol.% water. In hE15, this would be up to 0.74 vol.% water in the overall mixture. Japanese and German scientific evidence revealed the water is an inhibitor for corrosion by ethanol.

The experiments clearly show that water in fuel ethanol inhibits dry corrosion. At 10,000 ppm water in the E50 experiments by JARI and 3,500 ppm water in the E20 experiments by TU Darmstadt the alcoholate/alkoxide corrosion stopped. In the fuel ethanol this resembles 20,000 ppm or 2 volume% in the case of JARI and 5 x 3500 = 17,500 ppm of 1.75 volume% in the case of TU Darmstadt. The observations are in line with the fact that hydrous ethanol is known for being less corrosive than anhydrous ethanol. The reaction mechanism will be the same at lower-mid blends. When enough water is present in the fuel, the aluminum will react preferably with water to produce aluminum oxide, repairing the protective aluminum oxide layer, which is why the corrosion stops. The aluminum alcoholate / alkoxide does not make a tight oxide layer, which is why the corrosion continues. In other words, water is essential to repair the holes in the oxide layer. Based on the Japanese/German results, a minimum of 2 vol.% or 2.52 % m/m water is currently proposed in the revision of the hydrous ethanol specification for blending in petrol at E10+ levels. Water injection has additional positive effects on the engine performance (thermodynamic efficiency) and reduces overall CO2 emissions.

Overall, a transition from anhydrous to hydrous ethanol for gasoline blending is expected to make a significant contribution to ethanol's cost-competitiveness, fuel cycle net energy balance, air quality, and greenhouse gas emissions.

The level of blending above 10% (V/V) is chosen both from a technical (safety) perspective and to distinguish the product in Europe from regular unleaded petrol for reasons of taxes and customer clarity. Small-scale tests have shown many vehicles with modern engine types can run smoothly on this hydrous ethanol blend. Mixed tanking scenarios with anhydrous ethanol blends at 5% or 10% level do not induce phase separation. As avoiding mixing with E0, in particular at extremely low temperatures, in logistic systems and engines is not recommended, a separate specification for controlled usage is presented in a Netherlands Technical Agreement NTA 8115. The NTA 8115 is written for a worldwide application in trading and fuel blending. [70]

5 - E20, E25

E20 contains 20% ethanol and 80% gasoline, while E25 contains 25% ethanol. These blends have been widely used in Brazil since the late 1970s. As a response to the 1973 oil crisis, the Brazilian government made mandatory the blend of ethanol fuel with gasoline, fluctuating between 10% to 22% from 1976 until 1992. Due to this mandatory minimum gasoline blend, pure gasoline (E0) is no longer sold in Brazil. A federal law was passed in October 1993 establishing a mandatory blend of 22% anhydrous ethanol (E22) in the entire country. This law also authorized the Executive to set different percentages of ethanol within pre-established boundaries, and since 2003, these limits were fixed at a maximum of 25% (E25) and a minimum of 20% (E20) by volume. Since then, the government has set the percentage on the ethanol blend according to the results of the sugarcane harvest and ethanol production from sugarcane, resulting in blend variations even within the same year.

Since July 1, 2007, the mandatory blend was set at 25% of anhydrous ethanol (E25) by executive decree, and this has been the standard gasoline blend sold throughout Brazil most of the time as of

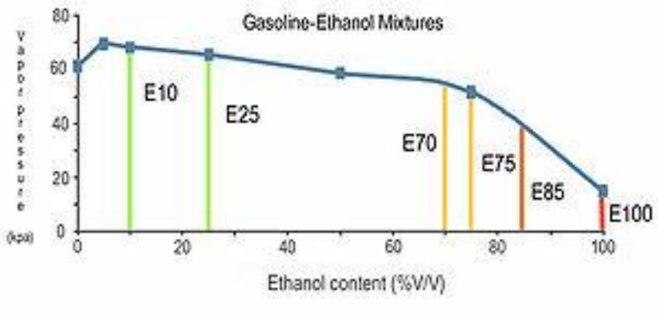
2011.[76] However, as a result of a supply shortage and the resulting high ethanol fuel prices, in 2010, the government mandated a temporary 90-day blend reduction from E25 to E20 beginning February 1, 2010. As prices rose abruptly again due to supply shortages that took place again between the 2010 and 2011 harvest seasons, some ethanol had to be imported from the United States, and in April 2011, the government reduced the minimum mandatory blend to 18%, leaving the mandatory blend range between E18 and E25.

All Brazilian automakers have adapted their gasoline engines to run smoothly with this range of mixtures, thus, all gasoline vehicles are built to run with blends from E20 to E25, defined by local law as "common gasoline type C".Some vehicles might work properly with lower concentrations of ethanol, but with a few exceptions, they are unable to run smoothly with pure gasoline, which causes engine knocking, as vehicles traveling to neighboring South American countries have demonstrated. Flex-fuel vehicles, which can run on any mixed of gasoline E20 - E25 up to 100% hydrous ethanol (E100 or hydrated ethanol) ratios, were first available in mid -2003. In July 2008, 86% of all new light vehicles sold in Brazil were flexible-fuel, and only two carmakers build models with a flex-fuel engine optimized to operate with pure gasoline (E0): Renault with the models Clio , Symbol, Logan, Sandero and Mégane, and Fiat with the Siena Tetrafuel.

Thailand introduced E20 in 2008, but shortages in ethanol supplies by mid-2008 caused a delay in the expansion of the E20 fueling station network in the country. By mid-2010, 161 fueling stations were selling E20, and sales have risen 80% since April 2009.[87] The rapid growth in E20 demand is because most vehicle models launched since 2009 were E20-compatible, and sales of E20 are expected to grow faster once more local automakers start producing small, E20 - compatible, fuel - efficient cars. The Thai government is promoting ethanol usage through subsidies, as ethanol costs four baht a liter more than gasoline.

A state law approved in Minnesota in 2005 mandates that ethanol comprise 20 % of all gasoline sold in this American state beginning in 2013. Successful tests have been conducted to determined the performance under E20 by current vehicles and fuel dispensing equipment designed for E10.

6 - E70 , E75



When the vapor pressure in the ethanol blend drops below 45 kPa, fuel ignition cannot be guaranteed on cold winter days, limiting the maximum ethanol blend percentage during the winter months to E75.

E70 contains 70 % ethanol and 30% gasoline, while E75 contains 75% ethanol. These winter blends are used in the United States and Sweden for E85 flexible-fuel vehicles during the cold weather, but still sold at the pump labeled as E85. The seasonal reduction of the ethanol content to an E85 winter blend is mandated to avoid cold starting problems at low temperatures.

In the US, this seasonal reduction of the ethanol content to E70 applies only in cold regions, where temperatures fall below 0 °C during the winter. In Wyoming for example, E70 is sold as E85 from October to May. In Sweden, all E85 flexible - fuel vehicles use an E75 winter blend. This blend was introduced since the winter 2006-07 and E75 is used from November until March.

For temperatures below − 15 °C , all E85 flex vehicles require an engine block heater to avoid cold starting problems. The use of this device is also recommended for gasoline vehicles when temperatures drop below − 23 °C . Another option when extreme cold weather is expected is to add more pure gasoline in the tank, thus reducing the ethanol content below the E70 winter blend, or simply not to use E85 during extreme low temperature spells.

7 - E85

E85, a mixture of 85 % ethanol and 15 % gasoline, is generally the highest ethanol fuel mixture found in the United States and several European countries, particularly in Sweden, as this blend is the standard fuel for flexible-fuel vehicles. This mixture has an octane rating of about 105, which is significantly lower than pure ethanol, but still higher than normal gasoline (87-95 octane, depending on country).

E85™
85% Ethanol

Logo used in the United States for E85 fuel

The 85% limit in the ethanol content was set to reduce ethanol emissions at low temperatures and to avoid cold starting problems during cold weather, at temperatures lower than 11 °C . A further reduction in the ethanol content is used during the winter in regions where temperatures fall below 0 °C and this blend is called Winter E85, as the fuel is still sold under the E85 label. A winter blend of E70 is mandated in some regions in the US, while Sweden mandates E75.

As of October 2010, nearly 3,000 E85 fuel pumps were in Europe, led by Sweden with 1,699 filling stations. The United States had 2,414 public E85 fuel pumps located in 1,701 cities by October 2010, mostly concentrated in the Midwest.

Thailand introduced E85 fuel by the end of 2008, and by mid-2010, only four E85 filling stations were available, with plans to expand to 15 stations by 2012.

8 - ED 95

ED 95 designates a blend of 95 % ethanol and 5% ignition improver; it is used in modified diesel engines where high compression is used to ignite the fuel , as opposed to the operation of gasoline engines, where spark plugs are used. This fuel was developed by Swedish ethanol producer SEKAB. Because of the high ignition temperatures of pure ethanol, the addition of ignition improver is necessary for successful diesel engine operation. A diesel engine running on ethanol also has a higher compression ratio and an adapted fuel system.

ED95 Bus in Sweden running on a modified diesel engine

This fuel has been used with success in many Swedish Scania buses since 1985, which has produced around 700 ethanol buses, more than 600 of them to Swedish cities, and more recently has also delivered ethanol buses for commercial service in Great Britain, Spain, Italy, Belgium, and Norway. As of June 2010 Stockholm has the largest ethanol ED95 bus fleet in the world.

As of 2010, the Swedish ED95 engine is in its third generation and already has complied with Euro 5 emission standards, without any kind of post-treatment of the exhaust gases. The ethanol-powered engine is also being certified as environmentally enhanced vehicle (EEV) in the Stockholm municipality. The EEV rule still has no date to enter into force in Europe and is stricter than the Euro 5 standard.

Nottingham became the first city in England to operate a regular bus service with ethanol-fueled vehicles. Three ED95 single-deck buses entered regular service in the city in March 2008. Soon after, Reading also introduced ED95 double-deck buses.

Under the auspices of the Bio Ethanol for Sustainable Transport project, more than 138 bio ethanol ED95 buses were part of demonstration trial at four cities, three in Europe, and one in Brazil, between 2006 and 2009. A total of 127 ED95 buses operated in Stockholm, five buses operated in Madrid, three in La Spezia, and one in Brazil.[2] In Brazil, the first Scania ED95 bus with a modified diesel engine was introduced as a trial in São Paulo city on December 2007, and since November 2009, two ED95 buses were in regular service. The Brazilian trial project ran for three years and performance and emissions were monitored by the National Reference Center on Biomass .

In November 2010, the municipal government of São Paulo city signed an agreement with UNICA, Cosan, Scania and *Viação Metropolitana*, a local bus operator, to introduced a fleet of 50 ethanol-powered ED95 buses by May 2011. Scania manufactures the bus engine and chassis in its plant located in São Bernardo do Campo, São Paulo, using the same technology and fuel as the ED95 buses already operating in Stockholm. The bus body is a Brazilian CAIO. The first ethanol-powered buses were delivered in May 2011, and the 50 buses will start regular service in June 2011 in the southern region of São Paulo. The 50 ED95 buses had a cost of R $ 20 million (US $ 12.3 million) and due to the higher cost of the ED95 fuel and the lower energy content of ethanol as compared to diesel, one of the firms participating in the cooperation agreement, Raísen supplies the fuel to the municipality at 70 % of the market price of regular diesel.

9 - E100

100 is pure ethanol fuel. Straight hydrous ethanol as an automotive fuel has been widely used in Brazil since the late 1970s for neat ethanol vehicle sand more recently for flexible-fuel vehicles. The ethanol fuel used in Brazil is distilled close to the azeotrope mixture of 95.63 % ethanol and 4.37 % water (by weight) which is approximately 3.5 % water by volume. The azeotrope is the highest concentration of ethanol that can be achieved by distillation. The

maximum water concentration according to the ANP specification is 4.9 vol.% (approximately 6.1 weight %) The E nomenclature is not adopted in Brazil, but hydrated ethanol can be tagged as E100, meaning it does not have any gasoline, because the water content is not an additive, but rather a residue from the distillation process. However, straight hydrous ethanol is also called E95 by some authors.

The first commercial vehicle capable of running on pure ethanol was the Ford Model T, produced from 1908 through 1927. It was fitted with a carburetor with adjustable jetting, allowing use of gasoline or ethanol, or a combination of both . At that time, other car manufacturers also provided engines for ethanol fuel use.[96] Thereafter, and as a response to the 1973 and 1979 energy crises, the first modern vehicle capable of running with pure hydrous ethanol (E100) was launched in the Brazilian market, the Fiat 147, after testing with several prototypes developed by the Brazilian subsidiaries of Fiat, Volkswagen, General Motors and Ford. As of September 2012, there were 1.1 million neat ethanol vehicles still in use in Brazil. Since 2003, Brazilian newer flex-fuel vehicles are capable of running on pure hydrous ethanol (E100) or blended with any combination of E20 to E25 gasoline (a mixture made with anhydrous ethanol), the national mandatory blend. As of September 2012, there were 17.1 million flexible - fuel vehicles running on Brazilian roads.

E100 imposes a limitation on normal vehicle operation, as ethanol's lower evaporative pressure (as compared to gasoline) causes problems when cold starting the engine at temperatures below 15 °C . For this reason, both pure ethanol and E100 flex-fuel vehicles are built with an additional small gasoline reservoir inside the engine compartment to help in starting the engine when cold by initially injecting gasoline. Once started, the engine is then switched back to ethanol. An improved flex-fuel engine generation was developed to eliminate the need for the secondary gas tank by warming the ethanol fuel during starting, and allowing them to start at temperatures as low as −5 °C , the lowest temperature expected anywhere in the Brazilian territory. The Polo E-Flex, launched in March 2009, was the first flex-fuel model without an auxiliary tank for cold start. The warming system, called Flex Start, was developed by Robert Bosch GmbH.

Swedish carmakers have developed ethanol-only capable engines for the new Saab Aero X BioPower 100 Concept E100, with a V6 engine which is fuelled entirely by E100 bio ethanol , and the limited edition of the Koenigsegg CCXR, a version of the CCX converted to use E85 or E100, as well as standard 98-octane gasoline, and currently the fastest and most powerful flex-fuel vehicle with its twin-supercharged V8 producing 1018 hp when running on bio fuel, as compared to 806 hp on 91-octane unleaded gasoline.

The higher fuel efficiency of E100 (compared to methanol) in high performance race cars resulted in Indianapolis 500 races in 2007 and 2008 being run on 100% fuel-grade ethanol.

10 - Use limitations

10 – 1 - Modifications to engines

The use of ethanol blends in conventional gasoline vehicles is restricted to low mixtures, as ethanol is corrosive and can degrade some of the materials in the engine and fuel system. Also, the engine has to be adjusted for a higher compression ratio as compared to a pure gasoline engine to take advantage of ethanol's higher oxygen content, thus allowing an improvement in fuel efficiency and a reduction of tailpipe emissions. The following table shows the required modifications to gasoline engines to run smoothly and without degrading any materials. This information is based on the modifications made by the Brazilian automotive industry at the beginning of the ethanol program in that country in the late 1970s, and reflects the experience of Volkswagen do Brasil.

10 – 2 - Other disadvantages

Disadvantages to ethanol fuel blends when used in engines designed exclusively for gasoline include lowered fuel mileage, metal corrosion, deterioration of plastic and rubber fuel system components, clogged fuel systems, fuel injectors, and carburetors, de lamination of composite fuel tanks, varnish buildup on engine parts, damaged or destroyed internal engine components, water absorption, fuel phase separation, and shortened fuel storage life. Many major auto, marine, motorcycle, lawn equipment, generator, and other internal combustion engine manufacturers have issued warnings and precautions about the use of ethanol-blended gasolines of any type in their engines, and the Federal Aviation Administration and major aviation engine manufacturers have prohibited the use of automotive gasolines blended with ethanol in light aircraft due to safety issues from fuel system and engine damage.

E 85

Logo used in the United States for E85 fuel

Contents

1 - Introduction

E85 is an abbreviation for an ethanol fuel blend of up to 85 % denatured ethanol fuel and gasoline or other hydrocarbon by volume. E85 is commonly used by flex-fuel vehicles in the United States and Europe. In the United States, government subsidies of ethanol in general and E85 in particular has encouraged a growing infrastructure for retail sale of E85, especially in corn growing states in the Midwest.

E85 allegedly has a number of advantages over conventional gasoline. One claimed advantage is a reduction in tailpipe emissions, if one disregards that E85 increases the emissions of acetaldehyde in vehicles.[1] Another advantage is a highly effective octane rating, reducing engine heat and wear, and increasing engine performance if an engine is tuned to run on E85, or able to automatically adjust to higher octane fuel. Because the ethanol component effectively displaces fossil fuels with energy harvested from renewable sources, in theory E85 is less carbon intensive than petroleum. Additionally, there is a greater potential for localized production of ethanol in agricultural areas and using waste materials. Also, a diversification of fuel sources reduces dependence on a particular type of fuel and may increase stability of supply.

Current factory-made E85 vehicles do not deliver as much fuel economy as gasoline vehicles. Some critics of flex-fuel vehicles claim that ethanol can produce fuel economy similar to that observed in gasoline engines, but automotive manufacturers fail to do the things that are necessary to do so .

2 - Controversy

2 - 1 - Corrosion debate

There is vehement debate regarding issues with fuel systems and E85. Allegedly, due to chemical differences between E85 and gasoline, fuel systems and engines not designed or modified to use E85 suffer increased wear and may fail prematurely. However, some researchers come to the opposite conclusion .

There is no disagreement that some of the environmental and social benefits of ethanol, and therefore E85, are highly dependent on raw materials used to produce the fuel. However, there is great disagreement as to ethanol's role in the pricing and availability of those raw materials.

2 – 2 - Food vs. fuel

Ethanol critics contend that production of ethanol from corn drives up world food prices, causing corn to be un affordable , or even unavailable at all. Ethanol advocates counter that allegation by pointing out that over 93 % of all corn grown in the U.S. is never fed to people, but is instead used as livestock feed. As livestock cannot digest starch efficiently, and dried corn is mostly starch, livestock do not digest much of the starch at all, and it is simply transformed into fecal matter , or manure , not meat , eggs , or milk. U.S. farmers grow more corn every year than people can buy; there is an annual surplus of corn in the U.S .

Ethanol advocates say that corn prices have increased due to manipulation of the commodities markets and because American corn companies sell more and more U.S.-grown corn to Mexico and China, creating more competition for corn buyers, and driving up its price. E85 critics contend that ethanol producers may not reduce carbon emissions, due to the petroleum and natural gas used in raising corn and refining it. E85 advocates reply by pointing to ethanol producers who do not do so, but instead use E85 or biodiesel fuel to transport E85, and use biomass as a heat source for the distillation of ethanol instead of petro-products like natural gas.

Some say that ethanol produced from waste materials or fast growing non-food crops such as switch grass is much more beneficial, but not yet economically practical at large scale. Others say that the world can easily replace all of its use of petroleum by simply making ethanol from the many crops that yield more ethanol per acre than corn yields, with existing technology, not future technology (Footnote 26), and that certain elements in the cellulosic ethanol field are more interested in patent rights than in producing the greatest amount of ethanol at the lowest price point.

3 - Availability and price

3 – 1 - North America

E85 is increasingly common in the United States, mainly in the Midwest where corn is a major crop and is the primary source material for ethanol-fuel production. As of November 7, 2012, there are over 2,400 gas stations that offer E85 fuel, according to Growth Energy, an enterprise which facilitates the offering of E85 and a service for finding E85 stations .

Prices vary by location: some prices were over 30 % less than regular gasoline; in other places it is only slightly less expensive.

3 – 2 - Europe

E85 as a fuel is widely used in Sweden; however, most of it is imported from Italy and Brazil.

E85 was formerly available from the Maxol chain in Ireland, where it was made from whey, a byproduct of cheese manufacturing. The availability ended in 2011, due to a severe excise-duty hike which rendered it economically unviable.

In Finland E85 is available from 26 St1 chain locations in Alavieska, Espoo, Helsinki, Hämeenlinna, Kajaani, Kemi, Keuruu, Kokkola, Kuopio, Lahti, Luumäki, Mustasaari, Mäntsälä, Pori, Porvoo, Raisio, Tampere, Turku, Vaasa and Vantaa.[3] The E85 sold by St1 is labeled as RE85 to indicate it is manufactured from bio-waste.

4 - Use in flexible - fuel vehicles

E85 ethanol is used in engines modified to accept higher concentrations of ethanol. Such flexible - fuel vehicles (FFV) are designed to run on any mixture of gasoline or ethanol with up to 85% ethanol by volume. There are a few major differences between FFVs and non-FFVs. One is the elimination of bare magnesium, aluminum, and rubber parts in the fuel system. Another is that fuel pumps must be capable of operating with electrically conductive ethanol instead of non-conducting dielectric gasoline fuel. Fuel-injection control systems have a wider range of pulse widths to inject approximately 34% more fuel. Stainless steel fuel lines, sometimes lined with plastic, and stainless-steel fuel tanks in place of terne fuel tanks are used. In some cases, FFVs use acid-neutralizing motor oil. For vehicles with fuel-tank-mounted fuel pumps, additional differences to prevent arcing, as well as flame arrestors positioned in the tank's fill pipe, are also sometimes used.

5 - Fuel economy

Ethanol promoters contend that automotive manufacturers currently fail to equal the fuel economy of gasoline because they fail to take advantages of characteristics which are superior in ethanol-based fuel blends. (Footnotes 19,20). They claim that some ethanol engines have already produced 22% more miles per gallon than identical gasoline engines (Footnote 19). Some critics of flex-fuel vehicles say that they fail to match gasoline fuel economy because flex-fuel vehicles are inadequate, not because E85 cannot deliver as much fuel economy.

Ethanol promoters claim that today's flex-fuel vehicles are much too inexact in measuring the ethanol content because car companies will not pay the high patent royalties demanded for fuel content sensors. They state that some flex-fuel vehicles have used wastefully high-flow fuel injectors which are not necessary and waste fuel all the time on either fuel. They state that flex-fuel systems also spray too much E85, and waste fuel in consequence. The technical term is "excessive fuel pulse width modulation". Other ethanol advocates also state that it is a mistake to base ethanol engine design on gasoline engine design, but that ethanol engines should be based on diesel engine design parameters instead. Using this approach, the EPA has produced an ethanol-only engine which achieves much higher brake thermal efficiency levels than gasoline engines achieve .

In contrast, ethanol critics contest the benefits of E85 by focusing on the fact that E85 has 33 % less energy content than "pure" gasoline (and 30% less than the E10 gasohol blend that is sold by almost all retailers in the US). Depending on the vehicle, this can result in a notable reduction in fuel economy and means that, in factory-made flex-fuel vehicles, while E85 is cheaper than gasoline per *gallon*, per *mile* it is far more expensive.

If ethanol advocates are correct, many flex-fuel vehicles fail to equal the mileage of gasoline-only engines because they do not preheat ethanol-blend fuels, or radically advance ignition timing for those fuels, or increase engine compression for E85 fuel , not because E85 contains less energy than gasoline. fuel economy is reduced for most factory-made FFVs (flexible-fuel vehicles) by about 20 to 30% when operated on E85 (summer blend). The Environmental Protection

Agency states on its website that several of the most current factory-made FFVs are still losing 25% fuel efficiency when running on E85.

For factory-made FFVs, more E85 is typically needed to do the same work as can be achieved with a lesser volume of gasoline. This difference is sometimes offset by the lower cost of the E85 fuel, depending on E85's current price discount relative to the current price of gasoline. As described earlier, the best thing for drivers to do is to record fuel usage with both fuels and calculate cost/distance for them. Only by doing that can the end-user economy of the two fuels be compared. For example, an existing pre-2003-model-year American-made FFV vehicle that normally achieves, say, 30 MPG on pure gasoline will typically achieve about 22 MPG, or slightly better, on E85 (summer blend.) When operated on E85 winter blend, which is actually E70 (70% ethanol, 30% gasoline), fuel economy will be higher than when operating on the summer blend.

To achieve any short-term operational fuel-cost savings, the price of E85 should therefore be 20% or more below the price of gasoline to equalize short term fuel costs for most older pre-2003 FFVs for both winter and summer blends of E85, which it typically is. Life-cycle costs over the life of the FFV engine are theoretically lower for E85, as ethanol is a cooler-and-cleaner burning fuel than gasoline. Provided that one takes a long-term life-cycle-operating-cost view, a continuous price discount of 20% to 25% below the cost of gasoline is probably about the break-even point in terms of vehicle life-cycle operating costs for operating most FFVs on E85 exclusively (for summer, spring / fall, and winter blends).

Fuel economy in fuel-injected non-FFVs operating on a mix of E85 and gasoline varies greatly depending on the engine and fuel mix. For a 60:40 blend of gasoline to E85 (summer blend), a typical fuel-economy reduction of around 23.7 % resulted in one person's[*who?*] carefully executed experiment with a 1998 Chevrolet S10 pickup with a 2.2L 4-cylinder engine, relative to the fuel economy achieved on pure gasoline. Similarly, for a 50 : 50 blend of gasoline to E85 (summer blend), a typical fuel - economy reduction of around 25%

resulted for the same vehicle. (Fuel-economy performance numbers were measured on a fixed commute of approximately 110 miles (180 km) roundtrip per day, on a predominantly freeway commute, running at a fixed speed (62 mph), with cruise control activated, air conditioning ON, at sea level, with flat terrain, traveling to/from Kennedy Space Center, FL). It is important to note, however, that if the engine had been specifically tuned for consumption of ethanol (higher compression, different fuel-air mixture, etc.) the mileage would have been much better than the results above. The aforementioned fact leads some to believe that the "FFV" engine is more of an infant technology rather than fully mature.

The amount of reduction in mileage, therefore, is highly dependent upon the particulars of the vehicle design, exact composition of the ethanol-gasoline blend, and state of engine tune (primarily fuel-air mixture and compression ratio). In order to offset this change in fuel economy there has been much legislation passed to subsidize the cost. The American Jobs Creation Act of 2004 created the Volumetric Ethanol Excise Tax Credit (VEETC) to subsidize the production costs. In 2008, the 2008 Farm Bill changed the 51-cent tax credit provided by VEETC to 45 cents. There have been other measures taken by congress to jump start ethanol production. For instance, the 2004 VEETC bill provided for a Small Ethanol Producer Tax Credit which gave tax credits to small ethanol producers. More recently the Tax Relief, Unemployment Insurance Reauthorization, and Job Creation Act of 2010 extended the tax cuts allowed by VEETC that were set to expire at the end of 2010 until the end of 2012.

So in order to save money at the pump with current flex-fuel vehicles available in the United States, the price of E85 must be much lower than gasoline. E85 was at least 20% less expensive in most areas, as recently as 2011. However as of March 2012, the difference in the retail price between E85 and gasoline is 15% or less in the vast majority of the United States. E85 also gets less MPG, at least in flex-fuel vehicles. In one test, a Chevy Tahoe flex-fuel vehicle averaged 18 MPG [U.S. gallons] for gasoline and 13 MPG for E85, or 28%

fewer MPG than gasoline. In that test, the cost of gas averaged $3.42, while the cost for E85 averaged $ 3.09, or 90 % of the cost of gasoline. In another test, however, a fleet of Ford Tauruses averaged only about 6% fewer miles per gallon in the ethanol-based vehicles as compared to traditional, gas-powered Tauruses.

6 - Octane and performance

E85 fuel dispenser at a regular gasoline station.

Alcohol fuels reach their peak torque a bit more quickly than gasoline does, so any vehicle that receives a very basic conversion to be able to run on E85 will be very slightly faster on E85.

As more effort is put into maximizing an engine to take advantage of E85's higher "octane", engines achieve greater power advantages. One car that has higher power on ethanol is the Koenig egg CCXR, which on ethanol is the third-most powerful production car, with 20% more hp on E85 than on gasoline. According to the manufacturer, this is due to the cooling properties of ethanol.E85 has an octane rating higher than that of regular gasoline's typical rating of 87, or premium gasoline's 91-93. This allows it to be used in higher-compression engines, which tend to produce more power per unit of displacement than their gasoline counterparts. The Renewable Fuels Foundation states in its *Changes in Gasoline IV* manual, "There is no requirement to post octane on an E85 dispenser. If a retailer chooses to post octane, they should be aware that the often cited 105 octane is incorrect. This number was derived by using ethanol’s blending octane value in gasoline. This is not the proper way to calculate the octane of E85. Ethanol’s true octane value should be used to calculate E85’s octane value. This results in an octane range of 94-96 (R+M)/2. These calculations have been confirmed by actual-octane engine tests."

Examples of this mis-citation can be found at the Iowa Renewable Fuels Association titled "E85 Facts" which cites a range of 100-105, and a document at the Texas State Energy Conservation Office titled "Ethanol" , which cites a 113 rating.

Use of E85 in an engine designed specifically for gasoline would result in a loss of the potential efficiency that it is possible to gain with this fuel. Use of gasoline in an engine with a high enough compression ratio to use E85 efficiently would likely result in catastrophic failure due to engine detonation, as the octane rating of gasoline is not high enough to withstand the greater compression ratios in use in an engine specifically designed to run on E85. (However, Flex Fuel Vehicles are designed to run on any mixture of gasoline and ethanol, from pure gasoline to E85, and avoid this problem.) Using E85 in a gasoline engine has the drawback of achieving lower fuel economy, as more fuel is needed per unit air (stoichiometric ratio) to run the engine in comparison with gasoline. The additional ethanol required for a stoichiometric fuel ratio helps compensate for lack of energy provided by ethanol's lower heating value (LHV), which is lower than the LHV of gasoline.

Some vehicles can actually be converted to use E85 despite not being specifically built for it. Because of the lower heating value E85 has a cooler intake charge — which, coupled with its high stability level from its high octane rating — has also been used as a "power adder" in turbocharged performance vehicles. These modifications have not only resulted in lower GHG emissions, but also resulted in 10 - 12 % power and torque increase at the wheels. Because of its low price (less than $ 2.00 / gal in some places) and high availability in certain areas people have started to turn to using it in place of high-end racing fuels, which typically cost over $ 10.00 / gal.

E85 consumes more fuel in flex-fuel type vehicles when the vehicle uses the same compression ratio for both E85 and gasoline, because of its lower stoichiometric fuel ratio and lower heating value. European car maker Saab, now defunct, produced a flex-fuel version of their 9 - 5 sedan, which consumes the same amount of fuel whether running E85 or gasoline.

7 - Emissions

When environmentalists concern themselves with emissions from combustion engines there are four primary types of pollutants scientists study. These emissions are hydrocarbons (HC), oxides of nitrogen (NO_x), carbon monoxide (CO) and carbon dioxide (CO_2). Because E85 is predominantly ethanol the tailpipe emissions are much different than that of regular gasoline. There have been numerous studies done to compare and contrast the different emissions and the effects these emissions have on the environment but the tests have been inconclusive. The tests have shown very little consistency if any at all because there are too many variables involved. The make and model of the vehicle, the way in which the ethanol was produced and the vehicles overall fuel efficiency all play a large role in the overall outcome of each study.[16] To address the problem of inaccuracy, engineers at the National Renewable Energy Laboratory combined data from all applicable emissions studies and compiled them into one data set. This compiled set of data showed that on average all emissions that are federally regulated showed a decrease or no statistically relevant difference between E85 and gasoline.

EPA's stringent tier-II vehicle emission standards require that FFVs achieve the same low emissions level regardless of whether E85 or gasoline is used. However, E85 can further reduce emissions of certain pollutants as compared to conventional gasoline or lower-volume ethanol blends. For example, E85 is less volatile than gasoline or low-volume ethanol blends, which results in fewer evaporative emissions. Using E85 also reduces carbon-monoxide emissions and provides significant reductions in emissions of many harmful toxics, including benzene, a known human carcinogen. However, E85 also increases emissions of acetaldehyde. EPA is conducting additional analysis to expand our understanding of the emissions impacts of E85.

Hydrogen Fuel

Contents

1 - Introduction

Hydrogen fuel is a zero - emission fuel which uses electro chemical cells, or combustion in internal engines, to power vehicles and electric devices. It is also used in the propulsion of spacecraft and can potentially be mass produced and commercialized for passenger vehicles and aircraft.

2 - Chemistry

Hydrogen is the first element on the periodic table, making it the lightest element on earth. It is also the most abundant element on the planet. However, since hydrogen gas is so light, it rises in the atmosphere and is there fore rarely found in its pure form, H_2 . In a flame of pure hydrogen gas, burning in air, the hydrogen (H_2) reacts with oxygen (O_2) to form water (H_2O) and releases heat. Other than water, hydrogen combustion may yield small amounts of nitrogen oxides.

Combustion heat enables hydrogen to act as a fuel. Nevertheless, hydrogen is an energy carrier, like electricity, not an energy resource. Energy firms must first produce the hydrogen gas, and that production induces environmental impacts . Hydrogen production always requires more energy than can be retrieved from the gas as a fuel later on . This is a limitation of the physical law of the conservation of energy.

Hydrogen lies in the first group and first period in the periodic table. Hydrogen is neither a metal nor a non metal but still is considered as non metal. It acts as a metalloid when compressed to high densities.

3 - Manufacturing

Because pure hydrogen does not occur naturally, it takes energy to manufacture it. There are different ways to manufacture it, such as , electrolysis and steam - methane reforming process. In electrolysis, electricity is run through water to separate the hydrogen and oxygen atoms. This method can be used by using wind, solar, geothermal, hydro, fossil fuels, biomass, and many other resources.[2] The more natural methods of making electricity (wind, solar, hydro, geothermal, biomass), rather than fossil fuels, would be better used as to continue the environment-friendly process of the fuel. Obtaining hydrogen from this process is being studied as a viable way to produce it domestically at a low cost. Steam-methane reforming process extracts the hydrogen from methane. However, this reaction causes a side production of carbon dioxide and carbon monoxide which are greenhouse gases and contribute to global warming . Even so, the current leading technology for producing hydrogen in large quantities is steam reforming of methane gas (CH_4). Other methods are discussed in the Hydrogen Production article.

4 - Energy

Once manufactured, hydrogen is an energy carrier (i.e. a store for energy first generated by other means). The energy is eventually delivered as heat when the hydrogen is burned. The heat in a hydrogen flame is a radiant emission from the newly formed water molecules. The water molecules are in an excited state on initial formation and then transition to a ground state; the transition unleashing thermal radiation. When burning in air, the temperature is roughly 2000°C.

5 - Uses

Hydrogen fuel can provide motive power for cars, boats and airplanes, portable fuel cell applications or stationary fuel cell applications, which can power an electric motor.

With regard to safety from unwanted explosions, hydrogen fuel in automotive vehicles is at least as safe as gasoline. ”

Indirect Land Use Change Impacts of Bio Fuels

Amazon rainforest.

Brazilian cerrado.

Contents

1 - Introduction

The indirect land use change impacts of bio fuels, also known as ILUC, relates to the unintended consequence of releasing more carbon emissions due to land - use changes around the world induced by the expansion of croplands for ethanol or biodiesel production in response to the increased global demand for bio fuels.

As farmers worldwide respond to higher crop prices in order to maintain the global food supply- and - demand balance, pristine lands are cleared to replace the food crops that were diverted elsewhere to bio fuels production. Because natural lands, such as rainforests and grasslands, store carbon in their soil and biomass as plants grow each year, clearance of wilderness for new farms translates to a net increase in greenhouse gas emissions. Due to this change in the carbon stock of the soil and the biomass, indirect land use change has consequences in the GHG balance of a bio fuel.

Other authors have also argued that indirect land use changes produce other significant social and environmental impacts, affecting biodiversity, water quality, food prices and supply, land tenure, worker migration, and community and cultural stability.

2 - History

The estimates of carbon intensity for a given bio fuel depend on the assumptions regarding several variables. As of 2008, multiple full life cycle studies had found that corn ethanol, cellulosic ethanol and Brazilian sugarcane ethanol produce lower greenhouse gas emissions than gasoline. None of these studies, however, considered the effects of indirect land-use changes, and though land use impacts were acknowledged, estimation was considered too complex and difficult to model. A controversial paper published in February 2008 in Scienc express by a team led by Searchinger from Princeton University concluded that such effects offset the (positive) direct effects of both corn and cellulosic ethanol and that Brazilian sugarcane performed better, but still resulted in a small carbon debt.

Malaysian cloud forest

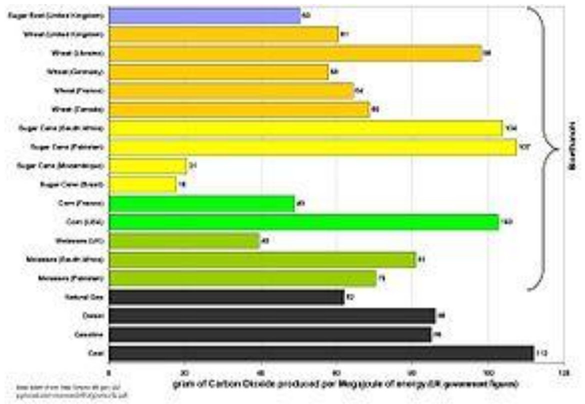
After the Searchinger team paper, estimation of carbon emissions from ILUC, together with the food vs. fuel debate, became one of the most contentious issues relating to bio fuels, debated in the popular media, scientific journals, op - eds and public letters from the scientific community, and the ethanol industry, both American and Brazilian. This controversy intensified in April 2009 when the California Air Resources Board (CARB) set rules that included ILUC impacts to establish the California Low- Carbon Fuel Standard that entered into force in 2011.

In May 2009 U.S. Environmental Protection Agency (EPA) released a notice of proposed rulemaking for implementation of the 2007 modification of the Renewable Fuel Standard (RFS). EPA's proposed regulations also included ILUC, causing additional controversy among ethanol producers. EPA's February 3, 2010 final rule incorporated ILUC based on modeling that was significantly improved over the initial estimates.

The UK Renewable Transport Fuel Obligation program requires the Renewable Fuels Agency (RFA) to report potential indirect impacts of bio fuel production, including indirect land use change or changes to food and other commodity prices. A July 2008 RFA study, known as the Gallager Review, found several risks and uncertainties, and that the "quantification of GHG emissions from indirect land-use change requires subjective assumptions and contains considerable uncertainty", and required further examination to properly incorporate indirect effects into calculation methodologies. A similarly cautious approach was followed by the European Union. In December 2008 the European Parliament adopted more stringent sustainability criteria for bio fuels and directed the European Commission to develop a methodology to factor in GHG emissions from indirect land use change.

3 - Studies and controversy

Before 2008, several full life cycle ("Well to Wheels" or WTW) studies had found that corn ethanol reduced transport-related greenhouse gas emissions. In 2007 a University of California, Berkeley team led by Farrel evaluated six previous studies, concluding that corn ethanol reduced GHG emissions by only 13 percent. However, 20 to 30 percent reduction for corn ethanol, and 85 to 85 percent for cellulosic ethanol, both figures estimated by Wang from Argonne National Laboratory, are more commonly cited. Wang reviewed 22 studies conducted between 1979 and 2005, and ran simulations with Argonne's GREET model. These studies accounted for direct land use changes. Several studies of Brazilian sugarcane ethanol showed that sugarcane as feedstock reduces GHG by 86 to 90 percent given no significant land use change. Estimates of carbon intensity depend on crop productivity, agricultural practices, power sources for ethanol distilleries and the energy efficiency of the distillery. None of these studies considered ILUC, due to estimation difficulties. Preliminary estimates by Delucchi from the University of California, Davis, suggested that carbon released by new lands converted to agricultural use was a large percentage of life-cycle emissions.



UK figures for the carbon intensity of bio ethanol and fossil fuels. Graph assumes all bio ethanols are burnt in country of origin and prior cropland was used to grow feedstock. No ILUC effects were included.

3 – 1 - Searchinger and Fargione studies

In February 2008 Searchinger concluded that ILUC affects the life cycle assessment and that instead of saving, both corn and cellulosic ethanol increased carbon emissions as compared to gasoline by 93 and 50 percent respectively. Ethanol from Brazilian sugarcane performed better, recovering initial carbon emissions in 4 years, while U.S. corn ethanol required 167 years and cellulosic ethanol required a

52 years payback period. The study limited the analysis a 30 year period, assuming that land conversion emits 25 percent of the carbon stored in soils and all carbon in plants cleared for cultivation. Brazil, China, and India were considered among the overseas locations where land use change would occur as a result of diverting U.S. corn cropland, and it was assumed that new cropland in each of these regions correspond to different types of forest, savanna or grassland based on the historical proportion of each converted to cultivation in these countries during the 1990s.

Fargione and his team published a separate paper in the same issue of Science express claiming that clearing lands to produce bio fuel feedstock created a carbon deficit. This deficit applies to both direct and indirect land use changes. The study examined six conversion scenarios: Brazilian Amazon to soybean biodiesel, Brazilian Cerrado to soybean biodiesel, Brazilian Cerrado to sugarcane ethanol, Indonesian or Malaysian lowland tropical rainforest to palm biodiesel, Indonesian or Malaysian peatland tropical rainforest to palm biodiesel, and U.S. Central grassland to corn ethanol. The carbon debt was defined as the amount of CO_2 released during the first 50 years of this process of land conversion. For the two most common ethanol feed stocks, the study found that sugarcane ethanol produced on natural cerrado lands would take ~17 years to repay its carbon debt, while corn ethanol produced on U.S. central grasslands would result in a repayment time of ~93 years. The worst-case scenario is converting Indonesian or Malaysian tropical peatland rainforest to palm biodiesel production, which would require ~420 years to repay.

3 - 1 – 1 - Criticism and controversy

The Searchinger and Fargione studies created controversy in both the popular media and in scientific journals. Wang and Haq from Argonne National Laboratory claiming: the assumptions were outdated; they ignored the potential of increased efficiency; and no evidence showed that "U.S. corn ethanol production has so far caused indirect land use in other countries." They concluded that Searchinger demonstrated that ILUC "is much more difficult to model than direct land use changes" . In his response Searchinger rebutted each technical objection and asserted that "... any calculation that ignores these emissions, however challenging it is to predict them with certainty, is too incomplete to provide a basis for policy decisions."

Another criticism, by Kline and Dale from Oak Ridge National Laboratory, held that Searchinger et al. and Fargione et al. "... do not provide adequate support for their claim that bio fuels cause high emissions due to land-use change", as their conclusions depends on a misleading because more comprehensive field research found that these land use changes "... are driven by interactions among cultural, technological, biophysical, economic, and demographic forces within a spational and temporal contest rather than by a single crop market". Fargione et al. responded in part that although many factors contributed to land clearing, this "observation does not diminish the fact that bio fuels also contribute to land clearing if they are produced on existing cropland or on newly cleared lands". Searching disagreed with all of Kline and Dale arguments.

The U.S. bio fuel industry also reacted, claiming that the "Searchinger study is clearly a 'worst case scenario' analysis ..." and that this study "relies on a long series of highly subjective assumptions ..." Searchinger rebutted each claim, concluding that NFA's criticisms were invalid. He noted that even if some of his assumptions are high estimates, the study also made many conservative assumptions.

	
Cattle ranching in Brazil.	*Slash and burn forest removal in Brazil.*

3 - 2 - Brazil

In February 2010 Lapola estimated that planned expansion of Brazilian sugarcane and soybean bio fuel plantations through 2020 would replace rangeland, with small direct land-use impact on carbon emissions. However, the expansion of the rangeland frontier into Amazonian forests, driven by cattle ranching would indirectly offset the savings. "Sugarcane ethanol and soybean biodiesel each contribute to nearly half of the projected indirect deforestation of 121,970 km^2 by 2020, creating a carbon debt that would take about 250 years to be repaid...."

The research also found that oil palm would cause the least land-use changes and associated carbon debt. The analysis also modeled livestock density increases and found that "a higher increase of 0.13 head per hectare in the average livestock density throughout the country could avoid the indirect land-use changes caused by bio fuels (even with soybean as the biodiesel feedstock), while still fulfilling all food and bio energy demands." The authors conclude that intensification of cattle ranching and concentration on oil palm are required to achieve effective carbon savings, recommending closer collaboration between the bio fuel and cattle-ranching sectors.

The main Brazilian ethanol industry organization (UNICA) commented that such studies missed the continuing intensification of cattle production already underway.

An study by Arima et al. published in May 2011 used spatial regression modeling to provide the first statistical assessment of ILUC for the Brazilian Amazon due to soy production. Previously, the indirect impacts of soy crops were only anecdotal or analyzed through demand models at a global scale, while the study took a regional approach. The analysis showed a strong signal linking the expansion of soybean fields in settled agricultural areas at the southern and eastern rims of the Amazon basin to pasture encroachments for cattle production on the forest frontier. The results demonstrate the need to include ILUC in measuring the carbon footprint of soy crops, whether produced for bio fuels or other end-uses.

The Arima study is based on 761 municipalities located in the Legal Amazon of Brazil, and found that between 2003 and 2008, soybean areas expanded by 39,100 sq-km in the basin's agricultural areas, mainly in Mato Grosso. The model showed that a 10% (3,910 sq-km) reduction of soy in old pasture areas would have led to a reduction in deforestation of up to 40% (26,039 sq-km) in heavily forested municipalities of the Brazilian Amazon. The analysis showed that the displacement of cattle production due to agricultural expansion drives land use change in municipalities located hundreds of kilometers away, and that the Amazonian ILUC is not only measurable but its impact is significant.

4 - Implementation

4 – 1 - United States

4 – 1 – 1 - California LCFS

On April 23, 2009, California Air Resources Board (CARB) approved the specific rules and carbon intensity reference values for the California Low-Carbon Fuel Standard (LCFS) that take effect January 1, 2011.[54][55] CARB's rulemaking included ILUC. For some bio fuels, CARB identified land use changes as a significant source of additional GHG emissions. It established one standard for gasoline and alternative fuels, and a second for diesel fuel and its replacements.

4 – 1 – 1 – 1 - Controversy

The public consultation process before the ruling, and the ruling itself were controversial, yielding 229 comments.[57] ILUC was one of the most contentious issues. On June 24, 2008, 27 scientists and researchers submitted a letter saying, "As researchers and scientists in the field of biomass to bio fuel conversion, we are convinced that there simply is not enough hard empirical data to base any sound policy regulation in regards to the indirect impacts of renewable bio fuels production. The field is relative new, especially when compared to the vast knowledge base present in fossil fuel production, and the limited analyses are driven by assumptions that sometimes lack robust empirical validation." The New Fuels Alliance, representing more than two-dozen bio fuel companies, researchers and investors, questioned the Board intention to include indirect land use change effects into account, wrote "While it is likely true that zero is not the right number for the indirect effects of any product in the real world, enforcing indirect effects in a piecemeal way could have very serious consequences for the LCFS.... The argument that zero is not the right number does not justify enforcing a different wrong number, or penalizing one fuel for one category of indirect effects while giving another fuel pathway a free pass."

On the other side, more than 170 scientists and economists urged that CARB, "include indirect land use change in the lifecycle analyses of heat-trapping emissions from bio fuels and other transportation fuels. This policy will encourage development of sustainable, low-carbon fuels that avoid conflict with food and minimize harmful environmental impacts.... There are uncertainties inherent in estimating the magnitude of indirect land use emissions from bio fuels, but assigning a value of zero is clearly not supported by the science."

Industry representatives complained that the final rule overstated the environmental effects of corn ethanol, and also criticized the inclusion of ILUC as an unfair penalty to domestic corn ethanol because deforestation in the developing world was being tied to U.S. ethanol production. The 2011 limit for LCFS means that Mid-west corn ethanol failed, unless current carbon intensity was reduced. Oil industry representatives complained that the standard left oil refiners with few options, such as Brazilian sugarcane ethanol, with its accompanying tariff. CARB officials and environmentalists counter that time and economic incentives will allow produces to adapt.

UNICA welcomed the ruling, while urging CARB to better reflect Brazilian practices, lowering their estimates of Brazilian emissions.

The only Board member who voted against the ruling explained that he had a "hard time accepting the fact that we're going to ignore the comments of 125 scientists", referring to the letter submitted by a group of scientists questioning the ILUC penalty. "They said the model was not good enough ... to use at this time as a component part of such an historic new standard." CARB advanced the expected date for an expert working group to report on ILUC with refined estimates from January 2012 to January 2011.

On December 2009 the Renewable Fuels Association (RFA) and Growth Energy, two U.S. ethanol lobbying groups, filed a lawsuit challenging LCFS' constitutionality. The two organizations argued that LCFS violated both the Supremacy Clause and the Commerce Clause, jeopardizing the nationwide ethanol market.

4 – 1 – 2 - EPA Renewable Fuel Standard

The Energy Independence and Security Act of 2007 (EISA) established new renewable fuel categories and eligibility requirements , setting mandatory lifecycle emissions limits. EISA explicitly mandated EPA to include "direct emissions and significant indirect emissions such as significant emissions from land use changes."

EISA required a 20 % reduction in lifecycle GHG emissions for any fuel produced at facilities that commenced construction after December 19, 2007 to be classified as a "renewable fuel"; a 50 % reduction for fuels to be classified as "biomass-based diesel" or "advanced bio fuel", and a 60% reduction to be classified as "cellulosic bio fuel". EISA provided limited flexibility to adjust these thresholds downward by up to 10 percent, and EPA proposed this adjustment for the advanced bio fuels category. Existing plants were grandfathered in.

On May 5, 2009, EPA released a notice of proposed rulemaking for implementation of the 2007 modification of the Renewable Fuel Standard, known as RFS2. The draft of the regulations was released for public comment during a 60-day period, a public hearing was held on 9 June 2009, and also a workshop was conducted on 10 – 11 June 2009.

EPA's draft analysis stated that ILUC can produce significant near-term GHG emissions due to land conversion, but that bio fuels can pay these back over subsequent years. EPA highlighted two scenarios, varying the time horizon and the discount rate for valuing emissions. The first assumed a 30 year time period uses a 0 percent discount rate (valuing emissions equally regardless of timing). The second scenario used a 100 year time period and a 2% discount rate.

On the same day that EPA published its notice of proposed rulemaking, President Obama signed a Presidential Directive seeking to advance bio fuels research and commercialization. The Directive established the Bio fuels Interagency Working Group, to develop policy ideas for increasing investment in next-generation fuels and for reducing their environmental footprint.

	
Sugarcane is the main feedstock for the production of ethanol fuel in Brazil	*Maize is the main feedstock for the production of ethanol fuel in the U.S.*

The inclusion of ILUC in the proposed ruling provoked complaints from ethanoland biodiesel producers. Several environmental organizations welcomed the inclusion of ILUC but criticized the consideration of a 100 year payback scenario, arguing that it underestimated land conversion effects. American corn growers, biodiesel producers, ethanol producers and Brazilian sugarcane ethanol producers complained about EPA's methodology, while the oil industry requested an implementation delay.

On June 26, 2009, the House of Representatives approved the American Clean Energy and Security Act 219 to 212, mandating EPA to exclude ILUC for a 5-year period, vis a vis RFS2. During this period, more research is to be conducted to develop more reliable models and methodologies for estimating ILUC, and Congress will review this issue before allowing EPA to rule on this matter. The bill failed in the U.S. Senate.

On February 3, 2010, EPA issued its final RFS2 rule for 2010 and beyond. The rule incorporated direct and significant indirect emissions including ILUC. EPA incorporated comments and data from new studies. Using a 30 year time horizon and a 0 % discount rate, EPA concluded that multiple bio fuels would meet this standard.

EPA's analysis accepted both ethanol produced from corn starch and bio butanol from corn starch as "renewable fuels". Ethanol produced from sugarcane became an "advanced fuel". Both diesel produced from algal oils and bio diesel from soy oil and diesel from waste oils, fats, and greases fell in the "biomass-based diesel" category. Cellulosic ethanol and cellulosic diesel met the "cellulosic bio fuel" standard.

The table summarizes the mean GHG emissions estimated by EPA modeling and the range of variations considering that the main source of uncertainty in the life cycle analysis is the GHG emissions related to international land use change.

4 – 1 – 2 – 1 - Reactions

UNICA welcomed the ruling, in particular, for the more precise lifecycle emissions estimate and hoped that classification the advanced bio fuel designation would help eliminate the tariff.

The U.S. Renewable Fuels Association (RFA) also welcomed the ruling, as ethanol producers "require stable federal policy that provides them the market assurances they need to commercialize new technologies", restating their ILUC objection.

RFA also complained that corn - based ethanol scored only a 21% reduction, noting that without ILUC, corn ethanol achieves a

52% GHG reduction. RFA also objected that Brazilian sugarcane ethanol "benefited disproportionally" because EPA's revisions lowered the initially equal ILUC estimates by half for corn and 93% for sugarcane.

Several Midwestern lawmakers commented that they continued to oppose EPA's consideration of the "dicey science" of indirect land use that "punishes domestic fuels".House Agriculture Chairman Collin Peterson said, "... to think that we can credibly measure the impact of international indirect land use is completely unrealistic, and I will continue to push for legislation that prevents unreliable methods and unfair standards from burdening the bio fuels industry."

EPA Administrator Lisa P. Jackson commented that the agency "did not back down from considering land use in its final rules, but the agency took new information into account that led to a more favorable calculation for ethanol".She cited new science and better data on crop yield and productivity, more information on co-products that could be produced from advanced bio fuels and expanded land-use data for 160 countries, instead of the 40 considered in the proposed rule.

4 – 2 - Europe

As of 2010, European Union and United Kingdom regulators had recognized the need to take ILUC into account, but had not determined the most appropriate methodology.

4 – 2 – 1 - UK Renewable Transport Fuel Obligation

The UK Renewable Transport Fuel Obligation (RTFO) program requires fuel suppliers to report direct impacts, and asked the Renewable Fuels Agency (RFA) to report potential indirect impacts, including ILUC and commodity price changes.[14] The RFA's July 2008 "Gallager Review", mentioned several risks regarding bio fuels and required feedstock production to avoid agricultural land that would otherwise be used for food production, despite concluding that "quantification of GHG emissions from indirect land - use change requires subjective assumptions and contains considerable uncertainty" . Some environmental groups argued that emissions from

ILUC were not being taken into account and could be creating more emissions.

4 – 2 – 2 - European Union

On December 17, 2008, the European Parliament approved the Renewable Energy Sources Directive (COM(2008)19) and amendments to the Fuel Quality Directive (Directive 2009/30),[107] which included sustainability criteria for bio fuels and mandated consideration of ILUC. The Directive established a 10 % bio fuel target. A separate Fuel Quality Directive set the EU's Low Carbon Fuel Standard, requiring a 6 % reduction in GHG intensity of EU transport fuels by 2020. The legislation ordered the European Commission to develop a methodology to factor in GHG emissions from ILUC by December 31, 2010, based on the best available scientific evidence.

In the meantime, the European Parliament defined lands that were ineligible for producing bio fuel feed stocks for the purpose of the Directives. This category included wetlands and continuously forested areas with canopy cover of more than 30 percent or cover between 10 and 30 percent given evidence that its existing carbon stock was low enough to justify conversion.

The Commission subsequently published terms of reference for three ILUC modeling exercises: one using a General Equilibrium model; one using a Partial Equilibrium mode land one comparing other global modeling exercises. It also consulted on a limited range of high-level options for addressing ILUCto which 17 countries[113] and 59 organizations responded. The United Nations Special Rapporteur on the Right to Food and several environmental organizations complained that the 2008 safeguards were inadequate. UNICA called for regulators to establish an empirical and "globally accepted methodology" to consider ILUC, with the participation of researchers and scientists from bio fuel crop - producing countries.

In 2010 some NGOs accused the European Commission of lacking transparency given its reluctance to release documents relating to the ILUC work . In March 2010 the Partial and General

Equilibrium Modeling results were made available, with the disclaimer that the EC had not adopted the views contained in the materials. These indicate that a 1.25 % increase in EU bio fuel consumption would require around 5,000,000 hectares of land globally.

The scenarios for varied from 5.6-8.6% of road transport fuels. The study found that ILUC effects offset part of the emission benefits, and that above the 5.6 % threshold, ILUC emissions increase rapidly increase. For the expected scenario of 5.6% by 2020, the study estimated that biodiesel production increases would be mostly domestic, while bio ethanol production would take place mainly in Brazil, regardless of EU duties. The analysis concluded that eliminating trade barriers would further reduce emissions, because the EU would import more from Brazil. Under this scenario,

"*direct emission savings from bio fuels are estimated at 18 Mt* CO_2*, additional emissions from ILUC at 5.3 Mt* CO_2 *(mostly in Brazil), resulting in a global net balance of nearly 13 Mt* CO_2 *savings in a 20 years horizon.*

The study also found that ILUC emissions were much greater for biodiesel from vegetable oil and estimated that in 2020 even at the 5.6% level were over half the greenhouse gas emissions from diesel.

As part of the announcement, the Commission stated that it would publish a report on ILUC by the end of 2010.

4 – 2 – 2 – 1 - Certification system

On June 10, 2010, the EC announced its decision to set up certification schemes for bio fuels, including imports as part of the Renewable Energy Directive. The Commission encouraged E.U. nations, industry and NGOs to set up voluntary certification schemes. EC figures for 2007 showed that 26 % of biodiesel and 31 % of bio ethanol used in the E.U. was imported, mainly from Brazil and the United States.

4 – 2 – 2 – 2 - Reactions

UNICA welcomed the EU efforts to "engage independent experts in its assessments" but requested that improvements because "... the report currently contains a certain number of inaccuracies, so once these are corrected, we anticipate even higher benefits resulting from the use of Brazilian sugarcane ethanol." UNICA highlighted the fact that the report assumed land expansion that "does not take into consideration the agro-ecological zoning for sugarcane in Brazil, which prevents cane from expanding into any type of native vegetation."

Critics said the 10 % figure was reduced to 5.6 % of transport fuels partly by exaggerating the contribution of electric vehicles (EV) in 2020, as the study assumed EVs would represent 20% of new car sales, two and six times the car industry's own estimate. They also claimed the study "exaggerates to around 45 percent the contribution of bio ethanol—the greenest of all bio fuels—and consequently downplays the worst impacts of biodiesel."

Environmental groups found that the measures "are too weak to halt a dramatic increase in deforestation ". According to Greenpeace, "indirect land-use change impacts of bio fuel production still are not properly addressed", which for them was the most dangerous problem of bio fuels

Industry representatives welcomed the certification system and some dismissed concerns regarding the lack of land use criteria. UNICA and other industry groups wanted the gaps in the rules filled to provide a clear operating framework.

Liquid Fuel

Contents

1 - Introduction

Liquid fuels are combustible or energy-generating molecules that can be harnessed to create mechanical energy, usually producing kinetic energy; they also must take the shape of their container. It is the fumes of liquid fuels that are flammable instead of the fluid.

Most liquid fuels in widespread use are derived from fossil fuels; however, there are several types, such as hydrogen fuel (for automotive uses), ethanol, and biodiesel, which are also categorized as a liquid fuel. Many liquid fuels play a primary role in transportation and the economy.

Liquid fuels are contrasted with solid fuels and gaseous fuels.

2 - General properties

Some common properties of liquid fuels are that they are easy to transport, and can be handled with relative ease. Also they are relatively easy to use for all engineering applications, and home use. (Fuels like Kerosene are rationed and available in government subsidized shops in India for home use.) Liquid fuels are also used most popularly in Internal combustion engines.

Some technically important properties include: flash point, fire point, cloud point, and pour point.

3 - Petroleum

Most liquid fuels used currently are produced from petroleum. The most notable of these is gasoline. Scientists generally accept that petroleum formed from the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth's crust.

3 – 1 - Gasoline

Gasoline is the most widely used liquid fuel. Gasoline, as it is known in United States and Canada, or petrol vitually everywhere else, is made of hydrocarbon molecules forming aliphatic compounds, or chains of carbons with hydrogen atoms attached. However, many aromatic compounds (carbon chains forming rings) such as benzene are found naturally in gasoline and cause the health risks associated with prolonged exposure to the fuel.

Production of gasoline is achieved by distillation of crude oil. The desirable liquid is separated from the crude oil in refineries. Crude oil is extracted from the ground in several processes, the most commonly seen may be beam pumps. To create gasoline, petroleum must first be removed from crude oil.

Liquid gasoline itself is not actually burned, but its fumes ignite, causing the remaining liquid to evaporate and then burn. Gasoline is extremely volatile and easily combusts, making any leakage potentially extremely dangerous. Gasoline sold in most countries carries a published octane rating. The octane number is an empirical measure of the resistance of gasoline to combusting prematurely, known as knocking. The higher the octane rating, the more resistant the fuel is to autoignition under high pressures, which allows for a higher compression ratio. Engines with a higher compression ratio, commonly used in race cars and high-performance regular-production automobiles, can produce more power; however, such engines require a higher octane fuel. Increasing the octane rating has, in the past, been achieved by adding 'anti-knock' additives such as lead-tetra-ethyl. Because of the environmental impact of lead additives, the octane rating is increased today by refining out the impurities that cause knocking.

3 - 2 - Diesel

Conventional diesel is similar to gasoline in that it is a mixture of aliphatic hydrocarbons extracted from petroleum. Diesel may cost more or less than gasoline, but generally costs less to produce because the extraction processes used are simpler. Some countries (particularly Canada) also have lower tax rates on diesel fuels.

After distillation, the diesel fraction is normally processed to reduce the amount of sulfur in the fuel. Sulphur causes corrosion in vehicles, acid rain and higher emissions of soot from the tail pipe (exhaust pipe). Historically, in Europe lower sulfur levels than in the United States were legally required. However, recent US legislation reduced the maximum sulphur content of diesel from 3,000 ppm to 500 ppm in 2007, and 15 ppm by 2010. Similar changes are also underway in Canada, Australia, New Zealand and several Asian countries. See also Ultra-low-sulfur diesel.

A diesel engine is a type of internal combustion engine which ignites fuel by injecting it into a combustion chamber previously compressed with air (which in turn raises the temperature) as opposed to using an outside ignition source, such as a spark plug.

3 – 3 - Kerosene

Kerosene is used in kerosene lamps and as a fuel for cooking, heating, and small engines. It displaced whale oil from lighting use. Jet fuel for jet engines is made in several grades (Avtur, Jet A, Jet A-1, Jet B, JP-4, JP-5, JP-7 or JP-8) that are kerosene-type mixtures. One form of the fuel known as RP-1 is burned with liquid oxygen as rocket fuel. These fuel grade kerosenes meet specifications for smoke points and freeze points.

In the mid-20th century, kerosene or "TVO" (Tractor Vaporising Oil) was used as a cheap fuel for tractors. The engine would start on gasoline, then switch over to kerosene once the engine warmed up. A "heat valve" on the manifold would route the exhaust gases around the intake pipe, heating the kerosene to the point where it can be ignited by an electric spark.

Kerosene is sometimes used as an additive in diesel fuel to prevent gelling or waxing in cold temperatures. However, this is not advisable in some recent vehicle diesel engines, as doing so may interfere with the engine's emissions regulation equipment.

4 - Natural gas and liquified petroleum gas

4 – 1 - Compressed natural gas

Natural gas, composed chiefly of methane, can be compressed to a liquid and used as a substitute for other traditional liquid fuels. Its combustion is very clean compared to other hydrocarbon fuels, but the fuel's low boiling point requires the fuel to be kept at high pressures to keep it in the liquid state. Though it has a much lower flash point than fuels such as gasoline, it is in many ways safer due to its higher auto ignition temperature and its low density, which causes it to dissipate when released in air.

4 – 2 - Liquified petroleum gas (LPG)

LP gas is a mixture of propane and butane, both of which are easily-compressible gases under standard atmospheric conditions. It offers many of the advantages of compressed natural gas (CNG), but is denser than air, does not burn as cleanly, and is much more easily compressed. Commonly used for cooking and space heating, LP gas and compressed propane are seeing increased use in motorized vehicles; propane is the third most commonly used motor fuel globally.

5 - Non - petroleum fossil fuels (Synthetic fuel)

When petroleum is not easily available, chemical processes such as the Fischer - Tropsch process can be used to produce liquid fuels from coal and / or natural gas. dr.Pier Luigi Caffese to new energy plan 2012Italian Govern introduce the concept of new non fossil liquid fuel,like: -windfuel from offshore wind -waterfuel from phs hydro or modular hydro -peak fuel from excess power -marine sea water fuel from marine phs – algae , marine plants fuel from big marine lakes(Caffese patent) -solar reactor fuels on marine lakes -fish fuels from marine fish farms on marine lake -alpine phs fuels -underground phs fuels -glucose bio butanol fuels -CARMA fuels synergies Rgas -refuels

6 - Biodiesel

Biodiesel is similar to diesel, but has differences akin to those between petrol and ethanol. For instance, biodiesel has a higher cetane rating (45 - 60 compared to 45-50 for crude-oil-derived diesel) and it acts as a cleaning agent to get rid of dirt and deposits. It has been argued that it only becomes economically feasible above oil prices of $80 (£40 or €60 as of late February, 2007) per barrel. This does however depend on locality, economic situation, government stance on biodiesel and a host of other factors- and it has been proven to be viable at much lower costs in some countries. Also, it yields about 10% less energy than ordinary diesel. Analogous to the use of higher compression ratios used for engines burning higher octane alcohols and petrol in spark-ignition engines, taking advantage of biodiesel's high cetane rating can potentially overcome the energy deficit compared to ordinary Number 2 diesel.

7 - Alcohols

Generally, the term alcohol refers to ethanol, the first organic chemical produced by humans, but any alcohol can be burned as a fuel. Ethanol and methanol are the most common, being sufficiently inexpensive to be useful.

7 – 1 - Methanol

Methanol is the lightest and simplest alcohol, produced from the natural gas component methane. Its application is limited primarily due to its toxicity (similar to gasoline), but also due to its high corrosivity and miscibility with water. Small amounts are used in some gasolines to increase the octane rating. Methanol-based fuels are used in some race cars and model airplanes.

Methanol is also called *methyl alcohol* or *wood alcohol*, the latter because it was formerly produced from the distillation of wood. It is also known by the name *methyl hydrate*.

7 - 2 - Ethanol

Ethanol, also known as grain alcohol or ethyl alcohol, is most commonly used in alcoholic beverages. However, it may also be used as a fuel, most often in combination with gasoline. For the most part, it is used in a 9:1 ratio of gasoline to ethanol to reduce the negative environmental effects of gasoline.

There is increasing interest in the use of a blend of 85% fuel ethanol blended with 15% gasoline. This fuel blend called E85, has a higher fuel octane than most premium gasolines. When used in a modern Flexible fuel vehicle, it delivers more performance to the gasoline it replaces at the expense of higher fuel consumption due to ethanol's lesser specific energy content.

Ethanol for use in gasoline and industrial purposes may be considered a fossil fuel because it is often synthesized from the petroleum product ethylene, which is cheaper than production from fermentation of grains or sugarcane.

7 – 2 - Butanol

Butanol is an alcohol which can be used as a fuel in most gasoline internal combustion engines without engine modification. It is typically a product of the fermentation of biomass by the bacterium *Clostridium acetobutylicum* (also known as the Weizmann organism). This process was first delineated by Chaim Weizmann in 1916 for the production of acetone from starch for making cordite, a smokeless gunpowder.

The advantages of butanol are its high octane rating (over 100) and high energy content, only about 10 % lower than gasoline, and subsequently about 50 % more energy- dense than ethanol, 100% more so than methanol. Butanol 's only major disadvantages are its high flashpoint 35 °C , toxicity (note that toxicity levels exist but are not precisely confirmed), and the fact that the fermentation process for renewable butanol emits a foul odour. The Weizmann organism can only tolerate butanol levels up to 2 % or so, compared to 14% for ethanol and yeast. Making butanol from oil produces no such odour, but the limited supply and environmental impact of oil usage defeats the purpose of alternative fuels. The cost of butanol is about $0.57-$0.58 per pound ($ 1250 – $ 1320 per metric ton or $4 approx. per US gallon). Butanol is much more expensive than ethanol (approx. $1.50 per gallon) and methanol.

On June 20, 2006, DuPont and BP announced that they were converting an existing ethanol plant to produce 9 million gallons of butanol per year from sugar beets. DuPont stated a goal of being competitive with oil at $ 30 – $ 40 per barrel without subsidies, so the price gap with ethanol is narrowing.

8 - Hydrogen

Liquified hydrogen is the liquid state of the element hydrogen. It is a common liquid rocket fuel for rocket applications and can be used as a fuel in an internal combustion engine or fuel cell. Various concept hydrogen vehicles have been lower volumetric energy, the hydrogen volumes needed for combustion are large. Hydrogen was liquefied for the first time by James Dewar in 1898.

9 - Ammonia

Ammonia (NH_3) has been used as a fuel before at times when gasoline is unavailable (e.g. for buses in Belgium during WWII). It has a volumetric energy density of 17 Megajoules per liter (compared to 10 for hydrogen, 18 for methanol, 21 for dimethyl ether and 34 for gasoline). It must be compressed or cooled to be a liquid fuel, although it does not require cryogenic cooling as hydrogen does to be liquified.

Vegetable Oil Fuel

Contents

1 - Introduction

Vegetable oil is an alternative fuel for diesel engines and for heating oil burners. For engines designed to burn diesel fuel, the viscosity of vegetable oil must be lowered to allow for proper atomization of the fuel, otherwise incomplete combustion and carbon build up will ultimately damage the engine.

2 - History

Rudolf Diesel was the father of the engine which bears his name. His first attempts were to design an engine to run on coal dust, but later designed his engine to run on vegetable oil. The idea, he hoped, would make his engines more attractive to farmers having a source of fuel readily available. In a 1912 presentation to the British

Institute of Mechanical Engineers, he cited a number of efforts in this area and remarked, "The fact that fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and the tar products are now."

Periodic petroleum shortages spurred research into vegetable oil as a diesel substitute during the 1930s and 1940s, and again in the 1970s and early 1980s when straight vegetable oil enjoyed its highest level of scientific interest. The 1970s also saw the formation of the first commercial enterprise to allow consumers to run straight vegetable oil in their automobiles, Elsbett of Germany. In the 1990s Bougainville conflict, islanders cut off from oil supplies due to a blockade used coconut oil to fuel their vehicles.

Academic research into straight vegetable oil fell off sharply in the 1980s with falling petroleum prices and greater interest in biodiesel as an option that did not require extensive vehicle modification.

3 - Application and usability

While engineers and enthusiasts have been experimenting with using vegetable oils as fuel for a diesel engine since at least 1900, it is only recently that the necessary fuel properties and engine parameters for reliable operation have become apparent. Only a handful of peer reviewed studies exist that show reliable long term use of vegetable oil.

3 – 1 - Modified fuel systems

Most diesel car engines are suitable for the use of straight vegetable oil (SVO), also commonly called pure plant oil (PPO), with suitable modifications. Principally, the viscosity and surface tension of the SVO / PPO must be reduced by preheating it, typically by using waste heat from the engine or electricity, otherwise poor atomization, incomplete combustion and carbonization may result. One common solution is to add a heat exchanger and an additional fuel tank for the petrodiesel or biodiesel blend and to switch between this additional tank and the main tank of SVO / PPO. The engine is started on diesel, switched over to vegetable oil as soon as it is warmed up and switched back to diesel shortly before being switched off to ensure that no vegetable oil remains in the engine or fuel lines when it is started from cold again. In colder climates it is often necessary to heat the vegetable oil fuel lines and tank as it can become very viscous and even solidify.

Single tank conversions have been developed, largely in Germany, which have been used throughout Europe. These conversions are designed to provide reliable operation with rapeseed oil that meets the German rapeseed oil fuel standard DIN 51605. Modifications to the engines cold start regime assist combustion on start up and during the engine warm up phase. Suitably modified indirect injection (IDI) engines have proven to be operable with 100% PPO down to temperatures of −10°C. Direct injection (DI) engines generally have to be preheated with a block heater or diesel fired heater. The exception is the VW Tdi (Turbocharged Direct Injection) engine for which a number of German companies offer single tank conversions. For long term durability it has been found necessary to increase the oil change frequency and to pay increased attention to engine maintenance.

3 – 2 - Unmodified indirect injection engines

Many cars powered by indirect injection engines supplied by in-line injection pumps, or mechanical Bosch injection pumps are capable of running on pure SVO / PPO in all but winter temperatures. Indirect injection Mercedes - Benz vehicles with in-line injection pumps and cars featuring the PSA XUD engine tend to perform reasonably, especially as the latter is normally equipped with a coolant heated fuel filter. Engine reliability would depend on the condition of the engine. Attention to maintenance of the engine, particularly of the fuel injectors, cooling system and glow plugs will help to provide longevity. Ideally the engine would be converted.

3 – 3 - Vegetable oil blending

The relatively high kinematic viscosity of vegetable oils must be reduced to make them compatible with conventional compression-ignition engines and fuel systems. Cosolvent blending is a low-cost and easy-to-adapt technology that reduces viscosity by diluting the vegetable oil with a low - molecular - weight solvent. This blending, or "cutting", has been done with diesel fuel, kerosene, and gasoline, amongst others; however, opinions vary as to the efficacy of this. Noted problems include higher rates of wear and failure in fuel pumps and piston rings when using blends.

3 – 4 - Home heating

When liquid fuels made from biomass are used for energy purposes other than transport, they are called bio liquids.

With often minimal modification, most residential furnaces and boilers that are designed to burn No. 2 heating oil can be made to burn either biodiesel or filtered, preheated waste vegetable oil (WVO). If cleaned at home, by the consumer, WVO can result in considerable savings. Many restaurants will receive a minimal amount for their used cooking oil, and processing to biodiesel is fairly simple and inexpensive. Burning filtered WVO directly is somewhat more problematic, since it is much more viscous, but it can be accomplished with suitable preheating. WVO can thus be an economical heating option for those with the necessary mechanical and experimental aptitude.

3 – 4 - 1 - Combined heat and power

A number of companies offer compressed ignition engine generators optimized to run on plant oils where the waste engine heat is recovered for heating.

4 - Properties

The main form of SVO / PPO used in the UK is rapeseed oil (also known as canola oil, primarily in the United States and Canada) which has a freezing point of -10°C . However the use of sunflower oil, which gels at around -12°C, is currently being investigated as a means of improving cold weather starting. Unfortunately oils with lower gelling points tend to be less saturated (leading to a higher iodine number) and polymerize more easily in the presence of atmospheric oxygen.

4 – 1 - Material compatibility

Polymerization of vegetable oil can have a detrimental effect on metals because it leads to oxidization. Copper and its alloys, such as brass, are affected, as are zinc and zinc-plating (galvanization) , tin , lead, iron, and steel · Stainless steel and aluminum are generally unaffected. Long-chain free fatty acids in vegetable oils are not corrosive .

4 – 2 - Temperature effects

Some Pacific island nations are using coconut oil as fuel to reduce their expenses and their dependence on imported fuels while helping stabilize the coconut oil market. Coconut oil is only usable where temperatures do not drop below 17 degrees Celsius (62 degrees Fahrenheit), unless two - tank SVO / PPO kits or other tank-heating accessories, etc. are used. Fortunately, the same techniques developed to use, for example, canola and other oils in cold climates can be implemented to make coconut oil usable in temperatures lower than 17 degrees Celsius.

5 - Availability

5 – 1 - Recycled vegetable oil

Recycled vegetable oil, also termed used vegetable oil (UVO), waste vegetable oil (WVO), used cooking oil, or yellow grease (in commodities exchange), is recovered from businesses and industry that use the oil for cooking.

As of 2000, the United States was producing in excess of 11 billion liters of recycled vegetable oil annually, mainly from industrial deep fryers in potato processing plants, snack food factories and fast food restaurants. If all those 11 billion liters could be recycled and used to replace the energy equivalent amount of petroleum (an ideal case), almost 1% of US oil consumption could be offset.[9] Use of used vegetable oil as a direct fuel competes with some other uses of the commodity, which has effects on its price as a fuel and increases its cost as an input to the other uses as well.

5 – 2 - Virgin vegetable oil

Virgin vegetable oil, also termed pure plant oil or straight vegetable oil, is extracted from plants solely for use as fuel. In contrast to used vegetable oil, is not a byproduct of other industries, and thus its prospects for use as fuel are not limited by the capacities of other industries . Production of vegetable oils for use as fuels is theoretically limited only by the agricultural capacity of a given economy. However, doing so detracts from the supply of other uses of pure vegetable oil. Oil from the fruit of the high - yield jatropha curcas tree , which grows in subtropical climates, is inedible to humans and therefore, its use as fuel does not compete with the demand for food.

6 - Legal implications

6 – 1 - Taxation of fuel

Taxation on SVO / PPO as a road fuel varies from country to country, and it is possible the revenue departments in many countries are even unaware of its use, or feel it too insignificant to legislate. Germany used to have 0 % taxation, resulting in it being a leader in most developments of the fuel use. However SVO / PPO as a road fuel began to be taxed at 0,09 € / liter from 1 January 2008 in Germany, with incremental rises up to 0,45 € / liter by 2012. However, in Australia it has become illegal to produce any fuel if it is to be sold unless a license to do so is granted by the federal government. This is a chargeable offense with a fine of up to 20,000 dollars but this bracket may alter circumstantially. Also a jail term may result if offenders are aware of the illegality of selling the fuel.

6 – 1 – 1 - Japan

The Japanese Government has also exempted the use of SVO as a fuel from road tax.

6 – 1 – 2 - Republic of Ireland

In the Republic of Ireland a pilot scheme is currently running, whereby as of April 2006, eight suppliers have been approved to sell SVO / PPO for use as a fuel without the payment of excise duty (Value Added Tax at 21% still applies). SVO from any other source still attracts excise duty at 36.8058 Euro cents per litre plus 21% VAT).

6 – 1 – 3 - France

Despite its prevalent use in France, it appears there has been no legislation to date to cover this.

6 – 1 – 4 - UK

Before 2011: In the UK it is legal once duty on the fuel is paid, or, in the case of using or producing less than 2,500 litres per year, no duty is necessary.

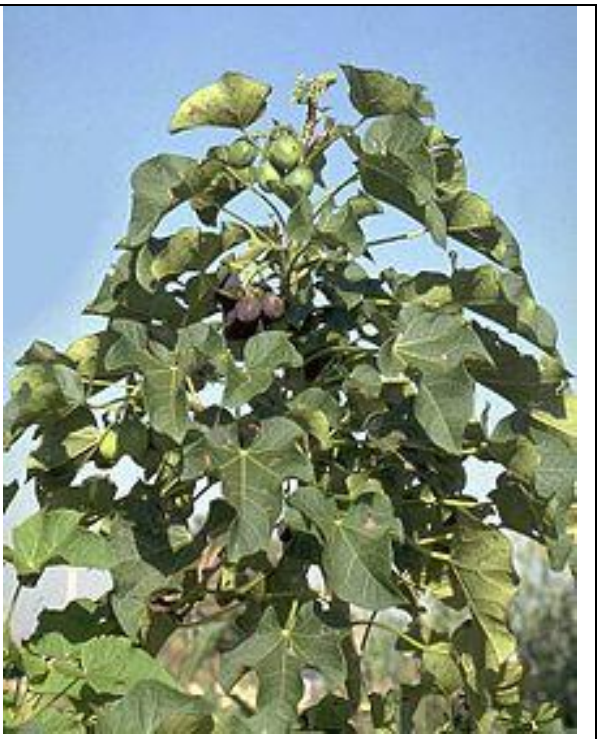
In the UK, drivers using SVO/PPO have in the past been prosecuted for failure to pay duty to Her Majesty's Revenue and Customs. The rate of taxation on SVO was originally set at a reduced rate of 27.1p per liter , but in late 2005, HMRC started to enforce the full diesel excise rate of 47.1p per liter.

HMRC argued that SVOs / PPOs on the market from small producers did not meet the official definition of "bio diesel" in Section 2AA of The Hydrocarbon Oil Duties Act 1979 (HODA), and consequently was merely a "fuel substitute" chargeable at the normal diesel rate. Such a policy seemed to contradict the UK Government's commitments to the Kyoto Protocol and to many EU directives and had many consequences, including an attempt to make the increase retroactive, with one organization being presented with a £16,000 back tax bill. This change in the rate of excise duty effectively removed any commercial incentive to use SVO/PPO, regardless of its desirability on environmental grounds; unless waste vegetable oil can be obtained free of charge, the combined price of SVO / PPO and taxation for its use usually exceeded the price of mineral diesel. HMRC's interpretation is widely challenged by the SVO / PPO industry and the UK pure Plant Oil Association (UKPPOA) was formed to represent the interests of people using vegetable oil as fuel and to lobby parliament.

Following a review in late 2006 , HM Revenue & Customs has announced changes regarding the administration and collection of excise duty of bio fuels and other fuel substitutes (Veg Oil). The changes came into effect on June 30, 2007. There is no longer a requirement to register to pay duty on vegetable oil used as road fuel for those who "produce" or use less than 2,500 liters per year. For those producing over this threshold the biodiesel rate now applies.

In 2011, the Duties associated with the use of Biodiesel changed to reflect a flat rate of 20 pence per litre of biodiesel used. No lower threshold now exists.

Jatropha curcas

	
Jatropha plantation in the dry center/west of the Paraguay Chaco	*Jatropha curcas*

Contents

1 - Introduction

Jatropha curcas is a species of flowering plant in the genus Jatropha in spurge family, Euphorbiaceae, that is native to the American tropics, most likely Mexico and Central America.[3] It is cultivated in tropical and subtropical regions around the world, becoming naturalized in some areas. The specific epithet, "*curcas*", was first used by Portuguese doctor Garcia de Orta more than 400 years ago and is of uncertain origin.[4] Common names include Barbados Nut, Purging Nut, Physic Nut, or JCL (abbreviation of *Jatropha curcas* Linnaeus).

J. curcas is a poisonous, semi-evergreen shrub or small tree, reaching a height of 6 m . It is resistant to a high degree of aridity, allowing it to be grown in deserts.

The seeds contain 27- 40 % oil (average : 34.4 %) that can be processed to produce a high - quality biodiesel fuel, usable in a standard diesel engine. The seeds are also a source of the highly poisonous toxalbumin curcin.

Scientific classification	
Kingdom:	Plantae
(unranked):	Angiosperms
(unranked):	Eudicots
(unranked):	Rosids
Order:	Malpighiales
Family:	Euphorbiaceae[1]
Genus:	*Jatropha*
Species:	*J. curcas*
Binomial name	
Jatropha curcas L .	

2 - Botanical features

Leaves: The leaves have significant variability in their morphology. In general, the leaves are green to pale green, alternate to sub opposite, and three- to five-lobed with a spiral phyllotaxis.

Flowers: male and female flowers are produced on the same inflorescence, averaging 20 male flowers to each female flower,[10] or 10 male flowers to each female flower . The petiole length ranges from 6 – 23 mm . The inflorescence can be formed in the leaf axil. Plants are monoecious and also presents hermaphroditic flowers occasionally.

Fruits : fruits are produced in winter, or there may be several crops during the year if soil moisture is good and temperatures are sufficiently high. Most fruit production is concentrated from midsummer to late fall with variations in production peaks where some plants have two or three harvests and some produce continuously through the season.

Seeds: the seeds are mature when the capsule changes from green to yellow. The seeds contain around 20% saturated fatty acids and 80 % unsaturated fatty acids, and they yield 25%–40% oil by weight. In addition, the seeds contain other chemical compounds, such as saccharose , raffinose , stachyose , glucose, fructose, galactose, and protein. The oil is largely made up of oleic and linoleic acids. Furthermore, the plant also contains curcasin, arachidic, linoleic, myristic, oleic, palmitic, and stearic acids and curcin.

Genome: the whole genome was sequenced by *Kazusa DNA Research Institute*, Chiba Japan in October 2010.

3 - Cultivation

Cultivation is uncomplicated. *Jatropha curcas* grows in tropical and subtropical regions. The plant can grow in wastelands and grows on almost any terrain, even on gravelly, sandy and saline soils. It can thrive in poor and stony soils, although new research suggests that the plant's ability to adapt to these poor soils is not as extensive as had been previously stated. Complete germination is achieved within 9 days. Adding manure during the germination has negative effects during that phase, but is favorable if applied after germination is achieved. It can be propagated by cuttings, which yields faster results than multiplication by seeds.

Jatropha curcas seeds

The flowers only develop terminally (at the end of a stem), so a good ramification (plants presenting many branches) produces the greatest amount of fruits. The plants are self-compatible.[10] Another productivity factor is the ratio between female and male flowers within an inflorescence, more female flowers mean more fruits. *Jatropha curcas* thrives on a mere 250 mm (10 in) of rain a year, and only during its first two years does it need to be watered in the closing days of the dry season. Ploughing and planting are not needed regularly, as this shrub has a life expectancy of approximately forty years. The use of pesticides is not necessary, due to the pesticidal and fungicidal properties of the plant. It is used in rural Bengal for dhobi itch (a common fungal infection of the skin).

While *Jatropha curcas* starts yielding from 9 –12 months time, the best yields are obtained only after 2 – 3 years time.

If planted in hedges, the reported productivity of *Jatropha* is from 0.8 kg. to 1.0 kg. of seed per meter of live fence. The seed production is around 3.5 tons / hectare (Seed production ranges from about 0.4 tons per hectare in first year to over 5 tons per hectare after 3 years).

4 - Propagation

Jatropha curcas has limited natural vegetative propagation and is usually propagated by seed. Propagation through seed (sexual propagation) leads to a lot of genetic variability in terms of growth, biomass, seed yield and oil content. Low seed viability and the recalcitrant nature of oil seeds also limit seed propagation. However, clonal techniques can help in overcoming these problems that hinder mass propagation of this tree-borne oilseed species. Vegetative propagation has been achieved by stem cuttings, grafting, budding as well as by air layering techniques.[14] The investigation leads to the recommendation that cuttings should be taken preferably from juvenile plants and treated with 200 micro gram per litre of IBA (rooting hormone) to ensure the highest level of rooting in stem cuttings. These vegetative methods have potential for commercial propagation of these plants.

5 - Processing

Seed extraction is made simple with the use of the Universal Nut Sheller, an appropriate technology designed by the Full Belly Project.

Oil content varies from 28 % to 30 % and 80 % extraction, one hectare of plantation will give 400 to 600 liters of oil if the soil is average.

The oily seeds are processed into oil, which may be used directly ("Straight Vegetable Oil") to fuel combustion engines or may be subjected to trans esterification to produce biodiesel. Jatropha oil is not suitable for human consumption, as it induces strong vomiting and diarrhea.

6 - Uses

6 – 1 - Bio fuel

When jatropha seeds are crushed, the resulting jatropha oil can be processed to produce a high - quality bio fuel or biodiesel that can be used in a standard diesel car or further processed into jet fuel, while the residue (press cake) can also be used as biomass feedstock to power electricity plants, used as fertilizer (it contains nitrogen, phosphorus and potassium), or as animal fodder. The cake can also be used as feed in digesters and gasifiers to produce biogas.

There are several forms of bio fuel, often manufactured using sedimentation, centrifugation, and filtration. The fats and oils are turned into esters while separating the glycerin. At the end of the process, the glycerin settles and the bio fuel floats. The process through which the glycerin is separated from the biodiesel is known as trans esterification. Glycerin is another by- product from Jatropha oil processing that can add value to the crop. Trans esterification is a simple chemical reaction that neutralizes the free fatty acids present in any fatty substances in Jatropha. A chemical exchange takes place between the alkoxy groups of an ester compound by an alcohol. Usually, methanol and ethanol alcohol are used for the purpose. The reaction occurs by the presence of a catalyst, usually sodium hydroxide (Na OH) or caustic soda and potassium hydroxide (KOH), which forms fatty esters (e.g., methyl or ethyl esters), commonly known as biodiesel. It takes approximately 10% of methyl alcohol by weight of the fatty substance to start the trans esterification process.

Estimates of *Jatropha* seed yield vary widely, due to a lack of research data, the genetic diversity of the crop, the range of environments in which it is grown, and *Jatropha*'s perennial life cycle. Seed yields under cultivation can range from 1,500 to 2,000 kilograms per hectare, corresponding to extractable oil yields of 540 to 680 liters per hectare . *Time* magazine recently cited the potential for as much as 1,600 gallons of diesel fuel per acre per year. The plant may yield more than four times as much fuel per hectare as soybean, and more than ten times that of maize (corn). A hectare of jatropha has been claimed to produce 1,892 liters of fuel. However, as it has not yet been domesticated or improved by plant breeders, yields are variable

Jatropha can also be intercropped with other cash crops such as coffee, sugar, fruits and vegetables.

In 2007 Goldman Sachs cited *Jatropha curcas* as one of the best candidates for future biodiesel production . However, despite its abundance and use as an oil and reclamation plant, none of the *Jatropha* species has been properly domesticated and, as a result, its productivity is variable, and the long-term impact of its large-scale use on soil quality and the environment is unknown.

In 2008 researchers at Daimler Chrysler Research explored the use of jatropha oil for automotive use, concluding that although jatropha oil as fuel "has not yet reached optimal quality, ... it already fulfills the EU norm for biodiesel quality". Archer Daniels Midland Company, Bayer Crop Science and Daimler AG have a joint project to develop jatropha as a bio fuel. Three Mercedes cars powered by Jatropha diesel have already put some 30,000 kilometres behind them. The project is supported by DaimlerChrysler and by the German Association for Investment and Development

6 – 1 – 1- Use as jet fuel

Aviation fuels may be more widely substituted with bio fuels such as jatropha oil than fuels for other forms of transportation. There are fewer planes than cars or trucks and far fewer jet fueling stations to convert than gas stations.

On December 30, 2008, Air New Zealand flew the first successful test flight from Auckland with a Boeing 747 running one of its four Rolls-Royce engines on a 50:50 blend of jatropha oil and jet A-1 fuel.[24][25] In the same press release, Air New Zealand announced plans to use the new fuel for 10 % of its needs by 2013. At the time of this test, jatropha oil was much cheaper than crude oil, costing an estimated $ 43 a barrel or about one-third of the June 4, 2008 closing price of $ 122.30 for a barrel of crude oil.

On January 7, 2009 Continental Airlines successfully completed a test flight from Houston, Texas using a 50/50 mixture of algae/jatropha - oil - derived bio fuel and Jet A in one of the two CFM56 engines of a Boeing 737 - 800 Next Generation jet. The two-hour test flight could mark another promising step for the airline industry to find cheaper and more environmentally friendly alternatives to fossil fuel.

On April 1, 2011 Inter jet completed the first Mexican aviation bio fuels test flight on an Airbus A320. The fuel was a 70:30 traditional jet fuel biojet blend produced from Jatropha oil provided by three Mexican producers, Global Energías Renovables (a wholly owned subsidiary of U.S.-based Global Clean Energy Holdings), Bencafser S.A. and Energy JH S.A. Honeywell's UOP processed the oil into Bio-SPK (Synthetic Paraffinic Kerosene). Global Energías Renovables operates the largest Jatropha farm in the Americas.

On October 28, 2011 Air China completed the first successful demonstration flight by a Chinese airline that used jatropha-based bio fuel. The mixture was a 50:50 mix of conventional jet fuel blended with jatropha oil from China National Petroleum Corp. The 747-400 powered one of its four engines on the fuel mixture during the 1-hour flight around Beijing airport.

6 – 1 – 2 - Use in developing world

Jatropha curcas seedlings in a greenhouse in Nicaragua

Currently the oil from *Jatropha curcas* seeds is used for making biodiesel fuel in Philippines, Pakistan and in Brazil, where it grows naturally and in plantations in the southeast, north, and northeast of Brazil. Likewise, jatropha oil is being promoted as an easily grown bio fuel crop in hundreds of projects throughout India and other developing countries. Large plantings and nurseries have been undertaken in India by many research institutions, and by women's self-help groups who use a system of microcredit to ease poverty among semiliterate Indian women. The railway line between Mumbai and Delhi is planted with *jatropha* and the train itself runs on 15-20% biodiesel.[20] In Africa, cultivation of *jatropha* is being promoted and it is grown successfully in countries such as Mali.[30] In the Gran Chaco of Paraguay, where a native variety (*Jatropha matacensis*) also grows, studies have shown the suitability of Jatropha cultivation and agro producers are starting to consider planting in the region.

6 – 1 – 2 - 1- Burma

Burma is also actively pursuing the use of jatropha oil. On 15 December 2005, then-head of state, Senior General Than Shwe, said "the States and Divisions concerned are to put 50,000 acres (200 km²) under the physic nut plants [Jatropha] each within three years totaling 700,000 acres (2,800 km²) during the period". On the occasion of Burma's Peasant Day 2006, Than Shwe described in his a message that "For energy sector which is an essential role in transforming industrial agriculture system, the Government is encouraging for cultivation of physic nut plants nationwide and the technical know how that can refine physic nuts to biodiesel has also identified." He would like to urge peasants to cultivate physic nut plants on a commercial scale with major aims for emergence of industrial agriculture system, for fulfilling rural electricity supply and energy needs, for supporting rural areas development and import substitute economy.

In 2006, the chief research officer at state-run Myanma Oil and Gas Enterprise said Burma hoped to completely replace the country's oil imports of 40,000 barrels a day with home-brewed, jatropha-derived bio fuel. Other government officials declared Burma would soon start exporting jatropha oil. Despite the military's efforts, the jatropha campaign apparently has largely flopped in its goal of making Burma self-sufficient in fuel.

Z.G.S. Bio energy has started Jatropha Plantation Projects in Northern Shan State, the company has begun planting Jatropha plants during late June 2007 and will start producing seeds by 2010.

6 – 1 – 3 - Controversies

As of 2011 skepticism about the "miracle" properties of *Jatropha* has been voiced. For example: "The idea that jatropha can be grown on marginal land is a red herring", according to Harry Stourton, business development director of UK-based Sun Bio fuels, which cultivates *Jatropha* in Mozambique and Tanzania. "It does grow on marginal land, but if you use marginal land you'll get marginal yields," he said.

An August 2010 article warned about the actual utility and potential dangers of reliance on *Jatropha* in Kenya. Major concerns included its invasiveness, which could disrupt local biodiversity, as well as damage to water catchment areas.

Jatropha curcas is lauded as being sustainable, and that its production would not compete with food production, but the jatropha plant needs water like every other crop to grow. This fact could create competition for water between the jatropha and other edible food crops. In fact, jatropha requires five times as much water per unit of energy as sugarcane and corn.

6 – 2 - Other uses

Leaves

The young leaves may be safely eaten, steamed or stewed. Cooked with goat meat, they are said to advantageously counteract its smell.

Pounded leaves are applied near horses' eyes to repel flies in India. Hydrogen cyanide (HCN) is present in the leaves. The extracts of the plants are dangerous to use but water can easily release it over if not too much extract is applied.

Flowers

The species is listed as a honey plant. Hydrogen cyanide is present.

Nuts

Can be construed for home cooking fuel in briquette form replacing charcoalized timber as in Haiti.

Some times roasted and eaten, although they are purgative.

They can be burned like candlenuts when strung on grass. HCN is present.

Used as a contraceptive in South Sudan.

Seeds

Interest exists in producing animal feed from the bio-waste once the oil is expressed, as in the case with Haiti, where Jatropha curcas grows prolifically and animal feed is in very sort supply.[41]

Similarly, Metsiyen in the Haitian culture dates back as a medicinal crop - thus the name "metsiyen"/"medsiyen". Some suggest it "calms the stomach".

Some mention of Metsiyen being used to ward off evil spirits in past Haitian culture where voodoo has been losing adherents for Christian faith.

Also used as a contraceptive in South Sudan.

The oil has been used for illumination, soap, candles, the adulteration of olive oil, and making Turkey red oil. Turkey red oil, also called sulphonated (or sulfated) castor oil, is the only oil that completely disperses in water. It is made by adding sulfuric acid to pure *Jatropha* oil. It was the first synthetic detergent after ordinary soap, as this allows easy use for making bath oil products. It is used in formulating lubricants, softeners, and dyeing assistants.

The seeds in the zone around Misantla, Veracruz are very appreciated by the population as food once they have been boiled and roasted. It is unclear if this is due to the existence of a non-toxic variety of Jatropha in Mexico and Central America, or if the seeds become edible once processed by cooking.

It is also similarly reported that Jatropha seeds are edible once the embryo has been removed. Again it may be so because of these seeds coming from a local non-toxic variety. HCN is present.

Roots

Their ashes are used as a salt substitute. HCN and rotenone are present.

Bark

Used as a fish poison. HCN is present.[49][*dead link*]

Latex

Strongly inhibits the watermelon mosaic virus.[50][*dead link*]

Sap

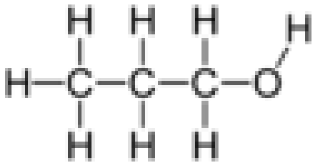
It stains linen. Sometimes used for marking.[51][*dead link*]

Shrub

Mexicans grow the shrub as a host for the lac insect, which is used in medicine as hepatoprotective and anti obesity drug. (Picture of lac insect here; drawing of insect, its larva and a colony here)

Used for erosion control,

1-Propanol

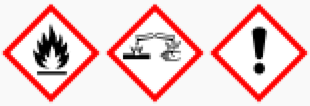


Contents

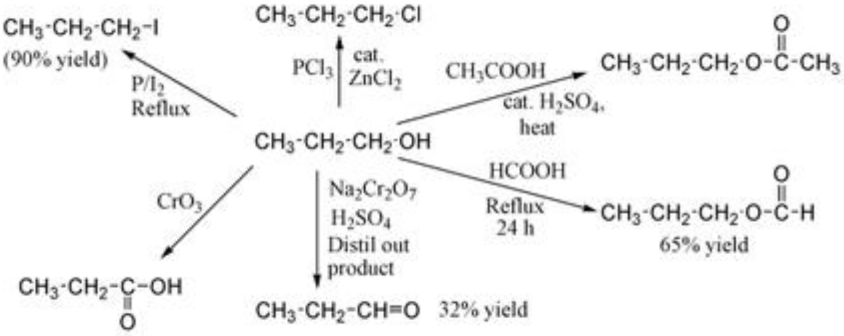
1 - Introduction

1- Propanol is a primary alcohol with the formula $CH_3CH_2CH_2OH$. This colorless liquid is also known as propan-1-ol, 1-propyl alcohol, *n*- propyl alcohol, *n*-propanol, or simply propanol. It is an isomer of isopropanol (2-propanol). It is formed naturally in small amounts during many fermentation processes and used as a solvent in the pharmaceutical industry mainly for resins and cellulose esters.

IUPAC name : Propan-1-ol	
Other names : *n*-Propyl alcohol *n*-Propanol Ethyl carbinol 1-Hydroxy propane Propanol Propionic alcohol Propionyl alcohol Propionylol Propyl alcohol Propylic alcohol Propylol	
Molecular formula	$C_3 H_8 O$
Molar mass	60 g mol^{-1}

Appearance	Colorless liquid
Density	803.4 mg cm^{-3}
Melting point	-126 °C
Boiling point	97 - 98 °C
Refractive index (n_D)	1.387
Viscosity	1.938 mPa s
Specific heat capacity, C	143.96 J K^{-1} mol^{-1}
Hazards	
GHS pictograms	
GHS signal word	DANGER
EU classification	 F Xi
Flash point	22 °C
Auto ignition temperature	371 °C
Explosive limits	13.7 %

2 - Chemical properties



1-Propanol shows the normal reactions of a primary alcohol. Thus it can be converted to alkyl halides; for example red phosphorus and iodine produce *n*-propyl iodide in 80% yield, while PCl_3 with catalytic Zn Cl_2 gives 1- chloropropane. Reaction with acetic acid in the presence of an H_2SO_4 catalyst under Fischer esterification conditions gives propyl acetate, while refluxing propanol overnight with formic acid alone can produce propyl formate in 65 % yield. Oxidation of 1-propanol with $Na_2Cr_2O_7$ and H_2SO_4 gives only a 36 %

yield of propionaldehyde, and therefore for this type of reaction higher yielding methods using PCC or the Swern oxidation are recommended. Oxidation with chromic acid yields propionic acid.

3 - Preparation

1-Propanol is manufactured by catalytic hydrogenation of propionaldehyde. The propion aldehyde is itself produced via the oxo process, by hydro formylation of ethylene using carbon monoxide and hydrogen in the presence of a catalyst such as cobalt octacarbonyl or a rhodium complex.

$$H_2C{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH{=}O$$
$$CH_3CH_2CH{=}O + H_2 \rightarrow CH_3CH_2CH_2OH$$

A traditional laboratory preparation of 1-propanol involves treating *n*-propyl iodide with moist Ag_2O.

1-Propanol was discovered in 1853 by Chancel, who obtained it by fractional distillation of fusel oil. Indeed 1-propanol is a major constituent of fusel oil, a by-product formed from certain amino acids when potatoes or grains are fermented to produce ethanol. This process is no longer a significant source of 1-propanol.

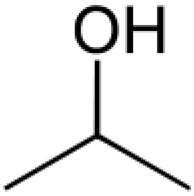
4 - Safety

1-Propanol is thought to be similar to ethanol in its effects on human body, but 2 - 4 times more potent. Oral LD_{50} in rats is 1870 mg/kg (compared to 7060 mg/kg for ethanol). It is metabolized into propionic acid. Effects include alcoholic intoxication and high anion gap metabolic acidosis. As of 2011, only one case of lethal 1-propanol poisoning was reported.

4 – 1 - Inhalation

Although this method is rare, it does indeed exist. Propanol might be much more convenient than ethanol for inhalation because of its potency with nebulizers.

Isopropyl Alcohol



Contents

1 - Introduction

Isopropyl alcohol is a common name for a chemical compound with the molecular formula C_3H_8O. It is a colorless, flammable chemical compound with a strong odor. It is the simplest example of a *secondary alcohol*, where the alcohol carbon is attached to two other carbons sometimes shown as $(CH_3)_2CHOH$. It is a structural isomer of propanol.

IUPAC name : isopropyl alcohol

Preferred IUPAC name : Propan-2- ol

Other names :
2-propanol , isopropanol , isopropyl alcohol , rubbing alcohol,

sec-propyl alcohol or *s*-propanol , I Pr OH	
Molecular formula	C_3H_8O
Molar mass	60 g mol^{-1}
Appearance	Colorless liquid
Density	0.786 g / cm^3 (20 °C)
Melting point	− 89 °C
Boiling point	82.5 °C
Solubility in water	miscible
Solubility	miscible in benzene, chloroform, ethanol, ether, glycerin soluble in acetone insoluble in salt solutions
Acidity (pK_a)	16.5
Refractive index (n_D)	1.3776
Viscosity	2.86 cP at 15 °C 1.96 cP at 25 °C 1.77 cP at 30 °C
GHS pictograms	⚠ 🔥
GHS signal word	Danger
Main hazards	Flammable
Flash point	11.7 °C (open cup) 13 °C (closed cup)
Auto ignition temperature	399 °C
LD_{50}	3600 mg / kg (oral, mouse), 12800 mg/kg (dermal, rabbit), LC_{50} = 53000 mg/m^3 (inhalation, mouse)
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

2 - Properties

Isopropyl alcohol is miscible in water, alcohol, ether and chloroform. It will dissolve ethyl cellulose, polyvinyl butyral, many oils, alkaloids, gums and natural resins . It is insoluble in salt solutions. Unlike ethanol or methanol, isopropyl alcohol can be separated from aqueous solutions by adding a salt such as sodium chloride, sodium sulfate, or any of several other inorganic salts, since the alcohol is much less soluble in saline solutions than in salt-free water. The process is colloquially called *salting out*, and causes concentrated isopropyl alcohol to separate into a distinct layer.

Isopropyl alcohol forms an azeotrope with water, which gives a boiling point of 80.37 ^{o}C and a composition of 87.7 wt % (91 vol%) isopropyl alcohol. Water-isopropyl alcohol mixtures have depressed melting points. It has a slightly bitter taste, and is not safe to drink.

Isopropyl alcohol becomes increasingly viscous with decreasing temperature. At temperatures below - 70 °C Isopropyl alcohol resembles maple syrup in viscosity.

Isopropyl alcohol has a maximum absorbance at 204 nm in an ultraviolet-visible spectrum .

3 - Reactions

Isopropyl alcohol can be oxidized to acetone, which is the corresponding ketone. This can be achieved using oxidizing agents such as chromic acid, or by dehydrogenation of isopropyl alcohol over a heated copper catalyst :

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$$

Isopropyl alcohol is often used as both solvent and hydride source in the Meerwein – Ponndorf - Verley reduction and other transfer hydrogenation reactions; it is oxidized to acetone. Isopropyl alcohol may be converted to 2-bromopropane using phosphorus tri bromide, or dehydrated to propene by heating with sulfuric acid.

Like most alcohols, isopropyl alcohol reacts with active metals such as potassium to form alkoxides which can be called *isopropoxides*. The reaction with aluminium (initiated by a trace of mercury) is used to prepare the catalyst aluminium iso propoxide.

4 - Production

In 1994, 1.5 million tones of isopropyl alcohol were produced in the United States, Europe, and Japan. This compound is primarily produced by combining water and propene in a hydration reaction. It is also produced by hydrogenating acetone.

There are two routes for the hydration process: indirect hydration via the sulfuric acid process, and direct hydration. The former process, which can use low-quality propene, predominates in the USA while the latter process, which requires high-purity propene, is more commonly used in Europe. These processes give predominantly isopropyl alcohol rather than 1-propanol because the addition of water or sulfuric acid to propene follows Markovnikov's rule.

4 – 1 - Indirect hydration

The indirect process reacts propene with sulfuric acid to form a mixture of sulfate esters. Subsequent hydrolysis of these esters by steam produces isopropyl alcohol, which is distilled. Diisopropyl ether is a significant by-product of this process; it is recycled back to the process and hydrolyzed to give the desired product.

4 – 2 - Direct hydration

Direct hydration reacts propene and water, either in gas or liquid phases, at high pressures in the presence of solid or supported acidic catalysts. Higher purity propylene (> 90 %) tends to be required for this type of process.

Both processes require that the isopropyl alcohol be separated from water and other by-products by distillation. Isopropyl alcohol and water form an azeotrope and simple distillation gives a material which is 87.9 % by weight isopropyl alcohol and 12.1 % by weight water . Pure (anhydrous) isopropyl alcohol is made by azeotropic distillation of the wet isopropyl alcohol using either diisopropyl ether or cyclo hexane as azeotroping agents.

4 – 3 - Hydrogenation of acetone

Crude acetone is hydrogenated in the liquid phase over Raney nickel or a mixture of copper and chromium oxide to give isopropyl alcohol. This process is useful when coupled with excess acetone production, such as the cumene process.

5 - Uses

In 1990, 45 thousand tones of isopropyl alcohol were used in the United States. The vast majority of isopropyl alcohol was used as a solvent for coatings or for industrial processes. Isopropyl alcohol in particular is popular for pharmaceutical applications,[6] presumably due to the low toxicity of any residues. Some isopropyl alcohol is used as a chemical intermediate. Isopropyl alcohol may be converted to acetone, but the cumene process is more significant. In that year, a tiny fraction (5.4 tones) was consumed for household use and in personal care products. It is also used as a gasoline additive.

5 – 1 - Solvent

Isopropyl alcohol dissolves a wide range of non-polar compounds. It also evaporates quickly and is relatively non-toxic, compared to alternative solvents. Thus it is used widely as a solvent and as a cleaning fluid, especially for dissolving oils.

Examples of this application include cleaning electronic devices such as contact pins (like those on ROM cartridges), magnetic tape and disk heads (such as those in audio and video tape recorders and floppy disk drives), the lenses of lasers in optical disc drives (e.g. CD, DVD) and removing thermal paste from heat sinks and IC packages (such as CPUs.) Isopropyl alcohol is used in keyboard, LCD and laptop cleaning, is sold commercially as a whiteboard cleaner, and is a strong but safer alternative to common household cleaning products. It is used to clean LCD and glass computer monitor screens (at some risk to the anti - reflection coating on some screens ' and used to give second - hand or worn non-vinyl phonograph records newer-looking sheen. It is effective at removing Hot-Melt Adhesive from a large variety of surfaces. Isopropyl alcohol should not be used to clean vinyl records as it may leach plasticizer from the vinyl making it more rigid . It is effective at removing residual glue from some sticky labels although some other adhesives used on tapes and paper labels are resistant to it. It can also be used to remove stains from most fabrics, wood, cotton, etc. In addition it can also be used to clean paint or other oil based products so that they may be reused, commonly known as "repainting." It is used as a wetting agent in the fountain solution used in lithographic printing, and often used as a solvent for French polishing shellac used in cabinet making.

5 – 2 - Intermediate

Isopropyl alcohol is esterified to give isopropyl acetate, another solvent. It reacts with carbon disulfide and sodium hydroxide to give sodium isopropyl xanthate , a herbicide and an ore flotation reagent. Isopropyl alcohol reacts with titanium tetrachloride and aluminium metal to give titanium and aluminium iso propoxides respectively, the former a catalyst, and the latter a chemical reagent.[6] This compound may serve as a chemical reagent in itself, by acting as a dihydrogen donor in transfer hydrogenation.

5 – 3 - Medical

Disinfecting pads typically contain a 60 – 70 % solution of isopropyl alcohol in water. A 75 % v / v solution in water may be used as a hand sanitizer. Isopropyl alcohol is used as a water-drying aid for the prevention of otitis externa, better known as swimmer's ear.

5 – 4 - Automotive

Isopropyl alcohol is a major ingredient in "gas dryer" fuel additives. In significant quantities, water is a problem in fuel tanks, as it separates from the gasoline, and can freeze in the supply lines at cold temperatures. It does not remove water from gasoline; rather, the alcohol solubilizes water in gasoline. Once soluble, water does not pose the same risk as insoluble water as it will no longer accumulate in the supply lines and freeze. Isopropyl alcohol is often sold in aerosol cans as a windshield de-icer. Isopropyl alcohol is also used to remove brake fluid traces from hydraulic braking systems, so that the brake fluid (usually DOT 3, DOT 4 or mineral oil) does not contaminate the brake pads, which would result in poor braking.

5 – 5 - Laboratory

As a biological specimen preservative, isopropyl alcohol provides a comparatively non-toxic alternative to formaldehyde and other synthetic preservatives. Isopropyl alcohol solutions of 90–99% are used to preserve specimens.

Isopropyl alcohol is often used in DNA extraction. It is added to a DNA solution in order to precipitate the DNA into a 'pellet' after centrifuging the DNA. This is possible because DNA is insoluble in isopropyl alcohol.

6 - Safety

Isopropyl alcohol vapor is denser than air and is flammable with a combustible range between 2 and 12.7 % in air. It should be kept away from heat and open flame. Isopropyl alcohol has also been reported to form peroxides, which may explode upon concentration . Isopropyl alcohol is a skin irritant.

7 - Toxicology

Isopropyl alcohol and its metabolite, acetone, act as central nervous system (CNS) depressants. Symptoms of isopropyl alcohol poisoning include flushing, headache, dizziness, CNS depression, nausea, vomiting, anesthesia, and coma. Poisoning can occur from ingestion, inhalation, or absorption; therefore, well-ventilated areas and protective gloves are recommended. Around 15 g of isopropyl alcohol can have a toxic effect on a 70 kg human if left untreated.[16] However, it is not nearly as toxic as methanol or ethylene glycol. Isopropyl alcohol does not cause an anion gap acidosis (in which a lowered blood serum pH causes depletion of bicarbonate anion) unlike ethanol and methanol. Isopropyl alcohol does however, produce an osmolal gap between the calculated and measured osmolalities of serum, as do the other alcohols. Overdoses may cause a fruity odor on the breath as a result of its metabolism to acetone, which is further metabolized to produce the nutrients acetate and glucose. Isopropyl alcohol is oxidized to form acetone by alcohol dehydrogenase in the liver.

8 - History

In 1920, Standard Oil first produced isopropyl alcohol by hydrating propene. Its major use at the time was not rubbing alcohol, but for oxidation to acetone, whose first major use was in World War One for the preparation of the explosive Cordite.

Butanol

Contents

1 - Introduction

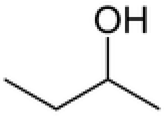
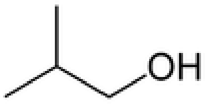
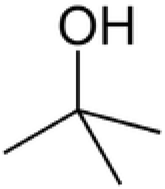
Butanol or butyl alcohol (some times also called *biobutanol* when produced biologically), is a primary alcohol with a 4 carbon structure and the molecular formula of C_4H_9OH. It belongs to the higher alcohols and branched-chain alcohols.

It is primarily used as a solvent, as an intermediate in chemical synthesis, and as a fuel.

There are four isomeric structures for butanol.

2 - Isomers

The unmodified term *butanol* usually refers to the straight chain isomer with the alcohol functional group at the terminal carbon, which is also known as *n*-butanol or 1-butanol. The straight chain isomer with the alcohol at an internal carbon is *sec*-butanol or 2-butanol. The branched isomer with the alcohol at a terminal carbon is isobutanol; 2-methyl-1-propanol, and the branched isomer with the alcohol at the internal carbon is *tert*-butanol; 2-methyl-2-propanol.

			
n-butanol	*sec-butanol*	*isobutanol*	*tert-butanol*

Butanol isomers, due to their different structures, have somewhat different melting and boiling points. n-Butanol and isobutanol have limited solubility, while the other two isomers are fully miscible with water. This is because all alcohols have a hydroxyl group which makes them polar which in turn tends to promote solubility in water. At the same time, the carbon chain of the alcohol resists solubility in water. Methanol, ethanol, and propanol are fully miscible with water, while n-butanol is only moderately miscible because of the balance between the two opposing solubility trends.

3 - Toxicity

Like many alcohols, butanol is considered toxic. It has shown low order of toxicity in single dose experiments to laboratory animals. and is considered safe enough for use in cosmetics. Brief, repeated overexposure with the skin can result in depression of the central nervous system, as with other short-chain alcohols. Exposure may also cause severe eye irritation and moderate skin irritation. The main dangers are from prolonged exposure to fumes. In extreme cases this includes suppression of the central nervous system and even death. Under most circumstances, butanol is quickly metabolized to carbon dioxide. It has not been shown to damage DNA or cause cancer.

4 - Uses

4 – 1 - Biobutanol

Butanol is considered as a potential bio fuel (butanol fuel). Butanol at 85 percent strength can be used in cars designed for gasoline (petrol) without any change to the engine (unlike 85% ethanol), and it contains more energy for a given volume than ethanol and almost as much as gasoline, so a vehicle using butanol would return fuel consumption more comparable to gasoline than ethanol. Butanol can also be used as a blended additive to diesel fuel to reduce soot emissions .

4 – 2 - Other uses

Butanol sees use as a solvent for a wide variety of chemical and textile processes, in organic synthesis and as a chemical intermediate. It is also used as a paint thinner and a solvent in other coating applications where it is used as a relatively slow evaporating latent solvent in lacquers and ambient-cured enamels. It finds other uses such as a component of hydraulic and brake fluids.

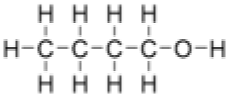
It is also used as a base for perfumes, but on its own has a highly alcoholic aroma.

Salts of butanol are chemical intermediates; for example alkali metal salts of tert-butanol are tert-butoxides.

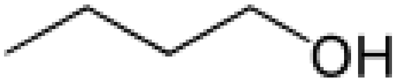
5 - Production

Since the 1950s, most butanol in the United States is produced commercially from fossil fuels. The most common process starts with propene (propylene), which is run through a hydroformylation reaction to form butyr aldehyde, which is then reduced with hydrogen to 1-butanol and/or 2-butanol. Tert-butanol is derived from isobutane as a co-product of propylene oxide production. Butanol can also be produced by fermentation of biomass by bacteria. Prior to the 1950s, *Clostridium acetobutylicum* was used in industrial fermentation processes producing butanol. Research in the past few decades showed results of other microorganisms that can produce butanol through fermentation.

n – Butanol (Butan – 1 - ol)



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H}$$



Contents

1 - Introduction

n-Butanol or *n*-butyl alcohol or normal butanol is a primary alcohol with a 4-carbon structure and the molecular formula C_4H_9OH. Its isomers include iso butanol , 2-butanol, and *tert*-butanol. Butanol is one of the group of "fusel alcohols" (from the German for "bad liquor"), which have more than two carbon atoms and have significant solubility in water.

n-Butanol occurs naturally as a minor product of the fermentation of sugars and other carbohydrates, and is present in many foods and beverages. It is also a permitted artificial flavorant in the United States, used in butter, cream, fruit, rum, whiskey, ice cream and ices, candy, baked goods and cordials. It is also used in a wide range of consumer products.

The largest use of *n*-butanol is as an industrial intermediate, particularly for the manufacture of butyl acetate (itself an artificial flavorant and industrial solvent). It is a petrochemical, manufactured from propylene and usually used close to the point of manufacture. Estimated production figures for 1997 are: United States 784,000 tones; Western Europe 575,000 tones; Japan 225,000 tones.

Systematic name ; Butan -1- ol	
Other names : Butalcohol Butanol 1-Butanol Butyl alcohol Butyl hydrate Butylic alcohol Butyralcohol Butyric alcohol Butyryl alcohol Hydroxybutane Propylcarbinol	
Molecular formula	$C_4H_{10}O$
Molar mass	74 g mol^{-1}
Appearance	Colourless liquid
Density	0.81 g cm^{-3}
Melting point	−90 °C, 183 K, -130 °F
Boiling point	118 °C
Solubility in water	73 g L^{-1} at 25°C
Refractive index (n_D)	1.399 (20 °C)
Viscosity	3 cP
EU classification	✖ Xn
Flash point	35 °C
Auto ignition temperature	343 °C
Explosive limits	1.4 –11.2 %

2 - Production

n-Butanol is produced industrially from the petrochemical feedstock propylene. Propylene is hydro formylated to butyr aldehyde (oxo process) in the presence of a rhodium-based homogeneous catalyst similar to Wilkinson's catalyst. The butyraldehyde is then hydrogenated to produce *n*-butanol.

3 - Industrial use

n-butanol is an intermediate in the production of butyl acrylate, butyl acetate, dibutyl phthalate, dibutyl sebacate, and other butyl esters, butyl ethers such as ethylene glycol mono butyl ether, di- and tri ethylene glycol mono butyl ether, and the corresponding butyl ether acetates. Other industrial uses include the manufacture of pharmaceuticals, polymers, pyroxylin plastics, herbicide esters, printing (e.g., 2,4-D, 2,4,5-T) and butyl xanthate. It is also used as a diluent/reactant in the manufacture of urea–formaldehyde and melamine–formaldehyde resins.

4 - Other uses

n-Butanol is used as an ingredient in perfumes and as a solvent for the extraction of essential oils. *n*-Butanol is also used as an extractant in the manufacture of antibiotics, hormones, and vitamins; a solvent for paints, coatings, natural resins, gums, synthetic resins, dyes, alkaloids, and camphor. Other miscellaneous applications of *n*-butanol are as a swelling agent in textiles, as a component of hydraulic brake fluids, cleaning formulations, degreasers, and repellents; and as a component of ore floation agents, and of wood-treating systems.

n-Butanol has been proposed as a substitute for diesel fuel and gasoline. It is produced in small quantities in nearly all fermentations (see fusel oil), but species of Clostridium produce much higher yields of butanol, and research is currently underway to increase the ultimate yield of bio butanol from biomass.

The production or, in some cases, use of the following substances may result in exposure to *n*-butanol: artificial leather, butyl esters, rubber cement, dyes, fruit essences, lacquers, motion picture, and photographic films, raincoats, perfumes, pyroxylin plastics, rayon, safety glass, shellac varnish, and waterproofed cloth.

4 – 1 - Occurrence in Nature

Alarm pheromones emitted by the Koschevnikov gland of honey bees contain n-butanol.

5 - Occurrence in food

n-Butanol occurs naturally as a result of carbohydrate fermentation in a number of alcoholic beverages, including beer,[11] grape brandies, wine, and whisky . It has been detected in the volatiles of hops, jack fruit , heat - treated milks, musk melon, cheese, southern pea seed, and cooked rice. *n*-Butanol is also formed during deep frying of corn oil, cottonseed oil, trilinolein, and triolein.

n-Butanol is used as an ingredient in processed and artificial flavourings, and for the extraction lipid-free protein from egg yolk, natural flavouring materials and vegetable oils, the manufacture of hop extract for beer making, and as a solvent in removing pigments from moist curd leaf protein concentrate.

6 - Metabolism and toxicity

n-Butanol is readily absorbed through the intestinal tract and lungs, and also to some extent through the skin. It is metabolized completely in vertebrates in a manner similar to ethanol: alcohol dehydrogenase converts *n*-butanol to butyr aldehyde; this is then converted to butyric acid by aldehyde dehydrogenase. Butyric acid can be fully metabolized to carbon dioxide and water by the β-oxidation pathway, of which it is naturally the penultimate step. In the rat, only 0.03 % of an oral dose of 2000 mg / kg was excreted in the urine.

The acute toxicity of *n*-butanol is relatively low, with oral LD_{50} values of 790 – 4360 mg / kg (rat; comparable values for ethanol are 7000 – 15000 mg / kg). No deaths were reported at an inhaled concentration of 8000 ppm (4- hour exposure, rats). At sub-lethal doses, *n*-butanol acts as a depressant of the central nervous system, similar to ethanol: one study in rats indicated that the intoxicating potency of *n*-butanol is some six times higher than that of ethanol, possibly because of its slower transformation by alcohol dehydrogenase.

n-Butanol is a natural component of many alcoholic beverages, albeit in low (but variable) concentrations. It (along with similar fusel alcohols) is reputed to be responsible for severe "hangovers", although experiments in animal models show no evidence for this.[31] An unknown dose *n*-Butanol was consumed by a 47-year-old male with no previous medical history, leading to a range of adverse health effects.

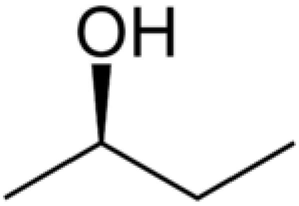
7 - Other hazards

Liquid *n*-butanol, as is common with most organic solvents, is extremely irritating to the eyes; repeated contact with the skin can also cause irritation. This is believed to be a generic effect of "defatting". No skin sensitization has been observed. Irritation of the respiratory pathways occurs only at very high concentrations (> 2400 ppm).

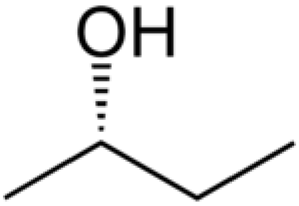
With a flash point of 29 °C (84 °F), *n*-butanol presents a moderate fire hazard: it is slightly more flammable than kerosene or diesel fuel but less flammable than many other common organic solvents. The depressant effect on the central nervous system (similar to ethanol intoxication) is a potential hazard when working with *n*-butanol in enclosed spaces, although the odour threshold (0.2–30 ppm) is far below the concentration which would have any neurological effect.

n-Butanol is of low toxicity to aquatic vertebrates and invertebrates. It is rapidly biodegraded in water, although an estimated 83 % partitions to air where it is degraded by hydroxyl radicals with a half-life of 1.2 – 2.3 days. It has low potential to bio accumulate. A potential hazard of significant discharges to watercourses is the rise in chemical oxygen demand (C.O.D.) associated with its biodegradation.

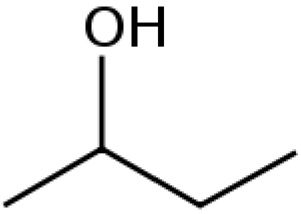
2-Butanol (Butan - 2 - ol)



(R)-(−) -2-butanol



(S)-(+)-2-butanol



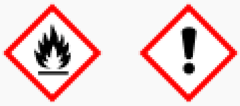
2-butanol

Contents

1 - Introduction

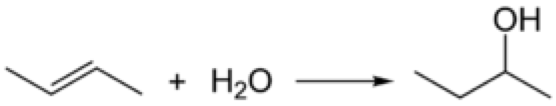
2-Butanol, or *sec*-butanol, is an organic compound with formula $CH_3CH(OH)CH_2CH_3$. This secondary alcohol is a flammable, colorless liquid that is soluble in 12 parts water and completely miscible with polar organic solvents such as ethers and other alcohols. It is produced on a large scale, primarily as a precursor to the industrial solvent methyl ethyl ketone. 2-Butanol is chiral and thus can be obtained as either of two stereoisomers designated as *(R)*-(−)-2-butanol and *(S)*-(+)-2-butanol. It is normally found as an equal mixture of the two stereo isomers — a racemic mixture.

IUPAC name : Butan -2 - ol	
Other names : *sec*-Butanol *sec*-Butyl alcohol 2-Butanol 2-Butyl alcohol	
Molecular formula	$C_4H_{10}O$
Molar mass	74 g mol^{-1}

Density	0.808 g cm^{-3}
Melting point	-115 °C
Boiling point	98-100 °C
Solubility in water	290 g dm^{-3}
Vapor pressure	1.67 kPa (at 20 °C)
Refractive index (n_D)	1.3978 (at 20 °C)
GHS pictograms	
Flash point	22–27 °C
Auto ignition temperature	405 °C
Explosive limits	1.7–9.8%

2 - Manufacture and applications

2-Butanol is manufactured industrially by the hydration of 1-butene or 2-butene:



Sulfuric acid is used as a catalyst for this conversion.

Although some 2-butanol is used as a solvent, it is mainly converted to butanone ("MEK"), which is an important industrial solvent and found in many domestic cleaning agents and paint removers. Volatile esters of 2-butanol have pleasant aromas and are used in small amounts as perfumes or in artificial flavors.

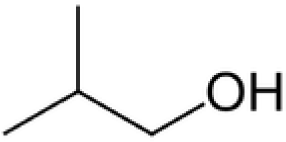
3 - Solubility

The solubility of sec-butanol is incorrect in most sources, including some of the most well-known references such as the Merck Index, the CRC Handbook of Chemistry and Physics, and Lange's Handbook of Chemistry. Even the International Programme on Chemical Safety lists the wrong solubility. This widespread error originated because of Beilstein's *Handbuch der Organischen Chemie* (*Handbook of Organic Chemistry*). This work cites a false solubility of 12.5 g / 100 ml water. Many other sources used this solubility, which has snowballed into a widespread error in the industrial world. The correct data (35.0 g / 100 ml at 20°C, 29 g/100 ml at 25°C, and 22 g/100 ml at 30°C) was first published in 1886 by Alexejew and then similar data was reported by other scientists including Dolgolenko and Dryer in 1907 and 1913, respectively. As petty of an error as this may seem, teachers and students have been frustrated by the error for years.

4 - Safety

Several explosions have been reported[4] during the conventional distillation of 2-butanol, apparently due to the buildup of peroxides with the boiling point higher than that of pure alcohol (and therefore concentrating in the still pot during distillation). As alcohols, unlike ethers, are not widely known to be capable of forming peroxide impurities, the danger is likely to be over looked.

Iso Butanol



Contents

1 - Introduction

Iso butanol (IUPAC nomenclature : 2-methyl-1-propanol) is an organic compound with the formula $(CH_3)_2CHCH_2OH$. This colorless, flammable liquid with a characteristic smell is mainly used as a solvent. Its isomers include *n*-butanol, 2-butanol, and *tert*-butanol, all of which are more important industrially.

IUPAC name : 2 - methyl -1- propanol	
Other names : Isobutyl alcohol, IBA, 2- methyl propyl alcohol	
Molecular formula	$C_4H_{10}O$
Molar mass	74 g / mol
Appearance	Colorless liquid
Density	0.802 g / cm^3, liquid
Melting point	-101.9 °C
Boiling point	107.89 °C
Solubility in water	8.7 mL / 100 mL
Refractive index (n_D)	1.3959
Viscosity	3.95 cP at 20 °C
EU classification	Irritant (Xi)
Flash point	28 °C (82 °F)

Auto ignition temperature	415 °C
Explosive limits	1.7 – 10.9 %

2 - Production

Iso butanol is produced by the carbonylation of propylene. Two methods are practiced industrially, hydro formylation is more common and generates a mixture of normal and iso butyr aldehydes, which are hydrogenated to the alcohols and then separated. Reppe carbonylation is also practiced.

Iso butanol is also produced naturally during the fermentation of carbohydrates and may also be a byproduct of the decay process of organic matter. Iso butanol, along with other low molecular weight alcohols can also be produced by some engineered microorganisms such as E. coli.

3 - Applications

Iso butanol has a variety of technical and industrial applications:

feedstock in the manufacture of isobutyl acetate, which is used in the production of lacquer and similar coatings, and in the food industry as a flavoring agent

precursor of derivative esters - isobutyl esters such as di iso butyl phthalate (DIBP) are used as plasticizers in plastics, rubbers, and other dispersions

paint solvent

varnish remover

ink ingredient

paint additive, to reduce viscosity, improve brush flow, and retard formation of oil residues (*blush*) on painted surfaces

gasoline additive, to reduce carburetor icing

automotive polish additive

automotive paint cleaner additive

chemical extractant in production of organic compounds

mobile phase in thin layer chromatography.

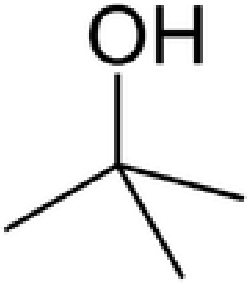
Iso butanol could possibly serve as an alternative to gasoline to fuel combustion engines. A process is being developed by Gevo.[5] A 1993 SAE technical paper addresses blending methanol, ethanol and iso butanol with unleaded gasoline for use as a motor fuel. A similar mixture is being used by Dyson Racing in the 2010 American LeMans Series. Gevo acquired Agri-Energy's Luverne, Minnesota, ethanol production facility to retrofit it to produce commercial quantities of iso butanol for motor fuel. The US Air Force A-10 Thunderbolt is the first aircraft to fly using Alcohol To Jet (ATJ) fuel

4 - Safety and regulation

Isobutanol is one of the least toxic of the butanols with an LD_{50} of 2460 mg/kg (rat, oral).

In March 2009, the Canadian government announced a ban on iso butanol use in cosmetics.

tert - Butyl Alcohol



Contents

1 - Introduction

tert-Butyl alcohol (TBA), or 2-methyl-2-propanol (2M2P), is the simplest tertiary alcohol. It is one of the three isomers of butanol. *tert*-Butanol is a clear liquid (or a colorless solid, depending on the ambient temperature) with a camphor-like odor. It is very soluble in water and miscible with ethanol and diethyl ether. It is unique among the isomers of butanol because it tends to be a solid at room temperature, with a melting point slightly above 25 °C.

IUPAC name : 2-Methylpropan - 2- ol	
Other names : *tert*-Butanol 2-Methyl-2-propanol	
Molecular formula	$C_4 H_{10} O$
Molar mass	74 g mol^{-1}
Appearance	Colorless liquid
Odor	Camphorous
Density	0.775 g / mL

Melting point	25-26 °C
Boiling point	82-83 °C
Solubility in water	miscible
log P	0.584
Vapor pressure	4.1 kPa (at 20 °C)
Refractive index (n_D)	1.387
Specific heat capacity, C	215.37 J K^{-1} mol^{-1}
EU classification	🔥 F ✖ Xn
Flash point	11 °C
Auto ignition temperature	480 °C
Explosive limits	2.4 – 8.0 %

2 - Natural occurrence

t-Butyl alcohol have been identified but not quantified, in beer and chickpeas. It is also found in cassava which is used as fermentation ingredient in certain alcoholic beverages.

3 - Preparation

Tert - Butyl alcohol is derived commercially from iso butane as a co - product of propylene oxide production. It can also be produced by the catalytic hydration of isobutylene, or by a Grignard reaction between acetone and methyl magnesium chloride.

4 - Applications

tert-Butyl alcohol is used as a solvent, as a denaturant for ethanol, as an ingredient in paint removers, as an octane booster for gasoline, as an oxygenate gasoline additive, and as an intermediate in the synthesis of other chemical commodities such as MTBE, ETBE, TBHP, other flavors and perfumes.

5 - Chemistry

As a tertiary alcohol, *tert*-butyl alcohol is more stable to oxidation and less reactive than the other isomers of butanol.

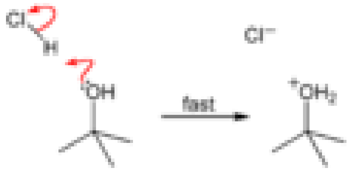
When *tert*-butyl alcohol is deprotonated with a strong base, the product is an alkoxide anion. In this case, it is *tert*-butoxide. For example, the commonly used organic reagent potassium *tert*-butoxide is prepared by refluxing dry *tert*-butanol with potassium metal.

$$K + t\mathrm{BuOH} \rightarrow t\mathrm{BuO}^{-}\mathrm{K}^{+} + {}^{1}/_{2}\,\mathrm{H}_2$$

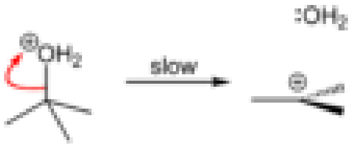
The *tert*-butoxide species is itself useful as a strong, non-nucleophilic base in organic chemistry. It is able to abstract acidic protons from the substrate molecule readily, but its steric bulk inhibits the group from participating in nucleophilic substitution, such as in a Williamson ether synthesis or an S_N2 reaction.

6 - Conversion to alkyl halide

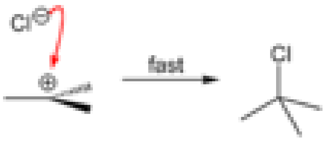
tert-Butyl alcohol reacts with hydrogen chloride to form *tert*-butyl chloride and water via an S_N1 mechanism.



Step 1

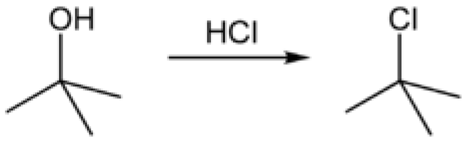


Step 2



Step 3

The overall reaction, therefore, is:



Because *tert*-butyl alcohol is a tertiary alcohol, the relative stability of the *tert*-butyl carbocation in the Step 2 allows the S_N1 mechanism to be followed. Primary alcohols generally undergo an S_N2 mechanism because the relative stability of a primary carbocation intermediate is very low. The tertiary carbocation in this case is stabilized through hyper conjugation where the neighboring C–H sigma bonds donate electrons into the empty p-orbital of the carbocation.

Butanol Fuel

Contents

1 - Introduction

Butanol may be used as a fuel in an internal combustion engine. Because its longer hydrocarbon chain causes it to be fairly non-polar, it is more similar to gasoline than it is to ethanol. Butanol has been demonstrated to work in vehicles designed for use with gasoline without modification. It has a four link hydrocarbon chain. It can be produced from biomass (as "bio butanol") as well as fossil fuels (as "petro butanol") ; but bio butanol and petro butanol have the same chemical properties.

2 - Production of bio butanol

Butanol from biomass is called biobutanol.[3] It can be used in unmodified gasoline engines.

2 – 1 - Technologies

Bio butanol can be produced by fermentation of biomass by the A.B.E. process. The process uses the bacterium *Clostridium acetobutylicum*, also known as the *Weizmann organism*. It was Chaim Weizmann who first used this bacterium for the production of acetone from starch (with the main use of acetone being the making of Cordite) in 1916. The butanol was a by-product of this fermentation (twice as much butanol was produced). The process also creates a recoverable amount of H_2 and a number of other by-products: acetic, lactic and propionic acids, iso propanol and ethanol.

Bio butanol can also be made using *Ralstonia eutropha* H16. This process requires the use of a electro-bioreactor and the input of carbon dioxide and electricity.

The difference from ethanol production is primarily in the fermentation of the feedstock and minor changes in distillation. The feedstocks are the same as for ethanol: energy crops such as sugar beets, sugar cane, corn grain, wheat and cassava, prospective non-food energy crops such as switchgrass and even guayule in North America, as well as agricultural byproducts such as straw and corn stalks.[6] According to DuPont, existing bio ethanol plants can cost-effectively be retrofitted to bio butanol production.

Additionally, butanol production from biomass and agricultural byproducts could be more efficient (i.e. unit engine motive power delivered per unit solar energy consumed) than ethanol or methanol production.

2 - 1 – 1 - Algae butanol

Bio butanol can be made entirely with solar energy, from algae (called Solalgal Fuel) or diatoms.

2 – 2 - Research

Although bio fuel demand has risen to over one billion liters (about 260 million US gallons) yearly , fermentation remains a largely inefficient method of butanol production. Under normal living conditions, *Clostridium* bacterial communities have a low yield of butanol per gram of glucose. Obtaining higher yields of butanol involves manipulation of the metabolic networks within bacteria to prioritize the synthesis of the bio fuel. Metabolic engineering and genetic engineering tools allow scientists to alter the states of reactions occurring in the organism, utilizing advanced techniques to create a bacterial strain capable of high butanol yield. Optimization can also be accomplished by the transfer of specific genetic information to other uni-cellular species, capitalizing on the traits of multiple organisms to achieve the highest rate of alcohol production.

2 – 2 – 1 - Using Alternate Carbon Sources

One promising development in bio butanol production technology was discovered in the late summer of 2011 - Tulane University's alternative fuel research scientists discovered a strain of *Clostridium*, called "TU-103", that can convert nearly any form of cellulose into butanol, and is the only known strain of *Clostridium*-genus bacteria that can do so in the presence of oxygen. The university's researchers have stated that the source of the "TU-103" *Clostridium* bacteria strain was most likely from the solid waste from one of the plains zebra at New Orleans' Audubon Zoo.

Metabolic engineering can be used to allow an organism to use a cheaper substrate such as glycerol instead of glucose. Because fermentation processes require glucose derived from foods, butanol production can negatively impact food supply . Glycerol is a good alternative source for butanol production. While glucose sources are valuable and limited, glycerol is abundant and has a low market price because it is a waste product of biodiesel production. Butanol production from glycerol is economically viable using metabolic pathways that exist in *Clostridium pasteurianum* bacterium.

A combination of succinate and ethanol can be fermented to produce butyrate (a precursor to butanol fuel) by utilizing the metabolic pathways present in a gram-positive anaerobic bacterium *Clostridium kluyveri*. Succinate is an intermediate of the TCA cycle, which metabolizes glucose. Anaerobic bacteria such as *Clostridium acetobutylicum* and *Clostridium saccharobutylicum* also contain these pathways. Succinate is first activated and then reduced by a two-step reaction to give 4-hydroxybutyrate, which is then metabolized further to crotonyl-coenzyme A (CoA) . Crotonyl-CoA is then converted to butyrate. The genes corresponding to these butanol production pathways from *Clostridium* were cloned to *E. coli*.

In 2012 researchers developed a method for storing electrical energy as chemical energy in higher alcohols (including butanol). These alcohols can then be used as liquid transportation fuels. The team led by James Liao genetically engineered lithoautotrophic microorganism known as *Ralstonia Eutropha* H16 to produce isobutanol and 3-methyl-1-butanol in an electro-bioreactor. Carbon dioxide is the sole carbon source for this process and electricity is used as the energetic component. The process they developed effectively separates the light and dark reactions that occur during photosynthesis. Solar panels are used to convert sunlight to electrical energy which is then converted using the microorganism to a chemical intermediate. The team is now in the process of scaling up the operation and believes this process will be more efficient than the biologic process.

2 – 2 – 2 - Improving Efficiency

In late 2012, A new discovery should make the alternative fuel butanol more attractive to the bio fuel industry. Scientist Hao Feng has found a way around the bottleneck that has frustrated producers in the past and could significantly reduce the cost of the energy involved in making it as well. His team was able to isolate the butanol molecules during the fermentation process so it does not kill the organisms and produces 100 % or more butanol. After the fermentation process, they used a process called cloud point separation to recover the butanol which used 4 times less energy.

Also in late 2012, utilizing systems metabolic engineering, a Korean research team at the formally the Korea Advanced Institute of Science and Technology (KAIST) has succeeded in demonstrating an optimized process to increase butanol production by generating an engineered bacterium. Professor Sang Yup Lee at the Department of Chemical and Bio molecular Engineering, KAIST, Dr. Do Young Seung at GS Caltex, a large oil refining company in Korea, and Dr.

Yu-Sin Jang at Bio fuel Chem, a startup butanol company in Korea, applied a systems metabolic engineering approach to improve the production of butanol through enhancing the performance of *Clostridium acetobutylicum*, one of the best known butanol-producing bacteria. In addition, the downstream process was optimized and an in situ recovery process was integrated to achieve higher butanol titer, yield, and productivity. The combination of systems metabolic engineering and bioprocess optimization resulted in the development of a process capable of producing more than 585 g of butanol from 1.8 Kg of glucose, which allows the production of this important industrial solvent and advanced bio fuel to be cost competitive.

The anaerobic bacteria *C. pasteurianum, C. acetobutylicum*, and other *Clostridium* species have metabolic pathways that convert glycerol to butanol through fermentation. However, the production of butanol from glycerol by fermentation in *C. Pasteurianum* is low. To counter this, a group of researchers used chemical mutagenesis to create a hyper butanol producing strain. The best mutant strain in this study "MBEL_GLY2" produced 10.8 grams butanol per 80 gram glycerol fed to the bacteria. This is an improvement compared to the 7.6 g butanol produced by the native bacteria.

Many organisms have the capacity to produce butanol utilizing an acetyl - CoA dependent pathway. The main problem with this pathway is the first reaction involving the condensation of two acetyl-CoA molecules to aceto acetyl - CoA. This reaction is thermo dynamically unfavorable due to the positive Gibbs free energy associated with it (dG = 6.8 kcal/mol).[19] Some experimentation has been done that involves increasing the carbon storage through the organism by utilizing carbon dioxide flow through photosynthetic organisms. To follow in this path of research, scientists have attempted to engineer reaction pathways that can enable photosynthetic organisms (like blue-green algae) to produce butanol more efficiently.

A study done by Ethan I. Lan and James C. Liao attempted to utilize the ATP produced during photosynthesis in blue-green algae to work around the thermodynamically unfavorable acetyl-CoA condensation to aceto acetyl-CoA. The native system was re-engineered to have acetyl - CoA react with ATP and CO_2 to form an intermediate, malonyl-CoA. Malonyl - CoA then reacts with another acetyl - CoA to form the desired aceto acetyl- CoA. The energy release from ATP hydrolysis (dG = -7.3 kcal/mol) makes this pathway significantly more favorable than standard condensation. Because blue-green algae generate NADPH during photosynthesis, it can be assumed that the cofactor environment is NADPH rich. Therefore, the native reaction pathway was further engineered to use NADPH rather than the standard NADH. All of these adjustments led to a 4-fold increase in butanol production, showing the importance of ATP and cofactor driving forces as a design principle in pathway engineering.

2 – 3 – Producers

DuPont and BP plan to make bio butanol the first product of their joint effort to develop, produce, and market next-generation bio fuels.[22] In Europe the Swiss company Butalco is developing genetically modified yeasts for the production of bio butanol from cellulosic materials. Gourmet Butanol, a United States based company, is developing a process that utilizes fungi to convert organic waste into bio butanol.

The number of bio butanol producers with commercial plants coming on line continues to grow monthly.[*citation needed*] At present, there are number of bio ethanol plants, which are being converted to biobutanol plants, which should increase the number of butanol producers as they come on - line .

3 - Distribution

Butanol better tolerates water contamination and is less corrosive than ethanol and more suitable for distribution through existing pipelines for gasoline . In blends with diesel or gasoline, butanol is less likely to separate from this fuel than ethanol if the fuel is contaminated with water. There is also a vapor pressure co-blend synergy with butanol and gasoline containing ethanol, which facilitates ethanol blending. This facilitates storage and distribution of blended fuels.

4 - Properties of common fuels

Fuel	Energy density	Air-fuel ratio	Specific energy	Heat of vaporization	RON	MON
Gasoline and biogasoline	32 MJ/L	14.6	2.9 MJ/kg air	0.36 MJ/kg	91–99	81–89
Butanol fuel	29.2 MJ/L	11.1	3.2 MJ/kg air	0.43 MJ/kg	96	78
Anhydrous Ethanol fuel	19.6 MJ/L	9.0	3.0 MJ/kg air	0.92 MJ/kg	107	89
Methanol fuel	16 MJ/L	6.4	3.1 MJ/kg air	1.2 MJ/kg	106	92

4 –1 - Energy content and effects on fuel economy

Switching a gasoline engine over to butanol would in theory result in a fuel consumption penalty of about 10%[29] but butanol's effect on mileage is yet to be determined by a scientific study. While the energy density for any mixture of gasoline and butanol can be calculated, tests with other alcohol fuels have demonstrated that the effect on fuel economy is not proportional to the change in energy density.

4 –2 - Octane rating

The octane rating of n-butanol is similar to that of gasoline but lower than that of ethanol and methanol. n-Butanol has a RON (Research Octane number) of 96 and a MON (Motor octane number) of 78 (with a resulting "(R+M) / 2 pump octane number" of 87, as used in North America) while t-butanol has octane ratings of 105 RON and 89 MON. t - Butanol is used as an additive in gasoline but cannot be used as a fuel in its pure form because its relatively high melting point of 25.5 °C causes it to gel and freeze near room temperature.

A fuel with a higher octane rating is less prone to knocking (extremely rapid and spontaneous combustion by compression) and the control system of any modern car engine can take advantage of this by adjusting the ignition timing. This will improve energy efficiency, leading to a better fuel economy than the comparisons of energy content different fuels indicate. By increasing the compression ratio, further gains in fuel economy, power and torque can be achieved. Conversely, a fuel with lower octane rating is more prone to knocking and will lower efficiency. Knocking can also cause engine damage. Engine design to run on 87 octane will not have any additional power/ fuel economy from at higher octane fuel.

4 –3 - Air - fuel ratio

Alcohol fuels, including butanol and ethanol, are partially oxidized and therefore need to run at richer mixtures than gasoline. Standard gasoline engines in cars can adjust the air-fuel ratio to accommodate variations in the fuel, but only within certain limits depending on model. If the limit is exceeded by running the engine on pure butanol or a gasoline blend with a high percentage of butanol, the engine will run lean, something which can critically damage components. Compared to ethanol, butanol can be mixed in higher ratios with gasoline for use in existing cars without the need for retrofit as the air-fuel ratio and energy content are closer to that of gasoline.

4 –4 - Specific energy

Alcohol fuels have less energy per unit weight and unit volume than gasoline. To make it possible to compare the net energy released per cycle a measure called the fuels specific energy is sometimes used. It is defined as the energy released per air fuel ratio. The net energy released per cycle is higher for butanol than ethanol or methanol and about 10 % higher than for gasoline.

4 –5 - Viscosity

The viscosity of alcohols increase with longer carbon chains. For this reason, butanol is used as an alternative to shorter alcohols when a more viscous solvent is desired. The kinematic viscosity of butanol is several times higher than that of gasoline and about as viscous as high quality diesel fuel.

Substance	Kinematic viscosity at 20°C
Butanol	3.64 cSt
Diesel	>3 cSt
Ethanol	1.52 cSt
Water	1.0 cSt
Methanol	0.64 cSt
Gasoline	0.4–0.8 cSt

4 – 6 - Heat of vaporization

The fuel in an engine has to be vaporized before it will burn. Insufficient vaporization is a known problem with alcohol fuels during cold starts in cold weather. As the heat of vaporization of butanol is less than half of that of ethanol, an engine running on butanol should be easier to start in cold weather than one running on ethanol or methanol.

5 - Potential problems with the use of butanol fuel

The potential problems with the use of butanol are similar to those of ethanol :

To match the combustion characteristics of gasoline, the utilization of butanol fuel as a substitute for gasoline requires fuel-flow increases (though butanol has only slightly less energy than gasoline, so the fuel-flow increase required is only minimal, maybe 10 %, compared to 40% for ethanol.)

Alcohol-based fuels are not compatible with some fuel system components.

Alcohol fuels may cause erroneous gas gauge readings in vehicles with capacitance fuel level gauging.

While ethanol and methanol have lower energy densities than butanol, their higher octane number allows for greater compression ratio and efficiency. Higher combustion engine efficiency allows for lesser greenhouse gas emissions per unit motive energy extracted.

Butanol is one of many side products produced from current fermentation technologies; as a consequnece, current fermentation technologies allow for very low yields of pure extracted butanol. When compared to ethanol, butanol is more fuel efficient as a fuel alternative, but ethanol can be produced at a much lower cost and with much greater yields.

Butanol is toxic at a rate of 20 g per liter and may need to undergo Tier 1 and Tier 2 health effects testing before being permitted as a primary fuel by the EPA.

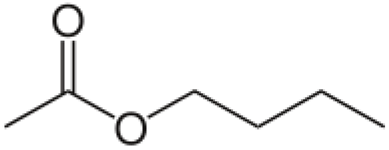
6 - Possible butanol fuel mixtures

Standards for the blending of ethanol and methanol in gasoline exist in many countries, including the EU, the US and Brazil. Approximate equivalent butanol blends can be calculated from the relations between the stochio metric fuel-air ratio of butanol, ethanol and gasoline. Common ethanol fuel mixtures for fuel sold as gasoline currently range from 5 % to 10 %. The share of butanol can be 60 % greater than the equivalent ethanol share, which gives a range from 8 % to 16 %. "Equivalent" in this case refers only to the vehicle's ability to adjust to the fuel. Other properties such as energy density, viscosity and heat of vaporization will vary and may further limit the percentage of butanol that can be blended with gasoline , Consumer acceptance may be limited due to the offensive smell of butanol. Plans are underway to market a fuel that is 85 % Ethanol and 15 % Butanol (E85B), so existing E85 internal combustion engines can run on a 100 % renewable fuel that could be made without using any fossil fuels. Because its longer hydrocarbon chain causes it to be fairly non-polar, it is more similar to gasoline than it is to ethanol. Butanol has been demonstrated to work in vehicles designed for use with gasoline without modification.

7 - Current use of butanol in vehicles

Currently no production vehicle is known to be approved by the manufacturer for use with 100 % butanol. As of early 2009, only few vehicles are approved for even using E85 fuel (i.e. 85 % ethanol + 15 % gasoline) in the USA. However, in Brazil all vehicle manufacturers (Fiat, Ford, VW, GM, Toyota, Honda, Peugeot, Citroen and others) produce flex fuel vehicles that can run on 100% ethanol or any mix of ethanol and gasoline. These flex fuel cars represent 90% of the sales of personal vehicles in Brazil, in 2009. BP and Dupont, engaged in a joint venture to produce and promote butanol fuel, claim[36] that "bio butanol can be blended up to 10%v/v in European gasoline and 11.5% v / v in US gasoline".

Butyl Acetate



Contents

1 - Introduction

n-Butyl acetate, also known as butyl ethanoate, is an organic compound commonly used as a solvent in the production of lacquers and other products. It is a colorless flammable liquid. Butyl acetate is found in many types of fruit, where along with other chemicals it imparts characteristic flavors and has a sweet smell of banana or apple. It is used as a synthetic fruit flavoring in foods such as candy, ice cream, cheeses, and baked goods.

The other three isomers of butyl acetate are: isobutyl acetate, *tert*-butyl acetate, and *sec*-butyl acetate.

IUPAC name : Butyl acetate
Systematic name : Butyl ethanoate
Other names : Acetic acid , *n*-butyl ester

Molecular formula	$C_6H_{12}O_2$
Molar mass	116 $g\ mol^{-1}$
Appearance	Colorless liquid with fruity odor
Density	0.88 g / cm^3
Melting point	-77 °C
Boiling point	127 °C
Solubility in water	10 g / L (20 °C)
Refractive index (n_D)	1.394 (20 °C)
Main hazards	Flammable
Flash point	27 °C

2 - Production

Butyl acetates are commonly manufactured by the Fischer esterification of a butanol isomer and acetic acid with the presence of catalytic sulfuric acid under reflux conditions.

3 - Occurrence in nature

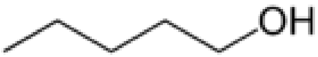
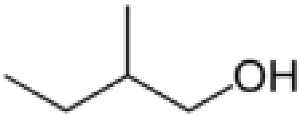
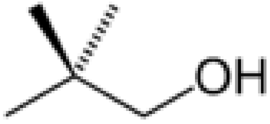
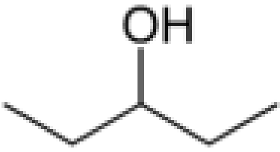
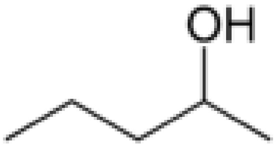
Apples, especially of the Red Delicious variety, are flavored in part by this chemical. The alarm pheromones emitted by the Koschevnikov gland of honey bees contain butyl acetate.

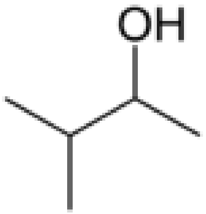
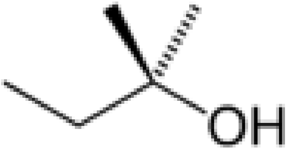
Amyl Alcohol

An amyl alcohol is any of 8 alcohols with the formula $C_5H_{11}OH$.[1] A mixture of amyl alcohols (also called amyl alcohol) can be obtained from fusel alcohol. Amyl alcohol is used as a solvent and in esterfication for example in the production of amyl acetate. Amyl alcohol as a distinct chemical compound refers to pentan-1-ol.

Eight structural isomers with molecular formula $C_5H_{12}O$ and all alcohols are known :

Amyl alcohol isomers

Common Name	**Structure**	**IUPAC Name**	**Boiling Point (°C)**
normal amyl alcohol		Pentan-1-ol	138.5
isobutyl carbinol or isoamyl alcohol or isopentyl alcohol		3-Methylbutan-1-ol	131.2
active amyl alcohol		2-Methylbutan-1-ol	128.7
tertiary butyl carbinol or neopentyl alcohol		2,2-Dimethylpropan-1-ol	113.1
3-Pentanol		Pentan-3-ol	115.3
methyl (n) propyl carbinol		Pentan-2-ol	118.8

methyl isopropyl carbinol		3-Methylbutan-2-ol	113.6
dimethyl ethyl carbinol or tertiary amyl alcohol		2-Methylbutan-2-ol	102

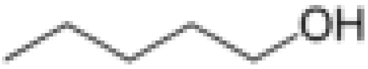
Three of these alcohols, active amyl alcohol (2-methylbutan-1-ol), methyl (n) propyl carbinol (pentan-2-ol), and methyl isopropyl carbinol (3-methylbutan-2-ol), are optically active, as they contain an asymmetric carbon atom.

The most important is isobutyl carbinol, this being the chief constituent of fermentation amyl alcohol, and consequently a constituent of fusel oil. It can be separated from fusel oil by shaking with strong brine solution, separating the oily layer from the brine layer and distilling it, the portion boiling between 125 and 140 °C. being collected. For further purification it may be shaken with hot limewater, the oily layer separated, dried with calcium chloride and fractionated, the fraction boiling between 128 and 132 °C only being collected. It may be synthesized from isobutanol by conversion into isovaleraldehyde, which is subsequently reduced to isobutyl carbinol by means of sodium amalgam.

It is a colourless liquid of density 0.8247 g / cm^3 (0 °C), boiling at 131.6 °C, slightly soluble in water, easily soluble in organic solvents. It possesses a characteristic strong smell and a sharp burning taste. Amyl alcohol has an oral LD50 of 200 mg/kg (mouse), suggesting that the chemical is significantly more toxic than ethanol. On passing its vapour through a red-hot tube, it decomposes with production of acetylene, ethylene, propylene, and other compounds. It is oxidized by chromic acid to iso valer aldehyde, and it forms crystalline addition compounds with calcium chloride and tin(IV) chloride.

The other amyl alcohols may be obtained synthetically. Of these, tertiary butyl carbinol has been the most difficult to obtain, its synthesis having first been reported in 1891, by L. Tissier by the reduction of a mixture of trimethyl acetic acid and tri methyl acetyl chloride with sodium amalgam. It is a solid that melts at 48 to 50 °C and boils at 112.3 °C.

1 – Pentanol

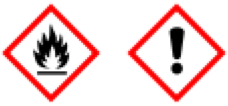
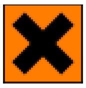


- Introduction

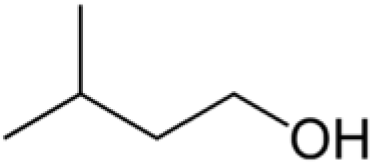
1-Pentanol, (or n-pentanol, pentan-1-ol), is an alcohol with five carbon atoms and the molecular formula $C_5H_{12}O$. 1-Pentanol is a colorless liquid with an unpleasant aroma. There are 8 alcohols with this molecular formula . The ester formed from butyric acid and 1-pentanol, pentyl butyrate, smells like apricot. The ester formed from acetic acid and 1-pentanol, amyl acetate (pentyl acetate), smells like banana.

Pentanol can be prepared by fractional distillation of fusel oil. To reduce the use of fossil fuels, research is underway to discover cost effective methods of utilizing fermentation to produce Bio-Pentanol. Pentanol can be used as a solvent for coating CDs and DVDs. Another use is a replacement for gasoline.

IUPAC name : Pentan -1- ol

Molecular formula	$C_5H_{12}O$
Molar mass	88 g mol^{-1}
Density	.811 g cm^{-3}
Melting point	-78 °C
Boiling point	137-139 °C
Solubility in water	22 g l^{-1}
Vapor pressure	200 Pa (at 20 °C)
Refractive index (n_D)	1.409
GHS pictograms	
GHS signal word	WARNING
EU classification	 Xn
Flash point	49 °C
Auto ignition temperature	300 °C

Iso Amyl Alcohol



Isoamyl alcohol (also known as isopentyl alcohol) is a clear, colorless alcohol with the formula $(CH_3)_2CHCH_2CH_2OH$. It is one of several isomers of amyl alcohol. It is a main ingredient in the production of banana oil, an ester found in nature and also produced as a flavouring in industry. It's also the main ingredient of Kovac's reagent, used for the bacterial diagnostic indole test.

It is also used as an antifoaming agent in the Chloroform:Isomyl Alcohol reagent.

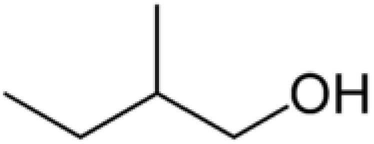
IUPAC name : 3-methyl-1-butanol

Other names :

Isopentyl alcohol , Isopentanol , Isobutylcarbinol

Molecular formula	$C_5 H_{12} O$
Molar mass	88 g / mol
Appearance	Clear , colorless liquid
Density	0.8104 g / cm^3 at 20 °C
Melting point	-117.2 °C
Boiling point	131.1 °C
Solubility in water	28 g / L
Solubility	very soluble in acetone , diethyl ether , ethanol
Viscosity	3.692 mPa·s
Flash point	43 °C
Auto ignition temperature	350 °C
Explosive limits	1.2 – 9 %

2 - Methyl – 1- butanol



1 - Introduction

2-Methyl-1-butanol (IUPAC name, also called active amyl alcohol) is an organic chemical compound. It is used as a solvent and an intermediate in the manufacture of other chemicals. 2-Methyl-1-butanol is a component of many mixtures of amyl alcohols sold industrially.

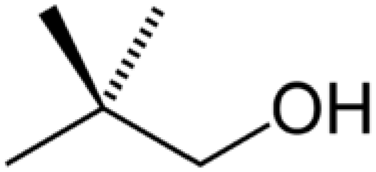
IUPAC name : 2-Methyl-1-butanol
Other names :
2-Methylbutan-1-ol , active amyl alcohol

Molecular formula	$C_5H_{12}O$
Molar mass	88 g / mol
Appearance	colorless liquid
Density	0.8152 g /cm^3
Melting point	-117.2 °C
Boiling point	127.5 °C
Solubility in water	31 g / L
Solubility	miscible with ethanol, diethyl ether ; very soluble in acetone
Vapor pressure	3 mm Hg
Viscosity	4.453 mPa·s
Auto ignition temperature	385 °C

2 - Reactions

2-Methyl-1-butanol can be derived from fusel oil (because it occurs naturally in fruits such as grapes) or manufactured by either the oxo process or via the halogenation of pentane.

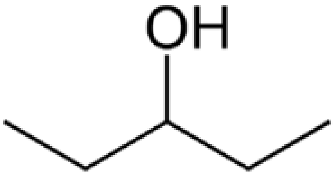
Neopentyl Alcohol



Neopentyl alcohol is a compound with formula $C_5H_{12}O$ or $(H_3C-)_3C-CH_2OH$. It is an alcohol derived from neopentane, or $C(CH_3)_4$.

IUPAC name **:** 2,2 - dimethylpropan -1- ol	
Other names : *tert*-butyl carbinol *tert*-butylmethanol neoamyl alcohol	
Molecular formula	$C_5 H_{12} O$
Molar mass	88 g mol^{-1}
Density	0.812 g/mL at 20 °C
Melting point	52.5 °C
Boiling point	113.5 °C
Solubility in water	36 g / L
Solubility	very soluble in ethanol , diethyl ether
Flash point	37 °C

3 – Pentanol



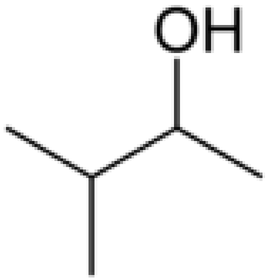
3 - Pentanol is one of the isomers of amyl alcohol.

IUPAC name : 3 - Pentanol

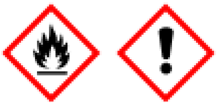
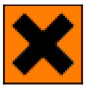
Other names : pentan – 3 - ol

Molecular formula	$C_5H_{12}O$
Molar mass	88 g / mol
Appearance	colorless liquid
Density	0.815 g / ml
Melting point	-63.68 °C
Boiling point	115.3 °C
Solubility in water	59 g / L
Solubility	soluble in acetone , benzene; very soluble in ethanol, diethyl ether
Vapor pressure	1.10 kPa
Specific heat capacity, *C*	$2.719\ J \cdot g^{-1} \cdot K^{-1}$
Flash point	41 °C
Autoignition temperature	435 °C
Explosive limits	1.2 – 9 %

3 - Methyl - 2 – butanol



IUPAC name : 3-Methylbutan -2 - ol

Molecular formula	$C_5H_{12}O$
Molar mass	88 g mol^{-1}
Appearance	Colorless liquid
Density	818 mg cm^{-3}
Boiling point	109 - 115 °C
Solubility in water	59 g dm^{-3}
Solubility in ethanol	miscible
Vapor pressure	1.20 kPa
GHS pictograms	
GHS signal word	WARNING
EU classification	 Xn
Flash point	34 °C

3- Methyl - 2 - butanol (IUPAC name, commonly called *sec*-isoamyl alcohol) is an organic chemical compound. It is used as a solvent and an intermediate in the manufacture of other chemicals.

tert - Amyl Alcohol

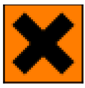
Contents

1 - Introduction

tert-Amyl alcohol (TAA), also known as 2-methyl-2-butanol (2M2B), is a speciality pentanol used primarily as a pharmaceutical or pigment solvent. It is a trace component in fermentation ethanol. It is a colorless liquid with a pungent odor of camphor, and soluble with water and other organic solvents.

Preferred IUPAC name : 2-Methyl-2-butanol
Systematic name : 2-Methylbutan-2- ol
Other names :
tert-Amyl alcohol , *t*-Amylol, *t*-Am OH , TAA
tert-Pentyl alcohol , *t*-Pentylol , Amylene hydrate
Dimethylethylcarbinol

Molecular formula	$C_5H_{12}O$
Molar mass	88 g mol^{-1}
Appearance	Colorless liquid
Odor	Camphorous
Density	805 mg cm^{-3}
Melting point	- 9 °C
Boiling point	101-103 °C
Solubility in water	120 g dm^{-3}
log P	1.095
Vapor pressure	1.6 kPa (at 20 °C)

Refractive index (n_D)	1.405
MSDS	hazard.com
GHS pictograms	 
GHS signal word	DANGER
EU classification	 F  Xn
Flash point	19 °C
Auto ignition temperature	437 °C
Explosive limits	9 %

2 - Natural occurrence

Fusel alcohols including TAA are a grain fermentation byproduct and therefore in most alcoholic beverages . TAA is also found in fried bacon and cassava. Trace quantities are in hops used to flavor beer.

3 - Industrial production

The oxo alcohol process is the principal commercial source of TAA. Minor quantities, mainly in Europe, are obtained from separation of fusel alcohols . The reaction of 2-methyl-2-butene (also known as iso amylene) with water in the presence of an acid catalyst yields TAA.

4 - Chemistry

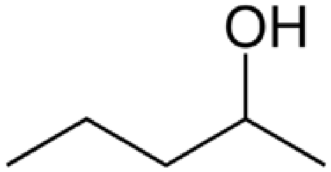
TAA is an isomer of amyl alcohol so it is also known as *tert*-Amyl alcohol. It is not expected to be susceptible to direct photolysis by sunlight.

5 - Pharmacology

Tertiary alcohols like TAA cannot be oxidized which makes them useful as drugs because they do not form toxic aldehyde and carboxylic acid metabolites.

TAA produces euphoria, sedative, hypnotic, and anticonvulsant effects similar to ethanol through ingestion or inhalation, and was previously used in medicine for these purposes . It is active in doses of 2,000 - 4,000 mg, making it 20 times more potent than ethanol. Its hypnotic potency is between chloral hydrate and paraldehyde and between benzodiazepines and ethanol. In humans, TAA is metabolized primarily via gluconoridation and oxidation to 2,3 – di hydroxy - 2 - methyl butane . An overdose produces symptoms similar to alcohol poisoning and is a medical emergency. The oral LD50 in rats is 1000 mg/kg. The subcutaneous LD50 in mice is 2100 mg/kg.

2 – Pentanol



- Introduction

2-Pentanol (IUPAC name, also called *sec*-amyl alcohol) is an organic chemical compound. It is used as a solvent and an intermediate in the manufacture of other chemicals. 2-Pentanol is a component of many mixtures of amyl alcohols sold industrially.

IUPAC name : 2-Pentanol

Other names : Pentan - 2- ol , *sec*- amyl alcohol

Molecular formula	$C_5 H_{12} O$
Molar mass	88 g / mol
Appearance	colorless liquid
Density	0.812 g / cm^3
Melting point	- 73 °C
Boiling point	119.3 °C
Solubility in water	45 g / L
Solubility	soluble in ethanol , diethyl ether , carbon tetrachloride , chloroform
Vapor pressure	0.804 kPa
Viscosity	3.470 mPa·s
Flash point	34 °C
Autoignition temperature	343 °C
Explosive limits	1.2– 9 %

Reactions

2-Pentanol can be manufactured by hydration of pentene.

Fusel Alcohol

Contents

1 - Introduction

Fusel alcohols, also sometimes called fusel oils, or potato oil in Europe, are a mixture of several alcohols (chiefly amyl alcohol) produced as a by - product of alcoholic fermentation. The word Fusel is German for "bad liquor".

2 - Classification

2 – 1 - Hazardous alcohols

Methanol (methyl alcohol) itself, while poisonous (LD50 5628 mg / kg , oral, rat), has a much weaker sedative effect than ethanol.

Isopropanol (isopropyl alcohol) is oxidized to form acetone by alcohol dehydrogenase in the liver but have occasionally been abused by alcoholics, leading to a range of adverse health effects.

2 – 2 - Alcohol faults

Mannitol, a wine fault

2 – 3 - Aroma alcohols

For desired alcohols other than ethanol in alcoholic beverages, see alcoholic beverage#Alcoholic beverages by alcohol type.

Excessive concentrations of some alcohols other than ethanol may cause off-flavors, sometimes described as "spicy", "hot", or "solvent-like". Some beverages, such as rum, whisky (especially Bourbon), incompletely rectified vodka (e.g. Siwucha), and traditional ales and ciders, are expected to have relatively high concentrations of non-hazardous alcohols as part of their flavor profile. However, in other beverages, such as Korn, vodka, and lagers, the presence of other alcohols than ethanol is considered a fault.

The compounds involved are chiefly:

2-methyl-1-butanol - sometimes called "active" amyl alcohol

iso amyl alcohol - also known as isopentyl alcohol

isobutyl alcohol - one of the least toxic of the butanols.

n-propyl alcohol

3 - Formation and removal

Fusel alcohols are formed when fermentation occurs :

at higher temperatures

at lower pH

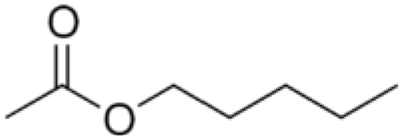
when yeast activity is limited by low nitrogen content

During distillation, fusel alcohols are concentrated in the "tails" at the end of the distillation run. They have an oily consistency, which is noticeable to the distiller, hence the other name "fusel oil". If desired, these heavier alcohols can be almost completely separated in a reflux still. Freeze distillation, on the other hand, does not remove fusel alcohols .

4 - Health effects

There is a popular belief that fusel alcohol contributes to hangover symptoms. However, these effects are under scientific debate. A Japanese study in 2003 concluded, "The fusel oil in whiskey had no effect on the ethanol-induced emetic response" in *Suncus murinus*. Additionally, consumption of fusel oils with ethanol suppressed subjects' subsequent taste aversion to alcohol, which suggested subjects' hangover symptoms were lessened.

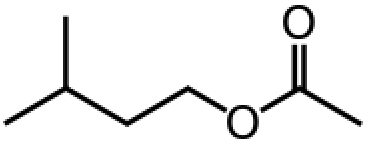
Amyl Acetate



IUPAC name : Pentyl acetate	
Other names :	
Acetic acid *n*-amyl ester	
Acetic acid pentyl ester	
n-Amyl acetate	
Amyl ethanoate	
Pear oil	
Pentyl ethanoate	
Molecular formula	$C_7H_{14}O_2$
Molar mass	130 g / mol
Density	0.876 g / cm³
Melting point	- 71 °C
Boiling point	149 °C
Solubility in water	10 g / l (20 °C)

Amyl acetate (pentyl acetate) is an organic compound and an ester with the chemical formula $CH_3COO\ [CH_2]_4CH_3$ and the molecular weight 130.19 g/mol. It has a scent similar to bananas and apples . The compound is the condensation product of acetic acid and 1- pentanol. However, esters formed from other pentanol isomers (amyl alcohols), or mixtures of pentanols, are often referred to as amyl acetate.

Iso Amyl Acetate



IUPAC name : 3-methylbut-1-yl ethanoate

Other names :

isopentyl acetate
banana oil
isopentyl ethanoate
pear essence
3-methylbutyl acetate
3-methylbutyl ethanoate

Molecular formula	$C_7H_{14}O_2$
Molar mass	130 g / mol
Density	0.876 g / cm^3
Melting point	−78 °C
Boiling point	142 °C
Flash point	25 °C

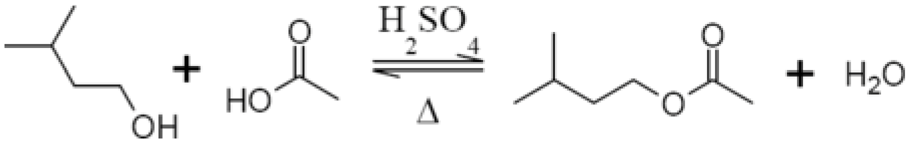
Contents

1 - Introduction

Iso amyl acetate, also known as isopentyl acetate, is an organic compound that is the ester formed from iso amyl alcohol and acetic acid. It is a colorless liquid that is only slightly soluble in water, but very soluble in most organic solvents. Isoamyl acetate has a strong odor (similar to Juicy Fruit, a foam banana sweet or a pear drop) which is also described as similar to both banana and pear. Banana oil is a term that is applied either to pure isoamyl acetate or to flavorings that are mixtures of isoamyl acetate, amyl acetate, and other flavors.

2 - Production

Iso amyl acetate is prepared by the acid catalyzed reaction (Fischer esterification) between iso amyl alcohol and glacial acetic acid as shown in the reaction equation below. Typically, sulfuric acid is used as the catalyst. Alternately, an acidic ion exchange resin can be used as the catalyst.



3 - Applications

Iso amyl acetate is used to confer banana flavor in foods. *Pear oil* commonly refers to a solution of isoamyl acetate in ethanol that is used as an artificial flavor.

It is also used as a solvent for some varnishes and nitrocellulose lacquers, as well as being a honey bee pheromone and can be used to attract large groups of honeybees to a small area. As a solvent and carrier for materials such as nitrocellulose, it was extensively used in the aircraft industry for stiffening and wind-proofing fabric flying surfaces, where it and its derivatives were generally known as 'dope'. Now that most aircraft are all-metal, such use is now limited to model aircraft, where it is still popularly used for strengthening tissue coverings and balsa wood.

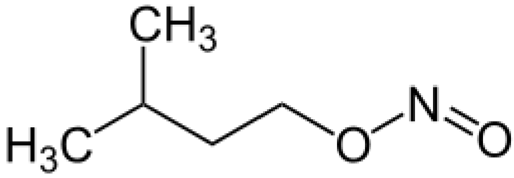
Because of its intense, pleasant odor and its low toxicity, isoamyl acetate is used to test the effectiveness of respirators or gas masks.

4 - Occurrence in nature

Banana oil is made naturally by the banana plant;[2] it is also produced synthetically.

Isoamyl acetate is released by a honey bee's sting apparatus where it serves as a pheromone beacon to attract other bees and provoke them to sting.

Amyl Nitrite



Contents

1 - Introduction

Amyl nitrite is the chemical compound with the formula $C_5H_{11}ONO$. A variety of isomers are known, but they all feature an amyl group attached to the nitrito functional group. The alkyl group is unreactive and the chemical and biological properties are mainly due to the nitrite group. Like other alkyl nitrites, amyl nitrite is bioactive in mammals, being a vasodilator, which is the basis of its use as a prescription medicine. As an inhalant, it also has a psychoactive effect, which has led to its recreational use.

IUPAC name **:** (3- methylbutyl) nitrite	
Other names : Isoamyl nitrite Nitramyl 3 - methyl -1-nitroso oxy butane Pentyl alcohol nitrite (ambiguous) Nitrous acid, pentyl ester (ambiguous) *poppers* (colloquial, street slang)	
Molecular formula	$C_5 H_{11} NO_2$
Molar mass	117.15 g mol^{-1}
Appearance	Colourless liquid

Density	0.872 g/cm^3, liquid (25 °C)
Boiling point	99 °C
Solubility in water	slightly soluble
Main hazards	vasodilator
Flash point	21 °C
Auto ignition temperature	209 °C

2 - Nomenclature

The term "amyl nitrite" encompasses several isomers. For example, a common form of amyl nitrite with the formula $(CH_3)_2CHCH_2CH_2ONO$ may be more specifically referred to as isoamyl nitrite. When the amyl group is a linear or normal (n) alkyl group, the resulting amyl nitrite would have the structural formula $CH_3(CH_2)_4ONO$.

Despite a very similar name to amyl nitrite, amyl nitrate has a different chemical composition and different properties.

3 - Synthesis and reactions

Alkyl nitrites are prepared by the reaction of alcohols with nitrous acid :

$C_5H_{11}OH + HONO \rightarrow C_5H_{11}ONO + H_2O$

The reaction is called esterification. Synthesis of alkyl nitrites is, in general, straightforward and can be accomplished in home laboratories. A common procedure includes the dropwise addition of concentrated sulfuric acid to a cooled mixture of an aqueous sodium nitrite solution and an alcohol. The intermediately-formed stoichiometric mixture of nitrous and nitric oxide then converts the alcohol to the alkyl nitrite, which, due to its low density, will form an upper layer that can be easily decanted from the reaction mixture.

Iso amyl nitrite decomposes in the presence of base to give nitrite salts and the iso amyl alcohol:

$C_5H_{11}ONO + NaOH \rightarrow C_5H_{11}OH + NaNO_2$

Amyl nitrite, like other alkyl nitrites, reacts with carbanions to give oximes.

Amyl nitrites are also useful as reagents in a modification of the Sandmeyer reaction. The reaction of the alkyl nitrite with an aromatic amine in a halogenated solvent produces a radical aromatic species, this then abstracts a halogen atom from the solvent. For the synthesis of aryl iodides diiodomethane is used, whereas bromoform is the solvent of choice for the synthesis of aryl bromides.

4 - Physiological effects

Amyl nitrite, in common with other alkyl nitrites, is a potent vasodilator (*i.e.,* it expands blood vessels, resulting in lowering of the blood pressure). Alkyl nitrites function as a source of nitric oxide, which signals for relaxation of the involuntary muscles. Physical effects include decrease in blood pressure, headache, flushing of the face, increased heart rate, dizziness, and relaxation of involuntary muscles, especially the blood vessel walls and the anal sphincter. There are no withdrawal symptoms. Overdose symptoms include nausea, emesis (vomiting), hypotension, hypoventilation, dyspnea (shortness of breath), and syncope (fainting). The effects set in very quickly, typically within a few seconds and disappear soon after (within minutes).

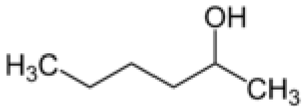
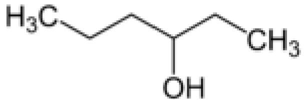
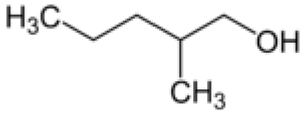
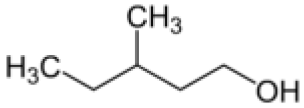
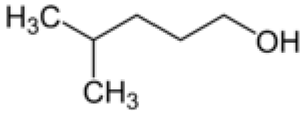
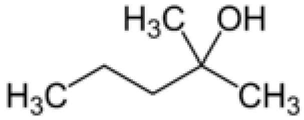
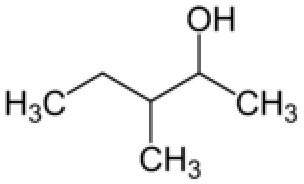
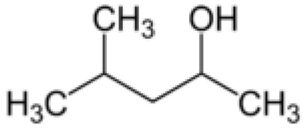
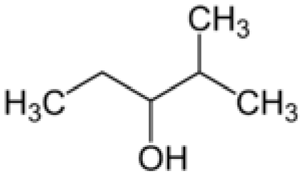
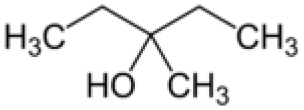
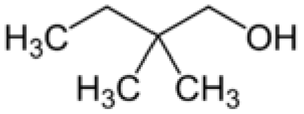
5 - Applications

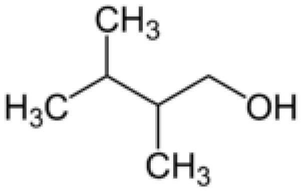
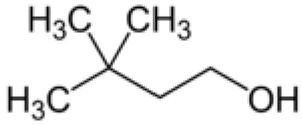
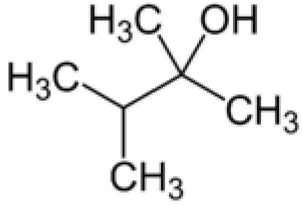
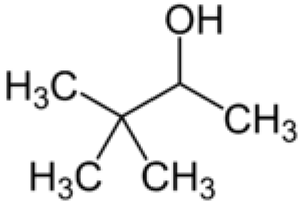
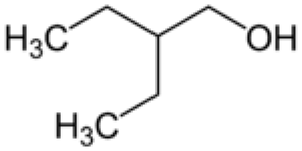
Amyl nitrite is employed medically to treat heart diseases such as angina and also to treat cyanide poisoning . It is also used as an inhalant drug that induces a brief euphoric state, and when combined with other intoxicant stimulant drugs such as cocaine or ecstasy (see MDMA), the euphoric state intensifies and is prolonged. Once some stimulative drugs wear off, a common side effect is a period of depression or anxiety, colloquially called a "come down"; amyl nitrite is sometimes used to combat these negative after-effects. This effect, combined with its dissociative effects, have led to its use as a recreational drug .

Amyl nitrite is also sometimes used as an antidote for cyanide poisoning. It can act as an oxidant, to induce the formation of methemoglobin. Methemoglobin in turn can sequester cyanide as cyano methemoglobin.

Hexanol

Hexanol may refer to any of the following isomeric organic compounds with the formula $C_6H_{13}OH$:

Structure	IUPAC Name	**Boiling Point (°C)**
	1-Hexanol	158
	2-Hexanol	136
	3-Hexanol	135
	2-Methyl-1-pentanol	147
	3-Methyl-1-pentanol	152
	4-Methyl-1-pentanol	151
	2-Methyl-2-pentanol	121
	3-Methyl-2-pentanol	134
	4-Methyl-2-pentanol	131
	2-Methyl-3-pentanol	126
	3-Methyl-3-pentanol	122
	2,2-Dimethyl-1-butanol	137

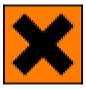
	2,3-Dimethyl-1-butanol	145
	3,3-Dimethyl-1-butanol	143
	2,3-Dimethyl-2-butanol	119
	3,3-Dimethyl-2-butanol	120
	2-Ethyl-1-butanol	146

1-Hexanol

Contents

1 - Interdiction

1-Hexanol is an organic alcohol with a six-carbon chain and a condensed structural formula of $CH_3(CH_2)_5OH$. This colorless liquid is slightly soluble in water, but miscible with ether and ethanol. Two additional straight chain isomers of 1-hexanol, 2-hexanol and 3-hexanol, exist, both of which differing by the location of the hydroxyl group. Many isomeric alcohols have the formula $C_6H_{13}OH$. It is used in the perfume industry.

IUPAC name ; Hexan - 1- ol	
Molecular formula	$C_6 H_{14} O$
Molar mass	102 g mol^{-1}
Density	813.6 mg cm^{-3}
Melting point	- 53 - - 41 °C
Boiling point	155 - 159 °C
Solubility in water	5.9 g dm^{-3} (at 20 °C)
Vapor pressure	100 Pa (at 25.6 °C)
Refractive index (n_D)	1.4178 (at 20 °C)
Specific heat capacity, *C*	243.2 J K^{-1} mol^{-1}
GHS signal word	WARNING
EU classification	 Xn
Flash point	59 °C
Auto ignition temperature	293 °C

2 - Preparation

Hexanol is produced industrially by the oligomerization of ethylene using tri ethyl aluminium followed by oxidation of the alkyl aluminium products. An idealized synthesis is shown :

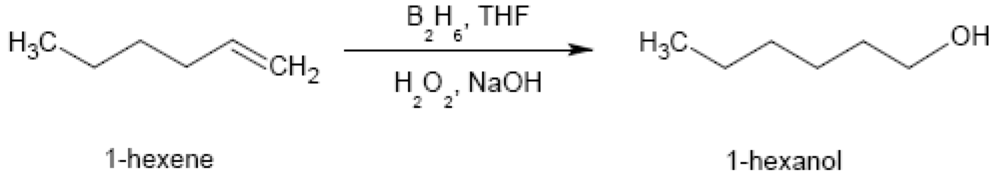
$Al(C_2H_5)_3 + 6C_2H_4 \rightarrow Al(C_6H_{13})_3$
$Al(C_6H_{13})_3 + 1½O_2 + 3H_2O \rightarrow 3HOC_6H_{13} + Al(OH)_3$

The process generates a range of oligomers that are separated by distillation.

2 – 1 - Alternative methods

Another method of preparation entails hydroformylation of 1-pentene followed by hydrogenation of the resulting aldehydes. This method is practiced in industry to produce mixtures of isomeric C_6 -alcohols, which are precursors to plasticizers.

In principle, 1-hexene could be converted to 1-hexanol by hydroboration (di borane in tetra hydro furan followed by treatment with hydrogen peroxide and sodium hydroxide):

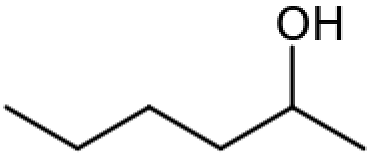


This method is instructive and useful in laboratory synthesis but of no practical relevance because of the commercial availability of inexpensive 1-hexanol from ethylene.

3 - Occurrence in Nature

1-Hexanol is believed to be a component of the odour of freshly mown grass. Alarm pheromones emitted by the Koschevnikov gland of honey bees contain 1-hexanol.

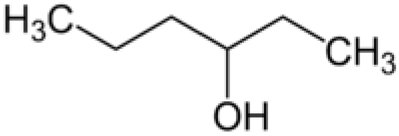
2 – Hexanol



2-Hexanol (or hexan-2- ol) is a six carbon alcohol in which the OH group is located on the second carbon atom. Its chemical formula is $C_6H_{14}O$ or $C_6H_{13}OH$. It is an isomer of the other hexanols. 2-Hexanol has a chiral center and can be resolved into enantiomers.

IUPAC name ; Hexan -2- ol	
Molecular formula	$C_6 H_{14} O$
Molar mass	102 g / mol
Density	0.81 g / mL
Boiling point	140 °C
Solubility in water	14 g / L
Solubility	soluble in ethanol, diethyl ether

3 – Hexanol



Contents

1 - Interdiction

3-Hexanol (IUPAC name, also called ethyl propyl carbinol) is an organic chemical compound. It occurs naturally in the flavor and aroma of plants such as pineapple and is used as a food additive to add flavor.

IUPAC name : 3-Hexanol

Other names :

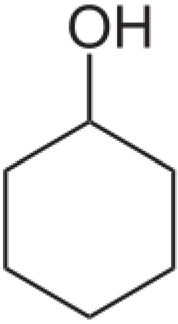
Hexan-3-ol, ethyl propyl carbinol

Molecular formula	$C_6H_{14}O$
Molar mass	102 g / mol
Appearance	colorless liquid
Density	0.819 g / cm^3
Boiling point	135 °C
Solubility in water	16 g / L
Solubility	miscible with diethyl ether ; very soluble in ethanol, acetone
Specific heat capacity, *C*	286.2 $J·mol^{-1}·K^{-1}$ (liquid)

2 - Reactions

3 - Hexanol can be synthesized by the hydroboration of unsaturated hexane compounds such as 3- hexyne.

Cyclo Hexanol



Contents

1 - Introduction

Cyclohexanol is the organic compound with the formula $(CH_2)_5CHOH$. The molecule is related to cyclohexane ring by replacement of one hydrogen atom by a hydroxyl group.[2] This compound exists as a deliquescent colorless solid, which, when very pure, melts near room temperature. Billions of kilograms are produced annually, mainly as a precursor to nylon.

IUPAC name : Cyclohexanol
Other names :
Cyclo hexyl Alcohol,
hexa hydro phenol,
hydro phenol,
hydroxy cyclo hexane,
Naxol

Molecular formula	$C_6 H_{12} O$
Molar mass	100 g / mol
Appearance	Colorless, viscous liquid. Hygroscopic

Odor	camphor - like
Density	0.9624 g / mL , liquid
Melting point	25.93 °C
Boiling point	161.84 °C
Solubility in water	3.60 g / 100 mL (20 °C) 4.3 g / 100 mL (30 °C)
Solubility	soluble in ethanol, ethyl etherm acetone, chloroform miscible with ethyl acetate, linseed oil, benzene
Refractive index (n_D)	1.4641
Viscosity	41.07 mPa·s (30 °C)
Main hazards	Flammable , skin irritant Reacts violently with oxidizing agents
Flash point	67 °C
Autoignition temperature	300 °C
Explosive limits	2.7 - 12 %
LD_{50}	2.06 g / kg (oral, rat)

2 - Production

Cyclo hexanol is produced by the oxidation of cyclohexane in air, typically using cobalt catalysts :

$$C_6H_{12} + 1/2\ O_2 \rightarrow C_6H_{11}OH$$

This process co-forms cyclo hexanone, and this mixture ("KA oil" for ketone-alcohol oil) is the main feedstock for the production of adipic acid. The oxidation involves radicals and the intermediacy of the hydro peroxide $C_6H_{11}O_2H$. Alternatively, cyclo hexanol can be produced by the hydrogenation of phenol:

$$C_6H_5OH + 3\ H_2 \rightarrow C_6H_{11}OH$$

This process can also be adjusted to favor the formation of cyclo hexanone.

3 - Basic reactions

Cyclo hexanol undergoes the main reactions expected for a secondary alcohol. Oxidation gives cyclo hexanone, which is converted on a large scale in industry to the oxime, a precursor to caprolactam. As a laboratory exercise, this oxidation can be effected with chromic acid. Esterification affords the commercially useful derivatives di cyclo hexyladipate and dicyclo hexyl phthalate, which are used as plasticizers. Heating in the presence of acid catalysts converts cyclo hexanol to cyclo hexene.

4 - Structure

Cyclo hexanol has at least two solid phases. One of them is a plastic crystal.

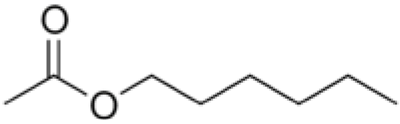
5 - Applications

As indicated above, cyclo hexanol is an important feedstock in the polymer industry, firstly as a precursor to nylons, but also to various plasticizers. Small amounts are used as a solvent.

6 - Safety

Cyclo hexanol is some what toxic : the TLV for the vapor for 8 h is 50 ppm. Few studies have been done on its carcinogenicity, but one study on rats found it to have co-carcinogenic effects.

Hexyl Acetate



Hexyl acetate is an ester with the molecular formula $C_8H_{16}O_2$. It is mainly used as a solvent for resins, polymers, fats and oils. It is also used as a paint additive to improve its dispersion on a surface.

Hexyl acetate is also used as a flavoring because of its fruity odor, and it is naturally present in many fruits and alcoholic beverages.

IUPAC name : Hexyl acetate

Other names :

n-Hexyl acetate ;

Capryl acetate ;

1-Hexyl acetate

Molecular formula	$C_8 H_{16} O_2$
Molar mass	144 g mol^{-1}
Appearance	Colorless liquid
Density	0.8673 g / cm^3
Melting point	- 80 °C
Boiling point	171.5 °C
Solubility in water	0.4 g / L (20 °C)

1 – Heptanol

Contents

1 - Introduction

1-Heptanol is an alcohol with a seven carbon chain and the structural formula of $CH_3(CH_2)_6OH$.[1] It is a clear colorless liquid that is very slightly soluble in water, but miscible with ether and ethanol.

Other names ; Heptyl alcohol , *n*-Heptyl alcohol , Enanthic alcohol	
Molecular formula	$C_7H_{16}O$
Molar mass	116 g mol^{-1}
Density	0.8187 g / cm³
Melting point	-34.6 °C
Boiling point	175.8 °C
Refractive index (n_D)	1.423
Flash point	3 °C (37 °F)

2 - Overview

There are three other isomers of heptanol that have a straight chain, 2-heptanol, 3-heptanol, and 4-heptanol, which differ by the location of the alcohol functional group.

Heptanol is commonly used in cardiac electrophysiology experiments to block gap junctions and increase axial resistance between myocytes. Increasing axial resistance will decrease conduction velocity and increase the heart's susceptibility to reentrant excitation and sustained arrhythmias.

1-Heptanol has a pleasant smell and is used in cosmetics for its fragrance.

2 – Heptanol

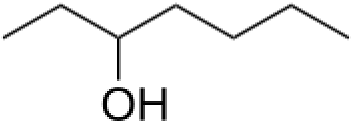
2-Heptanol is a chemical compound which is an isomer of heptanol. It is a secondary alcohol with the hydroxyl on the second carbon of the straight seven-carbon chain.

2-Heptanol is chiral, so (R)- and (S)- isomers exist.

IUPAC name : Heptan -2- ol
Other names : *s*-Heptyl alcohol

Molecular formula	$C_7H_{16}O$
Molar mass	116 g / mol
Density	0.817 g / mL
Boiling point	159 °C
Solubility in water	3.3 g/L
Solubility	soluble in : ethanol , diethyl ether
Viscosity	3.955 mPa·s
Flash point	71 °C

3 – Heptanol



3-Heptanol or heptan-3-ol is an organic alcohol with the chemical formula $C_7H_{16}O$.

3-Heptanol is chiral, so (R)- and (S)- isomers exist.

IUPAC name : Heptan - 3 - ol	
Molecular formula	$C_7H_{16}O$
Molar mass	116.20 g mol^{-1}

1 - Octanol

Contents

1 - Introduction

The term Octanol usually refers to the isomer, octan-1-ol, with the molecular formula $CH_3(CH_2)_7OH$. It is a fatty alcohol. Many other isomers are also known. Esters of octanol, such as octyl acetate, occur as components of essential oils. Octanol is manufactured for the synthesis of esters for use in perfumes and flavorings. It is used to model the partitioning of pharmaceutical products between water and the cytosol. Other uses include experimental medical procedures for controlling Essential Tremor and other types of involuntary neurological tremors.

IUPAC name : Octan -1- ol

Other names :

1- Octanol ; Capryl alcohol ; Octyl alcohol

Molecular formula	$C_8H_{18}O$
Molar mass	130 g mol^{-1}
Density	0.824 g / cm^3
Melting point	-16 °C
Boiling point	195 °C
Solubility in water	Insoluble

2 - Preparation

Octanol is produced industrially by the oligomerization of ethylene using tri ethyl aluminium followed by oxidation of the alkyl aluminium products . An idealized synthesis is shown:

$$Al(C_2H_5)_3 + 9\ C_2H_4 \rightarrow Al(C_8H_{17})_3$$

$$Al(C_8H_{17})_3 + 3\ O + 3\ H_2O \rightarrow 3\ HOC_8H_{17} + Al(OH)_3$$

The process generates a range of alcohols that are separated by distillation.

3 – Water / octanol partitioning (Partition coefficient)

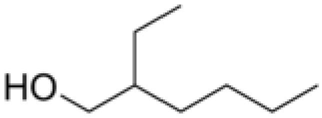
Octanol and water are immiscible. The distribution of a compound between water and octanol is used to calculate the partition coefficient 'P' of that molecule (often expressed as its logarithm to the base 10, log *P*). Water/ octanol partitioning is a relatively good approximation of the partitioning between the cytosol and lipid membranes of living systems.

Many dermal absorption models consider the stratum corneum/ water partition coefficient to be well approximated by a function of the water/ octanol partition coefficient of the form :

$$\log(K_{sc/w}) = a + b\log(K_{w/o})$$

Where a and b are constants , $K_{sc/w}$ is the stratum corneum/ water partition coefficient, and $K_{w/o}$ is the water/ octanol partition coefficient. The values of a and b vary between papers, but Cleek & Bunge have reported the values a = 0 , b = 0.74.

2 - Ethyl Hexanol

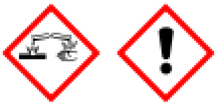
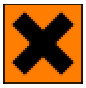


Contents

1 - Introduction

2 - Ethylhexanol (abbreviated 2-EH) is a fatty alcohol, an organic compound is a branched, eight-carbon chiral alcohol. It is a colorless liquid that is nearly insoluble in water but soluble in most organic solvents. It is produced on a massive scale as a precursor to plasticizers, some of which are controversial as potential endocrine disruptors.

IUPAC name : 2 - Ethyl hexan - 1- ol

Molecular formula	$C_8 H_{18} O$
Molar mass	130 g mol^{-1}
Appearance	Colourless liquid
Density	833 mg mL^{-1}
Melting point	−76 °C
Boiling point	180 - 186 °C
log P	2.721
Vapor pressure	30 Pa (at 20 °C)
Refractive index (n_D)	1.431
Specific heat capacity, *C*	317.5J K^{-1} mol^{-1}
GHS pictograms	
GHS signal word	DANGER
EU classification	 Xn
Flash point	81 °C
Auto ignition temperature	290 °C

Explosive limits	0.88 – 9.7 %
LD_{50}	1.97 g kg^{-1} (dermal, rabbit) 3.73 g kg^{-1} (oral, rat)

2 - Applications

Almost all 2-ethylhexanol is converted into the diesters bis(2-ethylhexyl) phthalate (DEHP), a plasticizer. Because it is a fatty alcohol, its esters tend to have emollient properties. For example, the sunscreen octocrylene contains a 2-ethylhexyl ester for this purpose. It is also commonly used as a low volatility solvent.

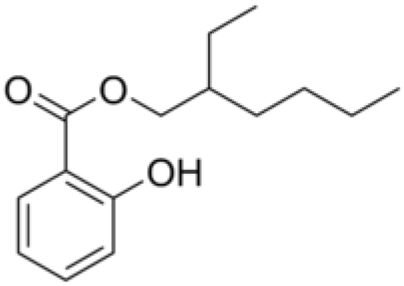
3 - Industrial production

2-Ethylhexanol is produced industrially by the aldol condensation of *n*-butyr aldehyde, followed by hydrogenation of the resulting hydroxy aldehyde. About 2,500,000 tons are prepared in this way annually. The *n* – butyr aldehyde is made by hydro formylation of propylene, either in a self - contained plant or as the first step in a fully integrated facility. Most facilities make *n*-butanol and iso butanol in addition to 2- ethyl hexanol.

4 - Nomenclature

Iso octanol and 2- ethyl hexanol are not synonyms. According to the Chemical Abstracts Service, iso octanol (CAS# 26952-21-6) refers to a different isomer of octanol, 6-methylheptan-1-ol.

Octyl Salicylate



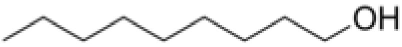
Octyl salicylate, or 2- ethylhexyl salicylate, is an organic compound used as an ingredient in sunscreens and cosmetics to absorb UVB (ultraviolet) rays from the sun.[1] It is an ester formed by the condensation of a salicylic acid with 2-ethylhexanol. It is a colorless oily liquid with a slight floral odor.

The salicylate portion of the molecule absorbs ultraviolet light, protecting skin from the harmful effects of exposure to sunlight. The ethyl hexanol portion is a fatty alcohol, adding emollient and oil-like (water resistant) properties.

IUPAC name :
2 - ethylhexyl 2 - hydroxy benzoate
Other names :
2-ethylhexyl salicylate ;
octisalate ;
benzoic acid , 2-hydroxy- , 2-ethylhexyl ester ;
ethyl hexyl salicylate ;
salicylic acid , 2- ethylhexyl ester ;
2 - ethylhexyl ester benzoic acid, 2-hydroxy- ;
2 - ethylhexyl ester salicylic acid ;
2- hydroxy- 2- ethylhexyl ester benzoic acid ;
benzoic acid, 2- hydroxy, 2- ethylhexyl ester ;

Molecular formula	$C_{15} H_{22} O_3$
Molar mass	250 g / mol
Density	1.014 g / cm^3
Melting point	< 25 °C
Boiling point	189 °C

1 – Nonanol



1-Nonanol is a straight chain fatty alcohol with nine carbon atoms and the molecular formula $CH_3(CH_2)_8OH$. It is a colorless to slightly yellow liquid with a citrus odor similar to citronella oil.

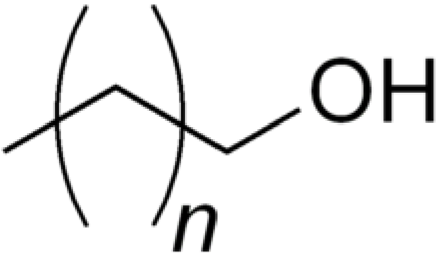
Nonanol occurs naturally in the oil of orange. The primary use of nonanol is in the manufacture of artificial lemon oil. Various esters of nonanol, such as nonyl acetate, are used in perfumery and flavors.

IUPAC name : 1-Nonanol

Other names :
Pelargonic alcohol;
Nonyl alcohol;
n-Nonyl alcohol

Molecular formula	$C_9H_{20}O$
Molar mass	144 g mol^{-1}
Appearance	Colorless liquid
Density	0.83 g / cm^3
Melting point	- 6 °C
Boiling point	214 °C
Solubility in water	1 g / L
Flash point	96 °C
LD_{50}	3560 mg / kg (oral, rat) 4680 mg / kg (dermal , rabbit)

Fatty Alcohol



Fatty alcohol

Contents

1 - Introduction

Fatty alcohols (or long - chain alcohols) are usually high-molecular-weight, straight - chain primary alcohols, but can also range from as few as 4 - 6 carbons to as many as 22 - 26, derived from natural fats and oils. The precise chain length varies with the source. Some commercially important fatty alcohols are lauryl, stearyl, and oleyl alcohols. They are colourless waxy solids, although impure samples may appear yellow. Fatty alcohols usually have an even number of carbon atoms and a single alcohol group (-OH) attached to the terminal carbon. Some are unsaturated and some are branched. They are widely used in industry.

2 - Production and occurrence

Most fatty alcohols in nature are found as waxes which are esters with fatty acids and fatty alcohols . They are produced by bacteria, plants and animals for purposes of buoyancy, as source of metabolic water and energy, biosonar lenses (marine mammals) and for thermal insulation in the form of waxes (in plants and insects).[3] Fatty alcohols were unavailable until the early 1900s. They were originally obtained by reduction of wax esters with sodium by the Bouveault–Blanc reduction process. In the 1930s catalytic hydrogenation was commercialized, which allowed the conversion of fatty acid esters, typically tallow, to the alcohols. In the 1940s and 1950s, petrochemicals became an important source of chemicals, and Karl Ziegler had discovered the polymerization of ethylene. These two developments opened the way to synthetic fatty alcohols.

2 – 1 - From natural sources

The traditional and still important source of fatty alcohols are fatty acid esters. Wax esters were formerly extracted from sperm oil, obtained from whales. An alternative plant source is jojoba. Fatty acid triesters, known as triglycerides, are obtained from plant and animal sources. These triesters are subjected to transesterification to give methyl esters, which in turn are hydrogenated to the alcohols. Although tallow is typically C16 - C18, the chain length from plant sources are more variable. Higher alcohols (C20 – C22) can be obtained from rapeseed. Shorter alcohols (C12 - C14) are obtained from coconut oil.

2 – 1 - From petro chemical sources

Fatty alcohols are also prepared from petrochemical sources. In the Ziegler process, ethylene is oligomerized using tri ethyl aluminium followed by air oxidation. This process affords even-numbered alcohols :

$$Al(C_2H_5)_3 + 18\ C_2H_4 \rightarrow Al(C_{14}H_{29})_3$$

$$Al(C_{14}H_{29})_3 + 1.5\ O_2 + 1.5\ H_2O \rightarrow 3\ HOC_{14}H_{29} + 0.5\ Al_2O_3$$

Alternatively ethylene can be oligomerized to give mixtures of alkenes, which are subjected to hydroformylation, this process affording odd-numbered aldehyde, which is subsequently hydrogenated. For example, from 1- decene, hydroformylation gives the C11 alcohol :

$C_8H_{17}CH{=}CH_2 + H_2 + CO \rightarrow C_8H_{17}CH_2CH_2CHO$

$C_8H_{17}CH_2CH_2CHO + H2 \rightarrow C_8H_{17}CH_2CH_2CH_2OH$

In the Shell higher olefin process, the chain-length distribution in the initial mixture of alkene oligomers is adjusted so as to more closely match market demand. Shell does this by means of an intermediate metathesis reaction.[4] The resultant mixture is fractionated and hydro formylated / hydrogenated in a subsequent step.

3 - Applications

Fatty alcohols are mainly used in the production of detergents and surfactants. They are components also of cosmetics, foods, and as industrial solvents. Due to their amphipathic nature, fatty alcohols behave as nonionic surfactants. They find use as emulsifiers, emollients and thickeners in cosmetics and food industry. About 50% of fatty alcohols used commercially are of natural origin, the remainder being synthetic.

3 – 1 - Nutrition

Very long chain fatty alcohols (VLCFA), obtained from plant waxes and bees wax have been reported to lower plasma cholesterol in humans. They can be found in unrefined cereal grains, beeswax, and many plant-derived foods. Reports suggest that 5 – 20 mg per day of mixed C24 – C34 alcohols, including octa cosanol and tri acontanol , lower low - density lipoprotein (LDL) cholesterol by 21 % – 29 % and raise high-density lipoprotein cholesterol by 8 % – 15 %.

Wax esters are hydrolyzed by a bile salt – dependent pancreatic carboxyl esterase, releasing long chain alcohols and fatty acids that are absorbed in the gastrointestinal tract. Studies of fatty alcohol metabolism in fibroblasts suggest that very long chain fatty alcohols, fatty aldehydes, and fatty acids are reversibly inter-converted in a fatty alcohol cycle. The metabolism of these compounds is impaired in several inherited human peroxisomal disorders, including adrenoleukodystrophy and Sjögren - Larsson syndrome.

4 - Safety

4 – 1 - Human Health

Fatty alcohols are relatively benign materials, with LD50s (oral, rat) ranging from 3.1- r g / kg for hexanol to 6 - 8 g / kg for octa decanol. For a 50 kg person, these values translate to more than 100 g. Tests of acute and repeated exposures have revealed a low level of toxicity from inhalation, oral or dermal exposure of fatty alcohols. Fatty alcohols are not very volatile and the acute lethal concentration is greater than the saturated vapor pressure. Longer chain (C12-C16) fatty alcohols produce fewer health effects than short chain (< C12). Short chain fatty alcohols are considered eye irritants, while long chain alcohols are not. Fatty alcohols exhibit no skin sensitization.

Repeated exposure to fatty alcohols produce low level toxicity and certain compounds in this category can cause local irritation on contact or low-grade liver effects (essentially linear alcohols have a slightly higher rate of occurrence of these effects). No effects on the central nervous system have been seen with inhalation and oral exposure. Tests of repeated bolus dosages of 1-hexanol and 1-octanol showed potential for CNS depression and induced respiratory distress. No potential for peripheral neuropathy has been found. In rats, the no observable adverse effect level (NOAEL) ranges from 200 mg/kg/day to 1000 mg/kg/day by ingestion. There has been no evidence that fatty alcohols are carcinogenic, mutagenic, or cause reproductive toxicity or infertility. Fatty alcohols are effectively eliminated from the body when exposed, limiting possibility of retention or bioaccumulation.

Margins of exposure resulting from consumer uses of these chemicals are adequate for the protection of human health as determined by the Organization for Economic Co - operation and Development (OECD) high production volume chemicals program.

4 – 2 - Environment

Fatty alcohols up to chain length C18 are biodegradable, with length up to C16 biodegrading within 10 days completely. Chains C16 to C18 were found to biodegrade from 62 % to 76 % in 10 days. Chains greater than C18 were found to degrade by 37 % in 10 days. Field studies at waste-water treatment plants have shown that 99 % of fatty alcohols lengths C12-C18 are removed.

Fate prediction using fugacity modeling has shown that fatty alcohols with chain lengths of C10 and greater in water partition into sediment. Lengths C14 and above are predicted to stay in the air upon release. Modeling shows that each type of fatty alcohol will respond independently upon environmental release.

4 – 3 - Aquatic Organisms

Fish, invertebrates and algae experience similar levels of toxicity with fatty alcohols although it is dependent on chain length with the shorter chain having greater toxicity potential. Longer chain lengths show no toxicity to aquatic organisms.

Chain Size	Acute Toxicity for fish	Chronic Toxicity for fish
< C11	1–100 mg / l	0.1 - 1.0 mg / l
C11- C13	0.1 - 1.0 mg / l	0.1 - < 1.0 mg / l
C14 - C15	NA	0.01 mg / l
> C16	NA	NA

This category of chemicals was evaluated under the Organization for Economic Co-operation and Development (OECD) high production volume chemicals program. No unacceptable environmental risks were identified.

5 - Common names and related compounds

Name	**Carbon atoms**
tert-Butyl alcohol	4 carbon atoms
tert-Amyl alcohol	5 carbon atoms
3-Methyl-3-pentanol	6 carbon atoms
Ethchlorvynol	7 carbon atoms
capryl alcohol (1-octanol)	8 carbon atoms
2-ethyl hexanol	8 carbon atoms
pelargonic alcohol (1-nonanol)	9 carbon atoms
capric alcohol (1-decanol, decyl alcohol)	10 carbon atoms
Undecyl alcohol (1-undecanol, undecanol, Hendecanol)	11 carbon atoms
Lauryl alcohol (Dodecanol, 1-dodecanol)	12 carbon atoms
Tridecyl alcohol (1-tridecanol, tridecanol, isotridecanol)	13 carbon atoms
Myristyl alcohol (1-tetradecanol)	14 carbon atoms
Pentadecyl alcohol (1-pentadecanol, pentadecanol)	15 carbon atoms
cetyl alcohol (1-hexadecanol)	16 carbon atoms
palmitoleyl alcohol (cis-9-hexadecen-1-ol)	16 carbon atoms
Heptadecyl alcohol (1-n-heptadecanol, heptadecanol)	17 carbon atoms
stearyl alcohol (1-octadecanol)	18 carbon atoms
Nonadecyl alcohol (1-nonadecanol)	19 carbon atoms
arachidyl alcohol (1-eicosanol)	20 carbon atoms
Heneicosyl alcohol (1-heneicosanol)	21 carbon atoms
behenyl alcohol (1-docosanol)	22 carbon atoms
erucyl alcohol (cis-13-docosen-1-ol)	22 carbon atoms
lignoceryl alcohol (1-tetracosanol)	24 carbon atoms
ceryl alcohol (1-hexacosanol)	26 carbon atoms
1-heptacosanol	27 carbon atoms
montanyl alcohol, cluytyl alcohol, or 1-octacosanol	28 carbon atoms
1-nonacosanol	29 carbon atoms
myricyl alcohol, melissyl alcohol, or 1-triacontanol	30 carbon atoms
1-dotriacontanol	32 carbon atoms
geddyl alcohol (1-tetratriacontanol)	34 carbon atoms
Cetearyl alcohol	

Category : Fatty Alcohols

A
Acetogenin
Arachidyl alcohol
B
Bactoprenol
Butanol
C
Cetostearyl alcohol
Cetyl alcohol
D
1-Decanol
Docosanol
Dodecanol
Dolichol
Dolichol monophosphate
1-Dotriacontanol
E
Ethchlorvynol
2-Ethylhexanol
F
Farnesol
1-(Furan-2-yl)undecan-1-ol
G
Geranylgeraniol
H
1-Heptacosanol
Heptanol
1-Hexacosanol
Hexanol
L
Linoleyl alcohol
N
1-Nonacosanol
1-Nonanol

O
1-Octacosanol
Octanol
Oleyl alcohol
P
Panaxytriol
Policosanol
Polidocanol
S
Sodium tetradecyl sulfate
Stearyl alcohol
T
1-Tetracosanol
1-Tetradecanol
Triacontanol
U
Undecanol

1 – Decanol

Contents

1 - Introduction

1- Decanol is a straight chain fatty alcohol with ten carbon atoms and the molecular formula $C_{10}H_{21}OH$. It is a colorless viscous liquid that is insoluble in water and has a strong odor.

IUPAC name : Decan -1- ol

Other names :
decyl alcohol , *n*-decyl alcohol , capric alcohol , epal 10 , antak , agent 504

Molecular formula	$C_{10}H_{22}O$
Molar mass	158 g / mol
Appearance	Viscous liquid
Density	0.8297 g/cm³
Melting point	6.4 °C
Boiling point	232.9 °C
Solubility in water	Insoluble
Viscosity	12.048 mPa.s (@ 25 °C)
Flash point	108 °C

2 - Uses

Decanol is used in the manufacture of plasticizers , lubricants, surfactants and solvents.

3 - Toxicity

Decanol causes a high irritability to skin and eyes, when splashed into the eyes it can cause permanent damage. Inhalation and ingestion can be harmful; it can also function as a narcotic. It is harmful in the environment.

Undecanol

Contents

1 - Introduction

Undecanol, also known by its IUPAC name **1- undecanol** or **undecan - 1 - ol** , and by its trivial names **undecyl alcohol** and **hendecanol**, is a fatty alcohol . Undecanol is a colorless, water insoluble liquid of melting point 19 ° C and boiling point 243 °C .

IUPAC name : Undecan -1- ol
Other names :
Undecanol , 1- Undecanol ,
Undecyl alcohol , 1- Hendecanol

Molecular formula	$C_{11}H_{24}O$
Molar mass	172 g / mol
Appearance	Colorless liquid
Density	0.8298 g / mL
Melting point	19 °C
Boiling point	243 °C
Solubility in water	Insoluble
Solubility in Ethanol and diethyl ether	Soluble
Flash point	> 82 °C

2 - Industrial uses and production

It has a floral citrus like odor, and a fatty taste and is used as a flavoring ingredient in foods. It is commonly produced by the reduction of 1-undecanal, the analogous aldehyde.

3 - Natural occurrence

1-Undecanol is found naturally in many foods such as fruits (including apples and bananas), butter, eggs and cooked pork.

4 - Toxicity

Undecanol can irritate the skin, eyes and lungs. Ingestion can be harmful, with the approximate toxicity of ethanol.

Dodecanol

Contents

1 - Introduction

Dodecanol, also known by its IUPAC name **1-dodecanol** or **dodecan-1-ol**, and by its trivial name **dodecyl alcohol** and **lauryl alcohol**, is a fatty alcohol. Dodecanol is a colourless, water insoluble solid of melting point 24 °C and boiling point 259 °C. It has a floral aroma. It can be obtained from palm kernel or coconut oil fatty acids and methyl esters by reduction.

Dodecanol is used to make surfactants, lubricating oils, pharmaceuticals, in the formation of monolithic polymers and as a flavor enhancing food additive.

In cosmetics, dodecanol is used as an emollient.

IUPAC name : Dodecan -1-ol

Other names :

Dodecanol , 1-Dodecanol , Dodecyl alcohol , Lauryl alcohol

Molecular formula	$C_{12}H_{26}O$
Molar mass	186
Appearance	Colorless solid
Density	0.8309
Melting point	24 °C
Boiling point	259 °C
Solubility in water	0.004 g / L
Solubility in ethanol and diethyl ether	Soluble
Flash point	127 °C

2 - Toxicity

Dodecanol is a mild skin irritant. It has about half the toxicity of ethanol, but it is very harmful to marine organisms.

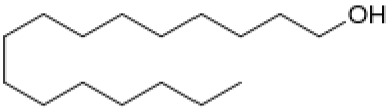
3 - Mutual solubility with water

The mutual solubility of 1- dodecanol and water has been quantified as follows.

Mutual Solubility of Water and 1-Dodecanol
(98 %, Melting Point 24 °C) , Weight %

Temperature, °C	**Solubility of Dodecanol in Water**	**Solubility of Water in Dodecanol**
29.5	0.04	2.87
40.0	0.05	2.85
50.2	0.09	2.69
60.5	0.15	2.96
70.5	0.09	2.70
80.3	0.14	2.89
90.8	0.18	2.96
standard deviation	0.02	0.01

Cetyl Alcohol



Contents

1 - Introduction

Cetyl alcohol, also known as **1-hexadecanol** and **palmityl alcohol**, is a fatty alcohol with the formula $CH_3 (CH_2)_{15} OH$. At room temperature, cetyl alcohol takes the form of a waxy white solid or flakes. The name **cetyl** derives from the whale oil (Latin: *cetus*) from which it was first isolated.

IUPAC name : Hexadecan-1-ol

Other names :

Cetanol , Cetyl alcohol , Ethal , Ethol , Hexa decanol , Hexadecyl alcohol , Palmityl alcohol

Molecular formula	$C_{16} H_{34} O$
Molar mass	242 $g\ mol^{-1}$
Appearance	White crystals
Density	0.811 g / cm^3
Melting point	49 °C
Boiling point	344 °C
Solubility in water	Insoluble
Flash point	185 °C

2 - Preparation

Cetyl alcohol was discovered in 1817 by the French chemist Michel Chevreul when he heated spermaceti, a waxy substance obtained from sperm whale oil, with caustic potash (potassium hydroxide). Flakes of cetyl alcohol were left behind on cooling.

With the demise of commercial whaling, cetyl alcohol is produced by hydrogenation of vegetable oils such as palm oil and coconut oil.

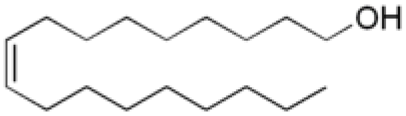
3 - Uses

Cetyl alcohol is used in the cosmetic industry as an opacifier in shampoos, or as an emollient, emulsifier or thickening agent in the manufacture of skin creams and lotions.[5] It is also employed as a lubricant for nuts and bolts.

4 - Side effects

People who suffer from eczema can be sensitive to cetyl alcohol, though this may be due to impurities rather than cetyl alcohol itself. Ironically, this ingredient is sometimes included in medications for the treatment of eczema.

Oleyl Alcohol



Oleyl alcohol, **octadecenol**, or **cis-9-octadecen-1-ol**, is a fatty alcohol coming from beef fat. It is also found in fish oil. Its chemical formula is $C_{18}H_{36}O$ or $CH_3(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_8OH$.

It is a non-ionic, unsaturated fatty alcohol.

It has uses as a nonionic surfactant, emulsifier, emollient and thickener in skin creams, lotions and many other cosmetic products, plasticizer for softening fabrics, surfactant and hair coating in shampoos and hair conditioners, and a carrier for medications.

IUPAC name : (Z) – Octadec - 9 – en -1- ol
Other names :
Octa decenol ,
cis-9-Octadecen -1- ol

Molecular formula	C18 H36 O
Molar mass	268 g/mol
Density	0.845- 0.855 g / cm3
Melting point	13 - 19 °C
Boiling point	330 - 360 °C
Solubility in water	Insoluble

Stearyl Alcohol

Stearyl alcohol (also known as *octadecyl alcohol* or *1-octadecanol*) is an organic compound with the formula $CH_3(CH_2)_{16}CH_2OH$. It is classified as a fatty alcohol. It takes the form of white granules or flakes, which are insoluble in water. It has a wide range of uses as an ingredient in lubricants, resins, perfumes and cosmetics. It is used as an emollient, emulsifier, and thickener in ointments of various sorts, and is widely used as a hair coating in shampoos and hair conditioners.

Stearyl alcohol is prepared from stearic acid or some fats by the process of catalytic hydrogenation. It has low toxicity.

IUPAC name ; Octadecan -1-ol
Other names :
Octa decyl alcohol , stearyl alcohol

Molecular formula	C18 H38 O
Molar mass	270 g / mol
Appearance	White solid
Density	0.812 g / cm³
Melting point	59.4 - 59.8 °C
Boiling point	210 °C at 15 mmHg (~2.0 kPa)
Solubility in water	1.1 x 10-3 mg / L

Docosanol

Contents

1 - Introduction

Docosanol, also known as **behenyl alcohol**, is a saturated fatty alcohol used traditionally as an emollient, emulsifier, and thickener in cosmetics , nutritional supplement (as an individual entity and also as a constituent of policosanol), and more recently, in a Food and Drug Administration (FDA) approved pharmaceutical, **Abreva** , approved as an antiviral agent for reducing the duration of cold sores caused by the herpes simplex virus.

Systematic name : Docosan -1- ol
Other names :
Behenic alcohol , Behenyl alcohol ,
Cachalot BE-22 , 1-Docosanol ,
n-Docosanol , Docosyl alcohol ,
Emery 3304 , Loxiol VPG 1451

Molecular formula	$C_{22}H_{46}O$
Molar mass	326 g mol−1
Melting point	70 °C
Boiling point	180 °C

2 - Mechanism and history of antiviral drug usage

Docosanol is thought to act by inhibiting the fusion of the human host cell with the viral envelope of the herpes virus, thus preventing its replication. This mechanism has not been demonstrated empirically.

The drug was licensed as an oral herpes medicine after clinical trials by the FDA in July 2000. It was shown to shorten the healing by 17.5 hours on average (95 % confidence interval: 2 to 22 hours) in a placebo - controlled trial. Three other trials showed negative results.

Marketed by Avanir Pharmaceuticals, Abreva was the first but not the only over-the-counter antiviral drug approved for sale in the United States and Canada. In Europe, it is marketed by Healthcare Brands under the name **Erazaban**. In March 2007 it was the subject of a US nationwide class-action suit against Avanir and Glaxo Smith Kline as the claim that it cut recovery times in half was found to have been misleading in a California court, but the case was eventually settled and the "cuts healing time in half" claim had not been used in product advertising for some years.

3 - Competition

The FDA has warned consumers to beware of over a dozen "Bogus STD Treatments" including Medavir, Herpaflor, Viruxo , C -Cure, and Never An Outbreak whose marketing makes unproven claims and the Warning Letters the FDA sent to the manufacturers, some of which have gone unheeded, stated that they were "dangerous to health when used in the manner recommended or suggested in their labeling."

On the other hand, another FDA-approved treatment for HSV-1 is Viroxyn (benzalkonium chloride), which a 2012 study found to be significantly more effective than Abreva,[14] and oral antivirals such as Famvir.

4 - Side effects

One of the most common side effects that has been reported from docosanol is headache. Headaches caused by the drug tend to be mild and can occur in any region of the head.

The intensity of the pain can, in some cases, interfere with the ability of remaining focused when working or when at school.

Skin irritation may also occur at the site of application. Usually, skin irritation is mild to moderate and does not need any further treatment. It may also diminish after prolonged use of docosanol.

The most serious side effects, although rare, are allergic reactions. Some of the patients experienced the symptoms of allergic reactions, including difficulty breathing, confusion, facial swelling, fainting, dizziness, hives or chest pain.[15] Allergic reactions are medical emergencies and individuals who experience them are recommended to seek immediate medical care in order to prevent further complications.

Other side effects may include:
Acne
Burning
Dryness
Itching
Rash
Redness
Acute diarrhea
Soreness
Swelling

5 - Contraindications

People who are allergic to one of the ingredients of Abreva are advised to avoid taking this medication. Also, it is not to be used by individuals who suffer from different medical conditions before consulting their health care provider. Interactions with docosanol may occur although there are no known specific interactions at this moment.

This topical has not been yet tested if it is safe to be used by pregnant women. Also, people who are taking other over-the-counter drugs, supplements or herbal preparations are recommended to consult their doctor prior to starting therapy. Nursing mothers are advised to avoid using this topical as it is not established if the active ingredients in the medicine pass into the breast milk. People who are allergic to docosanol or any other ingredient of the product are strongly advised not to use it.

Cosmetic products are recommended to be avoided while using docosanol mainly because they are likely to spread the unhealed infection and not because they interact with the topical. Lipstick is not contraindicated but it is recommended to be applied by using a different applicator to prevent spreading of the infection and recurrence. Cosmetics must be removed before applying the ointment. Also, it is important to know that herpes is highly contagious during outbreaks and patients are advised to avoid physical contact with other people as well as sharing the medicine.

Docosanol has not been specifically approved for treatment of children under 12 but is not expected to produce different side effects or problems than it does in adults. This topical is only intended for external, oral - facial use and should not be administered with the purpose of curing genital herpes or shingles.

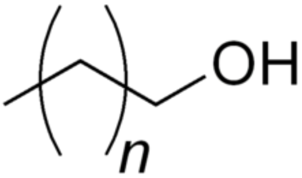
1 – Hexa Cosanol

1-Hexacosanol is a saturated primary fatty alcohol with a carbon chain length of 26 that is a white waxy solid at room temperature. It is freely soluble in chloroform and insoluble in water. It occurs naturally in the epicuticular wax and plant cuticle of many plant species.

IUPAC name : Hexacosan -1- ol

Molecular formula	C26 H54 O
Molar mass	382 g mol−1
Melting point	79 - 81 C
Boiling point	240 C

Policosanol



Contents

1 - Introduction

Policosanol (or **polycosanol**) is the generic term for a natural extract of plant waxes. It is used as a nutritional supplement intended to lower LDL cholesterol ("bad" cholesterol) and increase HDL cholesterol ("good" or "healthy" cholesterol) and to help prevent atherosclerosis, though some studies have raised questions about the effectiveness of policosanol.

Systematic (IUPAC) name :	
Octacosanol , triacontanol , etc.	
Clinical data	
AHFS / Drugs.com	International Drug Names
Formula	CH3 - (CH2) n - CH2OH n = 24 - 34
Mol. mass	(variable)

2 - Physical properties

Policosanol is a mixture of a few fatty alcohols derived from the waxes of such plants as sugar cane and yams, as well as beeswax. The most prevalent alcohol in poli cosanol is octa cosanol , followed by tri acontanol .

There is a much lower concentration of several other fatty alcohols : behenyl alcohol , lignoceryl alcohol , ceryl alcohol , 1-heptacosanol , 1-nonacosanol, 1-dotriacontanol, and geddyl alcohol.

Modulation of HMG - CoA reductase[3] and bile acid absorption inhibition have been proposed as mechanisms.

3 - Studies

Published studies have come to conflicting conclusions regarding the efficacy of policosanol in lowering LDL (i.e., "bad cholesterol") or raising HDL (i.e., "good cholesterol"). Despite a number of studies funded by the Cuban government, which produces and markets the drug , Older independent clinical clinical trials found no evidence of the efficacy of policosanol,[5] while more recent studies have found effect.

Cetostearyl Alcohol

Cetostearyl alcohol, **cetearyl alcohol** or **cetylstearyl alcohol** is a mixture of fatty alcohols, consisting predominantly of cetyl and stearyl alcohols and is classified as a fatty alcohol. It is used as an emulsion stabilizer, opacifying agent, and foam boosting surfactant, as well as an aqueous and nonaqueous viscosity-increasing agent. It imparts an emollient feel to the skin and can be used in water-in-oil emulsions, oil-in-water emulsions, and anhydrous formulations. It is commonly used in hair conditioners and other hair products.

Other names : Cetearyl alcohol ; Cetylstearyl alcohol ; Cetyl / stearyl alcohol	
Molecular formula	$CH3(CH2)nOH$; n = variable , typically 15 -17
Melting point	48-56 °C

Allyl Alcohol

Contents

1 - Introduction

Allyl alcohol (IUPAC name: 2-propenol) is an organic compound with the structural formula $CH_2=CHCH_2OH$. Like many alcohols, it is a water soluble, colourless liquid, but it is more toxic than typical small alcohols. Allyl alcohol is used as a raw material for the production of glycerol, but is also used as a precursor to many specialized compounds. Allyl alcohol is the smallest representative of the allylic alcohols.

IUPAC name : 2- propenol , Allyl alcohol	
Molecular formula	C3 H6 O
Molar mass	58 g mol−1
Density	0.854 g/ml
Melting point	− 129 °C
Boiling point	97 °C
Solubility in water	Miscible
Flash point	21 °C
Auto ignition temperature	378 °C
Explosive limits	2.5 – 18.0 %

2 - Production

Allyl alcohol can be obtained by many methods.[1] The hydrolysis of allyl chloride is the traditional route:

$CH_2CHCH_2Cl + NaOH \rightarrow CH_2CHCH_2OH + NaCl$

Allyl alcohol can also be made by the rearrangement of propylene oxide, a reaction that is catalyzed by potassium alum at high temperature. The advantage of this method relative to the allyl chloride route is that it does not generate salt. Also avoiding chloride-containing intermediates is the "acetoxylation" of propylene to allyl acetate :

$$CH_2{=}CHCH_3 + 1/2\ O_2 + CH_3CO_2H \rightarrow CH_2CHCH_2O_2CCH_3 + H_2O$$

Hydrolysis of this acetate gives allyl alcohol. Alternatively, propylene can be oxidized to acrolein, which upon hydrogenation gives the alcohol.

2 – 1 - Other methods

In principle allyl alcohol can be obtained by dehydrogenation of propanol. In the laboratory, it has been prepared by the reaction of glycerol and formic acid. Allyl alcohols in general can be prepared by allylic oxidation of allyl compounds by selenium dioxide.

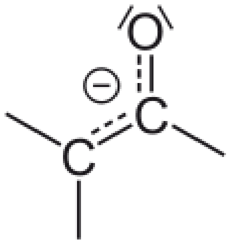
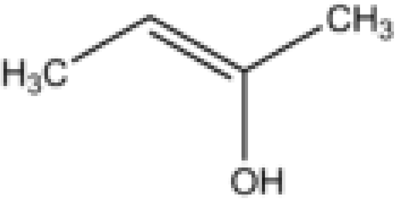
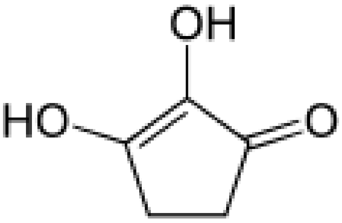
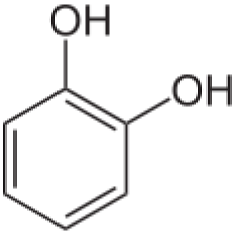
3 - Applications

Allyl alcohol is mainly converted to glycidol, which is a chemical intermediate in the synthesis of glycerol, glycidyl ethers, esters and amines. Also, a variety of polymerizable esters are prepared from allyl alcohol, e.g. diallyl phthalate.

4 - Safety

Allyl alcohol is more toxic than related alcohols. Its threshold limit value (TLV) is 2 ppm. It is a lacrymator.

Enol

	
Enolate	*Enol*
	
Reductone	*Enediol*

Contents

1 - Introduction

Enols (also known as alkenols) are alkenes with a hydroxyl group affixed to one of the carbon atoms composing the double bond. Alkenes with a hydroxyl group on both sides of the double bond are called enediols. Deprotonated anions of enols are called enolates. A reductone is a compound that has an enediol structure with an adjacent carbonyl-group.

The C = C double bond with adjacent alcohol gives enols and enediols their chemical characteristics, by which they present keto-enol tautomerism. In keto - enol tautomerism, enols interconvert with ketones or aldehydes.

The words enol and alkenol are portmanteaus of the words "alkene" (or just -ene, the suffix given to C=C double bonded alkenes) and "alcohol" (which represents the enol's hydroxyl group).

2 - Keto - enol tautomerism

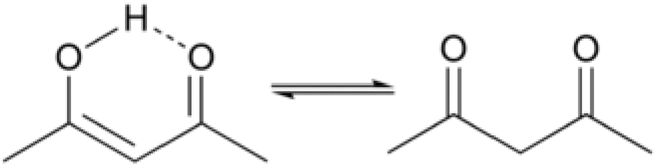
Keto-enol tautomers
Right the enol form

Enols interconvert with carbonyl compounds that have an α-hydrogen, like ketones and aldehydes. The compound is deprotonated on one side and protonated on another side, whereas a single bond and a double bond are exchanged. This is called keto-enol tautomerism.

The enol form is usually unstable, does not survive long, and changes into the keto (ketone). This is because oxygen is more electronegative than carbon and thus forms stronger bonds.

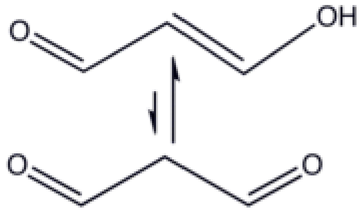
2 -1 - Tautomerism in multi-carbonyl compounds

In 1,3- dicarbonyl and 1,3,5-tricarbonyl compounds, however, the (mono-)enol form predominates. This is due to intramolecular hydrogen bonding and possibly to an easy internal proton transfer.



Hydrogen bond between carbonyls

Thus, at equilibrium, over 99 % of propanedial ($OHCCH_2CHO$) molecules exist as the mono-enol. The percentage is lower for 1,3-aldehyde ketones and diketones (acetyl acetone, for example, 80% enol form ·

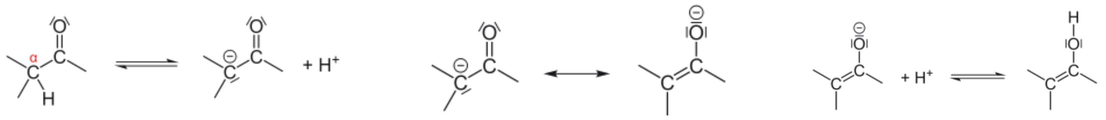


Propanedial, a 1,3-dicarbonyl

3 - Enolates

When *keto-enol tautomerism* occurs the keto or enol is deprotonated and an anion, which is called the enolate, is formed as intermediate. Enolates can exist in quantitative amounts in strictly Brønsted acid free conditions, since they are generally very basic. In enolates the anionic charge is delocalized over the oxygen and the carbon . Enolates are somewhat stabilized by this delocalization of the charge over three atoms. In valence bond theory, which is commonly employed in organic chemistry, this is explained by a phenomenon known as resonance.

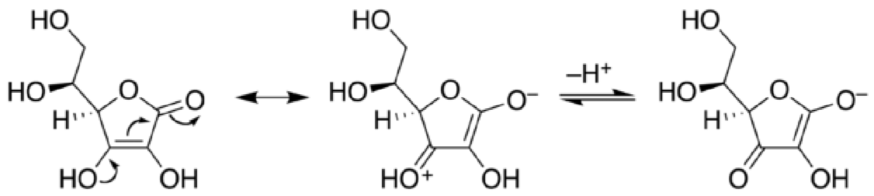
Keto – enol - tautomerism



Interconversion between keto form and enolate; deprotonation of the α-C-atom.

Enolate anion, described is terms of resonance. Left the carbanion.

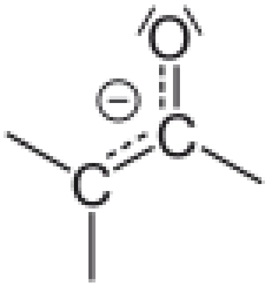
Interconversion between enolate and enol; protonation of the enolate.



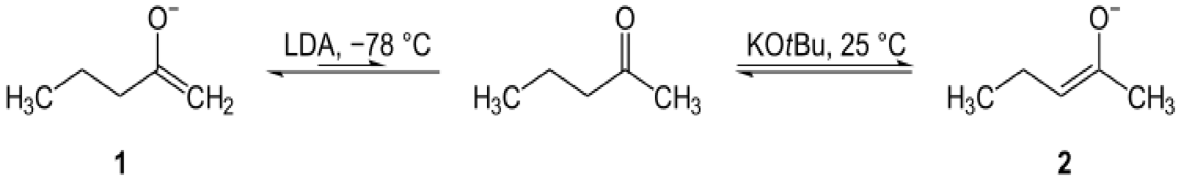
Movement of electron pairs in deprotonation of ascorbic acid (vitamin C), converting an enediol (left) into an enolate (right)

3 – 1 - Delocalization

The enolate ion is described as having a delocalized pi-bond. This is represented in valence bond theory by the resonance hybrid :

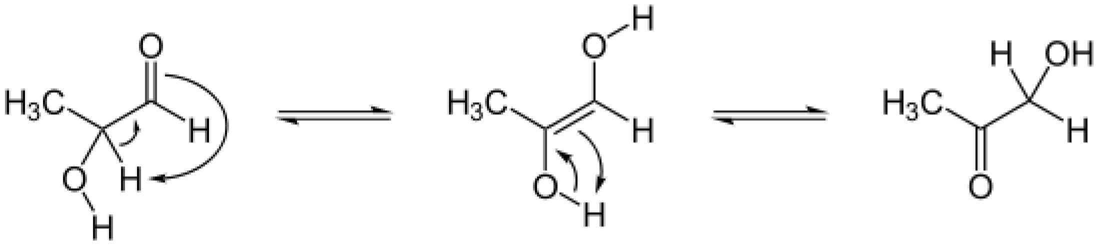


In ketones with α-hydrogens on both sides of the carbonyl carbon, selectivity of deprotonation may be achieved to generate two different enolate structures. At low temperatures (-78°C, i.e. dry ice bath), in aprotic solvents, and with bulky non-equilibrating bases (e.g. LDA) the "kinetic" proton may be removed. The "kinetic" proton is the one which is sterically most accessible. Under thermodynamic conditions (higher temperatures, weak base, and protic solvent) equilibrium is established between the ketone and the two possible enolates, the enolate favoured is termed the "thermodynamic" enolate and is favoured because of its lower energy level than the other possible enolate. Thus, by choosing the optimal conditions to generate an enolate, one can increase the yield of the desired product while minimizing formation of undesired products.



4 - Enediols

Enediols are alkenes with a hydroxyl group on both sides of the C=C double bond. Enediols are reaction intermediates in the Lobry-de Bruyn-van Ekenstein transformation.

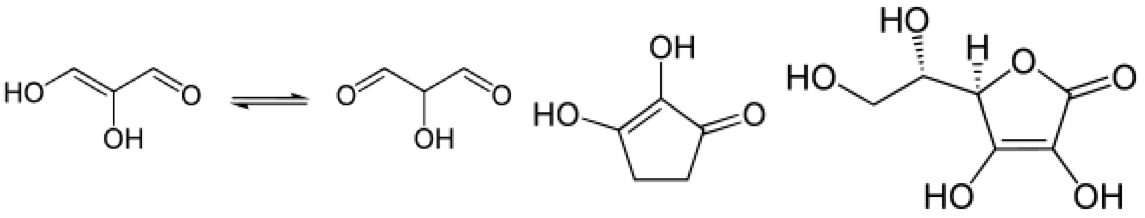


Ketol - enediol tautomerism. In the middle the enediol. Left and right two acyloin isomers.

5 - Reductones

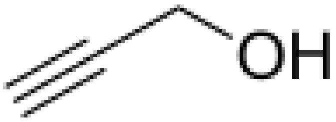
Enediols with a carbonyl group adjacent to the enediol group are called reductones. The enediol structure is stabilized by the resonance resulting from the tautomerism with the adjacent carbonyl. Therefore, the chemical equilibrium produces mainly the enediol form rather than the keto form. Reductones are strong reducing agents, thus efficacious antioxidants, and fairly strong acids . Examples of reductones are tartronaldehyde, reductic acid and ascorbic acid.

Examples of reductones



Tartronaldehyde *Reductic acid* *Ascorbic acid (Vitamin C)*

Propargyl Alcohol



Contents

1 - Introduction

Propargyl alcohol, or 2-propyn-1-ol, is an organic compound which is a simple alcohol containing an alkyne functional group. Propargyl alcohol is a clear colorless viscous liquid that is miscible with water and most polar organic solvents. It is insoluble in most hydrocarbon solvents.

Propargyl alcohol may be polymerized by either heat or base. It is used as a corrosion inhibitor, a metal complex solution, a solvent stabilizer and an electroplating brightener additive. It is also used as an intermediate in organic synthesis. Propargyl alcohol tautomerizes to an enone (α,β-unsaturated ketone). An enal is an α , β-unsaturated aldehyde.

Propargyl alcohol is a flammable liquid, toxic by inhalation, highly toxic by ingestion, toxic by skin absorption, and corrosive.

IUPAC name : 2- Propyn-1- ol	
Molecular formula	C3 H4 O
Molar mass	56.06 g mol−1
Density	0.9715 g/cm³
Melting point	- 51 °C
Boiling point	114-115 °C

2 - Preparation

Propargyl alcohol may be prepared by dehydro chlorination of 3-Chloro - 2- propen -1- ol by Na OH.

Sugar Alcohol

Contents

1 Introduction

A sugar alcohol (also known as a polyol , polyhydric alcohol, polyalcohol, or glycitol) is a hydrogenated form of carbohydrate, whose carbonyl group (aldehyde or ketone, reducing sugar) has been reduced to a primary or secondary hydroxyl group (hence the *alcohol*). Sugar alcohols have the general formula $H(HCHO)_{n+1}H$, where as sugars have $H(HCHO)_nHCO$. In commercial food stuffs sugar alcohols are commonly used in place of table sugar (sucrose), often in combination with high intensity artificial sweeteners to counter the low sweetness. Of these, xylitol is perhaps the most popular due to its similarity to sucrose in visual appearance and sweetness. Sugar alcohols do not contribute to tooth decay.

However, consumption of sugar alcohols does affect blood sugar levels. Sugar alcohols may also cause bloating and diarrhea when consumed in excessive amounts.

Some common sugar alcohols :

Name	Carbon
Methanol	1
Glycol	2
Glycerol	3
Erythritol	4
Threitol	4
Arabitol	5
Xylitol	5
Ribitol	5
Mannitol	6
Sorbitol	6
Galactitol	6
Fucitol	6
Iditol	6

Inositol (a cyclic sugar alcohol)	6
Volemitol	7
Isomalt	12
Maltitol	12
Lactitol	12
Maltotriitol	18
Maltotetraitol	24
Polyglycitol	

Both disaccharides and mono saccharides can form sugar alcohols; however, sugar alcohols derived from disaccharides (e.g. maltitol and lactitol) are not entirely hydrogenated because only one aldehyde group is available for reduction.

The simplest sugar alcohols, ethylene glycol and methanol, are sweet but notoriously toxic chemicals used in antifreeze. The more complex sugar alcohols are for the most part nontoxic.

2 - Sugar alcohols as food additives

Name	Sweetness relative to sucrose	Food energy (kcal / g)	Sweetness per food energy, relative to sucrose
Arabitol	0.7	0.2	14
Erythritol	0.812	0.213	15
Glycerol	0.6	4.3	0.56
HSH	0.4 – 0.9	3.0	0.52 – 1.2
Isomalt	0.5	2.0	1.0
Lactitol	0.4	2.0	0.8
Maltitol	0.9	2.1	1.7
Mannitol	0.5	1.6	1.2
Sorbitol	0.6	2.6	0.92
Xylitol	1.0	2.4	1.6
Compare with : Sucrose	1.0	4.0	1.0

As a group, sugar alcohols are not as sweet as sucrose, and they have less food energy than sucrose. Their flavor is like sucrose, and they can be used to mask the unpleasant aftertastes of some high intensity sweeteners. Sugar alcohols are not metabolized by oral bacteria, and so they do not contribute to tooth decay. They do not brown or caramelize when heated.

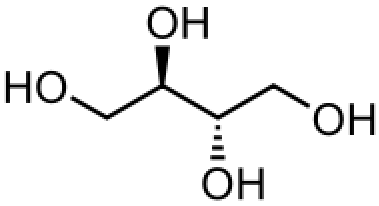
In addition to their sweetness, some sugar alcohols can produce a noticeable cooling sensation in the mouth when highly concentrated, for instance in sugar-free hard candy or chewing gum. This happens, for example, with the crystalline phase of sorbitol, erythritol, xylitol, mannitol, lactitol and maltitol. The cooling sensation is due to the dissolution of the sugar alcohol being an endothermic (heat-absorbing) reaction, one with a strong heat of solution.

Sugar alcohols are usually incompletely absorbed into the blood stream from the small intestines which generally results in a smaller change in blood glucose than "regular" sugar (sucrose). This property makes them popular sweeteners among diabetics and people on low-carbohydrate diets. However, like many other incompletely digestible substances, over consumption of sugar alcohols can lead to bloating, diarrhea and flatulence because they are not absorbed in the small intestine. Some individuals experience such symptoms even in a single-serving quantity. With continued use, most people develop a degree of tolerance to sugar alcohols and no longer experience these symptoms. As an exception, erythritol is actually absorbed in the small intestine and excreted unchanged through urine, so it has no side effects at typical levels of consumption.

The table above presents the relative sweetness and food energy of the most widely-used sugar alcohols. Despite the variance in food energy content of sugar alcohols, EU labeling requirements assign a blanket value of 2.4 kcal/g to all sugar alcohols.

People who have undergone gastric bypass surgery, specifically Roux-en-Y (RGB), should be careful not to eat too many sugar alcohols as doing so, with the exception of erythritol, can lead to "dumping".

Erythritol



Contents

1 Introduction

Erythritol ((2*R*,3*R*)-butane-1,2,3,4-tetraol) is a sugar alcohol (or polyol) that has been approved for use as a food additive in the United States and throughout much of the world. It was discovered in 1848 by British chemist John Stenhouse. It occurs naturally in some fruits and fermented foods.[3] At the industrial level, it is produced from glucose by fermentation with a yeast , *Moniliella pollinis* . It is 60 –70 % as sweet as table sugar yet it is almost noncaloric, does not affect blood sugar, does not cause tooth decay, and is partially absorbed by the body, excreted in urine and feces. It is less likely to cause gastric side effects than other sugar alcohols because of its unique digestion pathway. Under U.S. Food and Drug Administration (FDA) labeling requirements, it has a caloric value of 0.2 kilo calories per gram (95% less than sugar and other carbohydrates), though nutritional labeling varies from country to country. Some countries, such as Japan and the United States, label it as zero-calorie, while European Union regulations currently label it and all other sugar alcohols at 0.24 kcal / g.

2 - Erythritol and human digestion

In the body, most of the erythritol is absorbed into the bloodstream in the small intestine, and then for the most part excreted unchanged in the urine. About 10% enters the colon.[4] Because 90% of erythritol is absorbed before it enters the large intestine, it does not normally cause laxative effects, as are often experienced after consumption of other sugar alcohols (such as xylitol and maltitol), although extremely large doses can cause nausea and borborygmi.

3 - Side effects

Doses over 50g can cause a significant increase in nausea and borborygmi, and (rarely) erythritol can cause allergic urticaria.

In general, erythritol is free of side effects in regular use. When compared with other sugar alcohols, it is also much more difficult for intestinal bacteria to digest, so is less likely to cause gas or bloating than other polyols, such as maltitol, sorbitol, or lactitol.

4 - Physical properties

4 - 1 - Heat of solution

Erythritol has a strong cooling effect (endothermic, or positive heat of solution) when it dissolves in water, which is often combined with the cooling effect of mint flavors, but proves distracting with more subtle flavors and textures. The cooling effect is present only when erythritol is not already dissolved in water, a situation that might be experienced in an erythritol-sweetened frosting, chocolate bar, chewing gum, or hard candy. The cooling effect of erythritol is very similar to that of xylitol and among the strongest cooling effects of all sugar alcohols.

4 – 2 - Blending for sugar - like properties

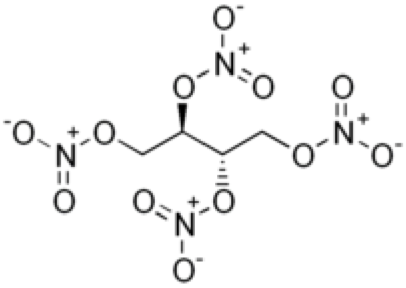
Erythritol is commonly used as a medium in which to deliver high-intensity sweeteners, especially stevia derivatives, serving the dual function of providing both bulk and a flavor similar to that of table sugar. Diet beverages made with this blend, thus, contain erythritol in addition to the main sweetener. Beyond high-intensity sweeteners, erythritol is often paired with other bulky ingredients that exhibit sugar - like characteristics to better mimic the texture and mouthfeel of sucrose. The cooling effect of erythritol is rarely desired, hence other ingredients are chosen to dilute or negate that effect. Erythritol also has a propensity to crystallize and is not as soluble as sucrose, so ingredients may also be chosen to help negate this disadvantage. Furthermore, erythritol is not hygroscopic, meaning it does not attract moisture, which can lead to the drying out of products, in particular baked goods, if another hygroscopic ingredient is not used in the formulation.

Inulin is oftentimes combined with erythritol because of inulin's offering a complementary negative heat of solution (exothermic, or warming effect when dissolved, which helps cancel erythritol's cooling effect) and noncrystallizing properties. However, inulin has a propensity to cause gas and bloating in those having consumed it in moderate to large quantities, in particular in individuals unaccustomed to it. Other sugar alcohols are sometimes used with erythritol, in particular isomalt, because of its minimally positive heat of solution, and glycerin, which has a negative heat of solution, moderate hygroscopicity, and noncrystallizing liquid form.

5 - Erythritol and bacteria

Erythritol has been certified as tooth - friendly . The sugar alcohol cannot be metabolized by oral bacteria, so does not contribute to tooth decay. Interestingly, erythritol exhibits some, but not all, of xylitol's tendency to "starve" harmful bacteria. Unlike xylitol, erythritol is actually absorbed into the bloodstream after consumption but before excretion. However, it is not clear at present if the effect of starving harmful bacteria occurs systemically.

Erythritol Tetra Nitrate



Contents

1 - Introduction

Erythritol tetranitrate (ETN) is an explosive compound chemically similar to PETN.[1] It is however thought to be 1/3 more sensitive to friction and impact. ETN is not well known, but in recent years has been used by amateur experimenters to replace PETN in improvised detonation cord or in boosters to initiate larger, less sensitive explosive charges. Due to the availability of erythritol as a natural sweetener and its relative ease of production in relation to PETN, ETN is a favoured home made explosive compound to the amateur experimenter.

Like many nitric esters, ETN acts as a vasodilator, and was the active ingredient in the original "sustained release" tablets, made under a process patent in the early 50s, called "nitroglyn". Ingesting ETN or prolonged skin contact can lead to absorption and what is known as a "nitro headache".

IUPAC name : [(*2R,3R*)-1,3,4-Trinitrooxybutan-2-yl] nitrate	
Molecular formula	$C_4H_6N_4O_{12}$
Molar mass	302.11 g mol^{-1}
Melting point	61 °C

Boiling point	Decomposes at 160 °C
Explosive data	
Shock sensitivity	Medium (2.0 Nm)
Friction sensitivity	Medium
Explosive velocity	8000 - 8100 m/s

2 - Properties

ETN has a relatively high velocity of detonation of 8000-8100 m/s at a density of 1.6 g/cm^3. It is white in color and odorless. ETN is commonly cast into mixtures with other high explosives. It is somewhat sensitive to shock and friction, so care should be taken while handling. ETN dissolves readily in acetone and other ketone solvents though for the purpose of recrystallization, slow cooling of a saturated solution in ethanol from 55 °C gives much better results with purer and better formed crystals.

Much like PETN, ETN is known for having a very long shelf life. Studies that directly observed the crystalline structure saw no signs of decomposition after four years of storage at room temperature.

3 - Oxygen balance

One quality this explosive has, that PETN does not, is a positive oxygen balance. Having a positive oxygen balance means that ETN possesses more than enough oxygen in its structure to fully oxidize all of its carbon and hydrogen upon detonation. This can be seen in the equation below.

$$C_4H_6N_4O_{12} \rightarrow 4\ CO_2 + 3\ H_2O + 2\ N_2 + \tfrac{1}{2}\ O_2$$

Whereas PETN decomposes to
:

$$C_5H_8N_4O_{12} \rightarrow 3\ CO_2 + 2\ CO + 4\ H_2O + 2\ N_2$$

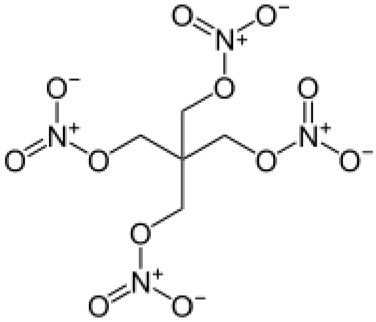
The carbon monoxide (CO) still requires oxygen to complete oxidation to carbon dioxide (CO_2).

Thus for every mole of ETN that decomposes, 1/2 free mole of O_2 is released. This could be used to oxidize an added metal dust or an oxygen deficient explosive such as TNT or PETN.

4 - Manufacture

Like other nitrated polyols, ETN is made by nitrating erythritol through the mixing of concentrated sulfuric acid and a nitrate salt. Ammonium nitrate is commonly used for this type of reaction. The erythritol is added to the mixture to begin its nitration. Much better yields can be obtained by using concentrated nitric acid in place of the nitrate salt, in which case the sulfuric acid is used simply to absorb water and act as a catalyst from the resulting esterification, driving the reaction.

Penta Erythritol Tetra Nitrate



Contents

1 - Introduction

Pentaerythritol tetranitrate (PETN), also known as PENT, PENTA, TEN, corpent, penthrite (or—rarely and primarily in German—as nitropenta), is the nitrate ester of pentaerythritol. Penta refers to the five carbon atoms of the neopentane skeleton.

PETN is most well known as an explosive. It is one of the most powerful high explosives known, with a relative effectiveness factor of 1.66.

PETN mixed with a plasticizer forms a plastic explosive.[3] As a mixture with RDX and other minor additives, it forms another plastic explosive called Semtex as well. The compound was discovered in the bombs used by the 2001 Shoe Bomber, in the 2009 Christmas Day bomb plot, and in the 2010 cargo plane bomb plot. On 7 September 2011, a bomb suspected to have used PETN exploded near the High Court of Delhi in India claiming 13 lives and injuring more than 70.

It is also used as a vasodilator drug to treat certain heart conditions, such as for management of angina.

IUPAC name : [3-Nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate	
Molecular formula	$C_5 H_8 N_4 O_{12}$
Molar mass	316.14 g mol−1
Appearance	White crystalline solid[1]
Density	1.77 g/cm3 at 20 °C
Melting point	141.3 °C
Boiling point	180 °C (decomposes above 150 °C)
Explosive data	
Shock sensitivity	Medium
Friction sensitivity	Medium
Explosive velocity	8400 m/s (density 1.7 g/cm3)
RE factor	1.66
Autoi gnition temperature	190 °C

2 - History

Penthrite was first synthesized in 1891 by Bernhard Tollens and P. Wigand by nitration of pentaerythritol. The production of PETN started in 1912, when it was patented by the German government. PETN was used by the German Army in World War I.

3 - Properties

PETN is practically insoluble in water (0.01 g / 100 ml at 50 °C) , weakly soluble in common nonpolar solvents such as aliphatic hydrocarbons (like gasoline) or tetrachloromethane, but soluble in some other organic solvents, particularly in acetone (about 15 g/100 g of the solution at 20 °C, 55 g / 100 g at 60 °C) and dimethylformamide (40 g / 100 g of the solution at 40 °C, 70 g / 100 g at 70 °C) . PETN forms eutectic mixtures with some liquid or molten aromatic nitro compounds, *e.g.* trinitrotoluene (TNT) or tetryl. Due to its highly symmetrical structure, PETN is resistant to attack by many chemical reagents; it does not hydrolyze in water at room temperature or in weaker alkaline aqueous solutions. Water at 100°C or above causes hydrolysis to dinitrate; presence of 0.1% nitric acid accelerates the reaction. Addition of TNT and other aromatic nitro derivatives lowers thermal stability of PETN.

The chemical stability of PETN is of interest, because of the use of PETN in aging stockpiles of weapons. A review has been published. Neutron radiation degrades PETN, producing carbon dioxide and some pentaerythritol dinitrate and trinitrate. Gamma radiation increases the thermal decomposition sensitivity of PETN, lowers melting point by few degrees Celsius, and causes swelling of the samples. Like other nitrate esters, the primary degradation mechanism is the loss of nitrogen dioxide; this reaction is autocatalytic. Studies were performed on thermal decomposition of PETN.

In the environment, PETN undergoes biodegradation. Some bacteria denitrate PETN to trinitrate and then dinitrate, which is then further degraded . PETN has low volatility and low solubility in water, and therefore has low bioavailability for most organisms. Its toxicity is relatively low, and its transdermal absorption also seems to be low. It poses a threat for aquatic organisms. It can be degraded to pentaerythritol by iron metal.

4 - Production

Production is by the reaction of pentaerythritol with concentrated nitric acid to form a precipitate which can be recrystallized from acetone to give processable crystals.

$$C(CH_2OH)_4 + 4\ HNO_3 \rightarrow C(CH_2ONO_2)_4 + 4\ H_2O$$

Variations of a method first published in a US Patent 2,370,437 by Acken and Vyverberg (1945 to Du Pont) forms the basis of all current commercial production.

PETN is manufactured by numerous manufacturers as a powder about the consistency of fine popcorn salt, or together with nitrocellulose and plasticizer as thin plasticized sheets (e.g. Primasheet 1000 or Detasheet). PETN residues are easily detectable in hair of people handling it. The highest residue retention is on black hair; some residues remain present even after washing.

5 - Explosive use

The most common use of PETN is as an explosive with high brisance. It is more difficult to detonate than primary explosives, so dropping or igniting it will typically not cause an explosion (at atmospheric pressure it is difficult to ignite and burns relatively slowly), but is more sensitive to shock and friction than other secondary explosives such as TNT or tetryl. Under certain conditions a deflagration to detonation transition can occur.

It is rarely used alone, but primarily used in booster and bursting charges of small caliber ammunition, in upper charges of detonators in some land mines and shells, and as the explosive core of detonation cord. PETN is the least stable of the common military explosives, but can be stored without significant deterioration for longer than nitroglycerin or nitrocellulose.

During World War II, PETN was most importantly used in exploding - bridgewire detonators for the atomic bombs. These exploding - bridgewire detonators gave more precise detonation, compared with primacord. PETN was used for these detonators because it was safer than primary explosives like lead azide: while it was sensitive, it would not detonate below a threshold amount of energy. Exploding bridgewires containing PETN remain used in current nuclear weapons. In spark detonators, PETN is used to avoid the need for primary explosives; the energy needed for a successful direct initiation of PETN by an electric spark ranges between 10 – 60 mJ.

Its basic explosion characteristics are :

Explosion energy: 5810 kJ / kg (1390 kcal / kg), so 1 kg of PETN has the energy of 1.24 kg TNT.

Detonation velocity: 8350 m / s (1.73 g/cm^3), 7910 m/s (1.62 g / cm^3), 7420 m/s (1.5 g / cm^3), 8500 m/s (pressed in a steel tube)

Volume of gases produced: 790 dm^3/kg (other value : 768 dm^3 / kg)

Explosion temperature: 4230 °C

Oxygen balance: - 6.31 atom - g/kg

Melting point: 141.3 °C (pure), 140 – 141 °C (technical)

Trauzl lead block test: 523 cm^3 (other values: 500 cm^3 when sealed with sand, or 560 cm^3 when sealed with water)

Critical diameter (minimal diameter of a rod that can sustain detonation propagation): 0.9 mm for PETN at 1 g/cm^3, smaller for higher densities (other value: 1.5 mm)

5 - 1 - In mixtures

PETN is used in a number of compositions. It is a major ingredient of the Semtex plastic explosive. It is also used as a component of pentolite, a 50 / 50 blend with TNT; a shaped charge of 8 ounces (0.23 kg) of pentolite, used in the M9A1 (bazooka) rockets, can penetrate up to 5 inches (130 mm) of armor . The XTX8003 extrudable explosive, used in the W68 and W76 nuclear warheads, is a mixture of 80 % PETN and 20 % of Sylgard 182, a silicone rubber. It is often phlegmatized by addition of 5 – 40 % of wax , or by polymers (producing polymer-bonded explosives); in this form it is used in some cannon shells up to 30 mm caliber, though unsuitable for higher calibers. It is also used as a component of some gun propellants and solid rocket propellants. Nonphlegmatized PETN is stored and handled with approximately 10 % water content. PETN alone cannot be cast as it explosively decomposes slightly above its melting point, but it can be mixed with other explosives to form castable mixtures.

PETN can be initiated by a laser . A pulse with duration of 25 nanoseconds and 0.5 – 4.2 joules of energy from a Q - switched ruby laser can initiate detonation of a PETN surface coated with a 100 nm thick aluminium layer in less than half microsecond.

PETN has been replaced in many applications by RDX, which is thermally more stable and has longer shelf life. PETN can be used in some ram accelerator types. Replacement of the central carbon atom with silicon produces Si-PETN, which is extremely sensitive.

5 - 2 - Terrorist use

In 1983, the "Maison de France" house in Berlin was brought to a near-total collapse by the detonation of 24 kilograms (53 lb) of PETN by terrorist Johannes Weinrich.

In 1999, Alfred Heinz Reumayr used PETN as the main charge for his fourteen improvised explosive devices that he constructed in a thwarted attempt to damage the Trans-Alaska Pipeline System.

In 2001, al-Qaeda member Richard Reid, the "Shoe Bomber", used PETN in the sole of his sneaker in his unsuccessful attempt to blow up American Airlines Flight 63 from Paris to Miami. He had intended to use the solid triacetone triperoxide (TATP) as a detonator.

In 2009, PETN was used in an attempt by al-Qaeda in the Arabian Peninsula to murder the Saudi Arabian Deputy Minister of Interior Prince Muhammad bin Nayef, by Saudi suicide bomber Abdullah Hassan al Asiri. The target survived and the bomber died in the blast. The PETN was hidden in the bomber's rectum, which security experts described as a novel technique.

On December 25, 2009, PETN was found in the underwear of Umar Farouk Abdulmutallab, the "Underwear bomber", a Nigerian with links to al-Qaeda in the Arabian Peninsula.[32]

According to U.S. law enforcement officials, he had attempted to blow up Northwest Airlines Flight 253 while approaching Detroit from Amsterdam . Abdulmutallab had tried, unsuccessfully , to detonate approximately 80 grams (2.8 oz) of PETN sewn into his underwear by adding liquid from a syringe; however , only a small fire resulted.

In the al-Qaeda in the Arabian Peninsula October 2010 cargo plane bomb plot, two PETN-filled printer cartridges were found at East Midlands Airport and in Dubai on flights bound for the U.S. on an intelligence tip. Both packages contained sophisticated bombs concealed in computer printer cartridges filled with PETN . The bomb found in England contained 400 grams (14 oz) of PETN, and the one found in Dubai contained 300 grams (11 oz) of PETN. Hans Michels, professor of safety engineering at University College London, told a newspaper that 6 grams (0.21 oz) of PETN " - around 50 times less than was used – would be enough to blast a hole in a metal plate twice the thickness of an aircraft's skin ." In contrast, according to an experiment conducted by a BBC documentary team designed to simulate Abdulmutallab's Christmas Day bombing, using a Boeing 747 airplane, even 80 grams of PETN was not sufficient to materially damage the airplane's fuselage.

5 - 3 - Detection

In the wake of terrorist PETN bomb plots, an article in *Scientific American* noted that even if all cargo were screened, PETN is difficult to detect because it has a very low vapor pressure at room temperature, meaning very little of it gets into the air around the bomb, where it can be detected.[4] *The Los Angeles Times* noted in November 2010 that because of its more stable molecules, and lower vapor, it is more difficult to detect by bomb-sniffing dogs and the trace swabs then used by the U.S. Transportation Security Administration.

Many technologies can be used to detect PETN , a number of which have been implemented in public screening applications, primarily for air travel. PETN is just one of a number of explosive chemicals typically of interest in that area, and it belongs to a family of common nitrate - based explosive chemicals which can often be detected by the same tests.

One technology, detectors that test swabs wiped on passengers and their baggage for traces of explosives, is generally reserved for travelers who are thought to merit additional scrutiny. A second type of machine, whole - body imaging scanners, use radio - frequency electromagnetic waves, low-intensity X- rays or T- rays of terahertz frequency to detect objects under clothing; these devices were of limited availability because of cost, privacy groups' opposition and industry concerns about bottlenecks.

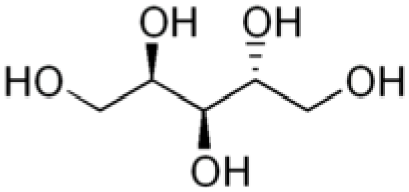
Both parcels in the 2010 cargo plane bomb plot were x-rayed without the bombs being spotted.[41] Qatar Airways said the PETN bomb "could not be detected by x-ray screening or trained sniffer dogs". The Bundeskriminalamt received copies of the Dubai x-rays, and an investigator said German staff would not have identified the bomb either. New airport security procedures followed in the U.S., largely to protect against PETN.

5 - 4 - Medical use

Like nitroglycerin (glyceryl trinitrate) and other nitrates, PETN is also used medically as a vasodilator in the treatment of heart conditions. These drugs work by releasing the signaling gas nitric oxide in the body. The heart medicine *Lentonitrat* is nearly pure PETN.

Monitoring of oral usage of the drug by patients has been performed by determination of plasma levels of several of its hydrolysis products, pentaerythritol dinitrate, pentaerythritol mononitrate and pentaerythritol, in plasma using gas chromatography-mass spectrometry.

Arabitol

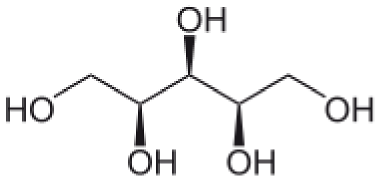


Arabitol or arabinitol is a sugar alcohol. It can be formed by the reduction of either arabinose or lyxose. Some organic acid tests check for the presence of D-arabinitol, which may indicate overgrowth of intestinal parasites such as Candida albicans or other yeast/fungus species.

IUPAC name :
(2R,4R)-pentane-1,2,3,4,5-pentol
Other names : Arabinitol , Lyxitol

Molecular formula	C5 H12 O5
Molar mass	152.14 g/mol
Appearance	Prismatic crystals
Melting point	103 °C
Solubility in water	Miscible

Xylitol



Contents

1 - Introduction

Xylitol (Greek: *xyl[on]*, "wood" + suffix *-itol*, used to denote sugar alcohols), categorized as a polyalcohol (alditol), has interesting applications in hygiene and nutraceutical formulations and products. Xylitol has the formula $(CHOH)_3(CH_2OH)_2$ and is an achiral isomer of pentane-1,2,3,4,5-pentol. Xylitol could function as a diabetic sweetener which is roughly as sweet as sucrose with 33 % fewer calories. Unlike other natural or synthetic sweeteners, xylitol is actively beneficial for dental health by reducing caries to a third in regular use and tooth remineralization, and also has been shown to reduce the incidence of acute middle ear infection.

Xylitol is naturally found in low concentrations in the fibers of many fruits and vegetables, and can be extracted from various berries, oats, and mushrooms, as well as fibrous material such as corn husks and sugar cane bagasse, and birch. However, industrial production starts from xylan (a hemicellulose) extracted from hardwoods or corncobs, which is hydrolyzed into xylose and catalytically hydrogenated into xylitol.

IUPAC name :
(2R,4S)-Pentane-1,2,3,4,5-pentol
Other names :
1,2,3,4,5-Pentahydroxypentane ;
Xylite

Molecular formula	$C_5 H_{12} O_5$
Molar mass	152. g mol−1
Density	1.52 g / cm³
Melting point	92 – 96 °C
Boiling point	216 °C
Solubility in water	~ 1.5 g / mL

2 - Production

Xylitol was discovered almost simultaneously by German and French chemists in the late 19th century, and was first popularized in Europe as a safe sweetener for people with diabetes that would not affect insulin levels. Its dental significance was researched in Finland in the early 1970s, when scientists at Turku University showed it had significant dental benefits.[6] Those became known as the "Turku sugar studies". Today, using hardwood or maize sources, the largest manufacturer globally is the Danish company Danisco, with several other suppliers from China . Xylitol is produced by hydrogenation of xylose, which converts the sugar (an aldehyde) into a primary alcohol.

3 - Properties

One gram of xylitol contains 2.4 kilocalories (Cal), as compared to one gram of sugar, which has 3.87 Cal.[9] Xylitol has virtually no aftertaste, and is advertised as "safe for diabetics and individuals with hyperglycemia." This tolerance is attributed to the lower effect of xylitol on a person's blood sugar, compared to that of regular sugars as it has a very low glycemic index of 7 (glucose has a GI of 100).

4 - Medical applications

4- 1 - Dental care

Xylitol is a “tooth - friendly”, nonfermentable sugar alcohol. It appears to have more dental health benefits than other polyalcohols. The structure of xylitol contains a tridentate ligand, $(H- C- OH)_3$ that can rearrange with polyvalent cations like Ca^{2+}. This interaction allows for Ca^{2+} to be transported through the gut wall barrier and through saliva may remineralize enamel before dental caries form.

Early studies from Finland in the 1970s found compared to chewing sucrose-flavored gum, xylitol resulted in nearly two fewer cavities or missing teeth. Cavity - causing bacteria prefer six - carbon sugars or disaccharides, while xylitol is non - fermentable and can not be used as an energy source, interfering with bacterial growth and reproduction. The harmful micro-organisms are starved in the presence of xylitol, allowing the mouth to remineralize damaged teeth with less interruption. This same property renders it unsuitable for making bread as it interferes with the ability of yeast to digest sugars.[14] At least 6 grams of xylitol per day is thought to be needed for dental efficacy; for most chewing gum or breath mints this would require 12 pieces per day.

Xylitol also inhibits the growth of *Streptococcus pneumoniae*, as well as the attachment of *Haemophilus influenzae* on the nasopharyngeal cells.

However, despite these promising conjectures two systematic reviews of clinical trials could not find conclusive evidence that xylitol was indeed superior to other polyols such as sorbitol or equal to that of topical fluoride in its anti-caries effect.

Xylitol - based products are allowed by the U.S. Food and Drug Administration to make the medical claim that they do not promote dental cavities.

4 – 2 - Diabetes

Possessing approximately 33 % fewer calories, xylitol is a lower- calorie alternative to table sugar. Absorbed more slowly than sugar, it does not contribute to high blood sugar levels or the resulting hyperglycemia caused by insufficient insulin response. This characteristic has also proven beneficial for people suffering from metabolic syndrome, a common disorder that includes insulin resistance , hypertension, hypercholesterolemia , and an increased risk for blood clots. Xylitol is used as a sweetener in medicines, chewing gum and pastilles.

4 – 3 - Ear and upper respiratory infections

Studies have shown xylitol chewing gum can help prevent acute otitis media the act of chewing and swallowing assists with the disposal of earwax and clearing the middle ear, while the presence of xylitol prevents the growth of bacteria in the eustachian tubes (auditory or pharyngotympanic tubes) which connect the nose and ear.[22] When bacteria enter the body, they adhere to the tissues using a variety of sugar complexes. The open nature of xylitol and its ability to form many different sugar-like structures appears to interfere with the ability of many bacteria to adhere. In a double-blind, randomized, controlled trial, saline solutions of xylitol significantly reduced the number of nasal coagulase-negative *Staphylococcus* bacteria. The researchers attributed the benefits to the increased effectiveness of endogenous antimicrobial factors.[23] In a very small case series, nasally administered xylitol reduced ear complaints in children previously having chronic complaints, on the order of almost one a month, by more than 92%. The author also reported beneficial effects on asthma with nasal administration.

5 - Safety

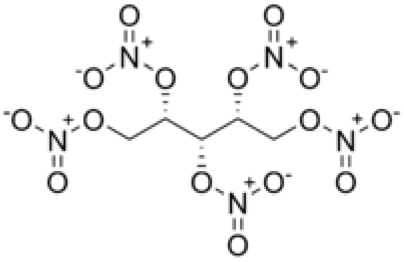
Xylitol has no known toxicity in humans. In one study, the participants consumed a diet containing a monthly average of 1.5 kg of xylitol with a maximum daily intake of 430 g with no apparent ill effects. Like most sugar alcohols, it has a laxative effect because sugar alcohols are not fully broken down during digestion; albeit one-tenth the strength of sorbitol . The effect depends upon the individual. In one study of 13 children, four experienced diarrhea when consuming over 65 grams per day. Studies have reported adaptation occurs after several weeks of consumption.

As with other sugar alcohols, with the exception of erythritol, consumption in excess of one's laxation threshold (the amount of sweetener that can be consumed before abdominal discomfort sets in) can result in temporary gastrointestinal side effects, such as bloating, flatulence, and diarrhea. Adaptation, an increase of the laxation threshold, occurs with regular intake. Xylitol has a lower laxation threshold than some sugar alcohols, but is more easily tolerated than others such as mannitol and sorbitol.

5 – 1 - Dogs

Dogs that have ingested foods containing xylitol (greater than 100 milligrams of xylitol consumed per kilogram of bodyweight) have presented with low blood sugar (hypoglycemia), which can be life-threatening.[28] Low blood sugar can result in a loss of coordination, depression, collapse and seizures in as little as 30 minutes.[29] Intake of doses of xylitol (greater than 500 – 1000 mg/kg bwt) has been implicated in liver failure in dogs, which can be fatal.

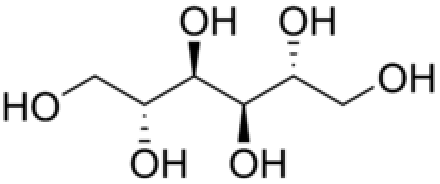
Xylitol Penta Nitrate



Xylitol pentanitrate is a rarely used liquid explosive compound with extremely high viscosity formed by completely nitrating xylitol, a sugar alcohol compound with five carbon atoms. In pure form it is a white crystalline explosive, much like other fully nitrated polyols. However, during synthesis lower nitrated forms are produced, which produce a viscous liquid mixture that is hard to purify.

IUPAC name : 1,2,3,4,5-Pentakis-nitrooxy-pentane	
Molecular formula	$C_5H_7N_5O_{15}$
Molar mass	377 g / mol

Mannitol



Contents

1 - Introduction

Mannitol is a white, crystalline sugar alcohol with the chemical formula ($C_6H_8(OH)_6$). It is used as an osmotic diuretic agent and a weak renal vasodilator. It was originally isolated from the secretions of the flowering ash and called manna after its resemblance to the Biblical food. It is also referred to as mannite and manna sugar. In plants, it is used to induce osmotic stress. Its fetal safety is "C" in Briggs' Reference Guide to Fetal and Neonatal Risk.

Systematic (IUPAC)	
(2R,3R,4R,5R)-Hexan-1,2,3,4,5,6-hexol	
Trade names	Osmitrol
Routes	Intravenous Oral
Pharmacokinetic data	

Bioavailability	~7 %
Metabolism	Hepatic, negligible.
Half-life	100 minutes
Excretion	Renal: 90 %
Formula	C6 H14 O6
Mol. mass	182

2 - Chemistry

Mannitol is a sugar alcohol; that is, it is derived from a sugar by reduction, with a molecular weight of 182 g / mol , and a density of 1.52 g/mL. Other sugar alcohols include xylitol and sorbitol. Mannitol and sorbitol are isomers, the only difference being the orientation of the hydroxyl group on carbon 2 . Aqueous solutions of mannitol are mildly acidic and sometimes such solutions are treated to lower the pH . D - Mannitol has a solubility of 22g mannitol / 100 mL water (25 °C) , and a relative sweetness of 50 (sucrose =100). It melts between 165 and 169 °C , and boils at 295 °C , indicating a greater boiling point at STP conditions.

3 - Obtaining mannitol

3 – 1 - Industrial synthesis

Mannitol is commonly formed via the hydrogenation of fructose, which is formed from either starch or sucrose (common table sugar). Although starch is a cheaper source than sucrose, the transformation of starch is much more complicated. Eventually, it yields a syrup containing about 42 % fructose, 52 % dextrose, and 6 % maltose. Sucrose is simply hydrolyzed into an invert sugar syrup, which contains about 50 % fructose. In both cases, the syrups are chromatographically purified to contain 90 – 95 % fructose. The fructose is then hydrogenated over a nickel catalyst into mixture of isomers sorbitol and mannitol. Yield is typically 50 % : 50 %, although slightly alkaline reaction conditions can slightly increase mannitol yields.

3 – 2 - Biological syntheses

Mannitol is one of the most abundant energy and carbon storage molecules in nature, produced by a plethora of organisms, including bacteria, yeasts, fungi, algae, lichens, and many plants. Fermentation by microorganisms is a possible alternative to traditional industrial synthesis, producing much higher yields of mannitol, with minimal to no side products. A fructose to mannitol metabolic pathway, known as the mannitol cycle in fungi, has been discovered in a type of red algae (*Caloglossa leprieurii*), and it is highly possible that other microorganisms employ similar such pathways.[8] A class of lactic acid bacteria, labeled heterofermentive because of their multiple fermentation pathways, convert either three fructose molecules or two fructose and one glucose molecule into two mannitol molecules, and one molecule each of lactic acid, acetic acid, and carbon dioxide. Feedstock syrups containing medium to large concentrations of fructose (for example, cashew apple juice, containing 55 % fructose: 45 % glucose) can produce yields 200 g mannitol per liter of feedstock. Further research is being conducted, studying ways to engineer even more efficient mannitol pathways in lactic acid bacteria, and also studying the use of other microorganism, such as yeast[7] and E. coli bacteria in mannitol productions. When food grade strains of any of the aforementioned microorganisms are used, the mannitol and the organism itself are directly applicable to food products, avoiding the need for careful separation of micro organism and mannitol crystals. Although this is a promising method, steps are needed to scale it up to industrially needed quantities.

3 – 3 - Natural product extraction

Since mannitol is found in a wide variety of natural products, including almost all plants, it can be directly extracted from natural products, rather than chemical or biological syntheses. In fact, in China, isolation from seaweed is the most common form of mannitol production. Mannitol concentrations of plant exudates can range from 20 % in seaweeds to 90 % in the plane tree. Traditionally, mannitol is extracted by the Soxhlet extraction, utilizing ethanol, water, and methanol to steam and then hydrolyze the crude material. The mannitol is then recrystallized from the extract, generally resulting in yields of about 18 % of the original natural product. Another up and coming method of extraction is by using supercritical and subcritical fluids. These fluids are at such a stage that there is no difference between the liquid and gas stages, and are therefore more diffusive than normal fluids. This is considered to make them much more effective mass transfer agents than normal liquids. The super-/sub-critical fluid is pumped through the natural product, and the mostly mannitol product is easily separated from the solvent and minute amount of byproduct. Supercritical carbon dioxide extraction of olive leaves has been shown to require less solvent per measure of leaf than a traditional extraction - 141.7 g CO_2 versus 194.4 g ethanol per 1 g (0.035 oz) olive leaf. Heated, pressurized, subcritical water is even cheaper, and is shown to have dramatically greater results than traditional extraction. It requires only 4.01 g water per 1 g of olive leaf, and gives a yield of 76.75 % mannitol. Both super- and sub-critical extractions are cheaper, faster, purer, and more environmentally friendly than the traditional extraction. However, the required high operating temperatures and pressures are causes for hesitancy in the industrial use of this technique .

4 - Uses

4 – 1 - Medical applications

Mannitol is used clinically in osmotherapy to reduce acutely raised intracranial pressure until more definitive treatment can be applied, e.g., after head trauma. It is also used to treat patients with oliguric renal failure. It is administered intravenously, and is filtered by the glomeruli of the kidney, but is incapable of being reabsorbed from the renal tubule, resulting in decreased water and Na^+ reabsorption via its osmotic effect. Consequently, mannitol increases water and Na^+ excretion, thereby decreasing extracellular fluid volume .

Mannitol can also be used as a facilitating agent for the transportation of pharmaceuticals directly into the brain. The arteries of the blood – brain barrier are much more selective than normal arteries. Normally, molecules can diffuse into tissues through gaps between the endothelial cells of the blood vessels. However, what enters the brain must be much more rigorously controlled. The endothelial cells of the blood–brain barrier are connected by tight junctions, and simple diffusion through them is impossible. Rather, active transport is necessary, requiring energy, and only transporting molecules that the arterial endothelial cells have receptor signals for. Mannitol is capable of opening this barrier by temporarily shrinking the endothelial cells, simultaneously stretching the tight junctions between them . An intracarotid injection of high molarity mannitol (1.4–1.6M), causes the contents of the artery to be hyperosmotic to the cell. Water leaves the cell and enters the artery in order to recreate an osmotic equilibrium. This loss of water causes the cells to shrivel and shrink, stretching the tight junctions between the cells . The newly formed gap reaches its peak width five minutes after mannitol injection, and stays widely open for thirty minutes. During this timespan, drugs injected into the artery can easily diffuse though the gaps between cells directly into the brain.[11] This makes mannitol indispensable for delivering various drugs directly to the brain (e.g., in the treatment of Alzheimer's disease, or in chemotherapy for brain tumors.) .

Mannitol is commonly used in the circuit prime of a heart lung machine during cardiopulmonary bypass. The presence of mannitol preserves renal function during the times of low blood flow and pressure, while the patient is on bypass. The solution prevents the swelling of endothelial cells in the kidney, which may have otherwise reduced blood flow to this area and resulted in cell damage.

Mannitol is also the basis of Bronchitol which was developed by the Australian pharmaceutical company Pharmaxis as a treatment for cystic fibrosis and bronchiectasis. The mannitol is orally inhaled as a dry powder through what is known as an osmohaler and osmotically draws water into the lungs to thin the thick, sticky mucus characteristic of cystic fibrosis. This is intended to make it easier for the sufferer to cough the mucus up during physiotherapy. The critical characteristic of the mannitol is its particle size distribution. Pharmaxis has also developed Aridol – a diagnostic test for airway hyperresponsiveness based on mannitol.

Mannitol is also the first drug of choice for the treatment of acute glaucoma in veterinary medicine. It is administered as a 20% solution IV. It dehydrates the vitreous humor and, thus, lowers the intraocular pressure. However, it requires an intact blood-ocular barrier to work .

Mannitol can also be used to temporarily encapsulate a sharp object (such as a helix on a lead for an artificial pacemaker) while it is passed through the venous system. Because the mannitol dissolves readily in blood, the sharp point will become exposed at its destination.

Mannitol may be administered in cases of severe Ciguatera poisoning. Severe ciguatoxin, or "tropical fish poisoning" can produce stroke-like symptoms.

Mannitol is the primary ingredient of Mannitol Salt Agar, a bacterial growth medium, and is used in others.

In oral doses larger than 20 g, mannitol acts as an osmotic laxative, and is sometimes sold as a laxative for children ·

4 – 2 - In foods

Mannitol does not stimulate an increase in blood glucose, and is therefore used as a sweetener for people with diabetes, and in chewing gums. It also has a low glycemic index Although mannitol has a higher heat of solution than most sugar alcohols, its comparatively low solubility reduces the cooling effect usually found in mint candies and gums. However, when mannitol is completely dissolved in a product, it induces a strong cooling effect . Also, it has a very low hygroscopicity- it does not pick up water from the air until the humidity level is 98 %. This makes mannitol very useful as a coating for hard candies, dried fruits, and chewing gums, and it is often included as an ingredient in candies and chewing gum . The pleasant taste and mouthfeel of mannitol also makes it a popular excipient for chewable tablets.

4 – 3 - In analytical chemistry

Mannitol can be used to form a complex with boric acid. This increases the acid strength of the boric acid permitting better precision in volumetric analysis of this acid.

4 – 4 - In illicit drugs

Mannitol is sometimes used as an adulterant or cutting agent for heroin, methamphetamines, cocaine, or other illicit drugs. In popular culture, when it is used in this manner, it is often referred to as *baby laxative*.

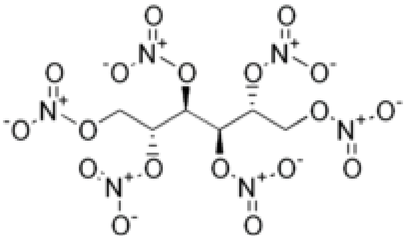
5 Controversy

The three studies that initially found that high - dose mannitol was effective in cases of severe head injury have been the subject of a recent investigation . Although several authors are listed with Dr. Julio Cruz, it is unclear whether the authors had knowledge of how the patients were recruited. Further, the Federal University of São Paulo, which Dr. Cruz gave as his affiliation, has never employed him. Currently, therefore, the Cochrane review recommending high-dose mannitol has been withdrawn pending re-evaluation, as there is some evidence that mannitol may worsen cerebral edema.

6 - Toxicology

Mannitol is contraindicated in patients with anuria and congestive heart failure.

Mannitol Hexa Nitrate



Mannitol hexanitrate is a powerful explosive. Physically, it is a powdery solid at normal temperature ranges, with density 1.6g/cc. The chemical name is hexanitromannitol and it is also known as nitromannite, MHN, nitromannitol, nitranitol, or mannitrin. It is less stable than nitroglycerin, and it is used in detonators.

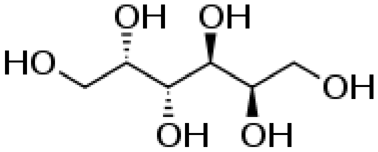
Mannitol hexanitrate is a secondary explosive formed by the nitration of mannitol, a sugar alcohol. The product is used in medicine as a vasodilator and as an explosive in blasting caps. Its sensitivity is considerably high, particularly at high temperatures (>75 °C) where it is more sensitive than nitroglycerine.

It has the highest brisance of any known conventional explosive, even more than nitroglycerine.

IUPAC name :
(2R,3R,4R,5R)-Hexane-1,2,3,4,5,6-hexol-1,2,3,4,5,6-hexanitrate
Other names : Mannitol hexanitrate , Nitromannite , Nitromannitol , Nitranitol , Mannitrin

Molecular formula	$C_6 H_8 N_6 O_{18}$
Molar mass	452
Density	1.604 g / cc
Melting point	112 °C = 234 °F

Galactitol



Galactitol (dulcitol) is a sugar alcohol, the reduction product of galactose. In people with galactokinase deficiency , a form of galactosemia , excess dulcitol forms in the lens of the eye leading to cataracts.

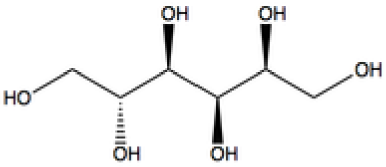
Galactitol is produced from galactose in a reaction catalyzed by aldose reductase. Galactose itself comes from the metabolism of the disaccharide lactose into glucose and galactose.

The other common galactose metabolism defect is a defect in galactose-1-phosphate uridylyltransferase, an autosomal recessive disorder, which also causes a buildup of galactitol as a result of increased concentrations of galactose-1-phosphate and galactose. The toxicity associated with galactose-1-phosphate uridylyltransferase deficiency is associated with symptoms of hepatosplenomegaly and mental retardation in addition to the cataracts caused by galactitol buildup.

IUPAC name :
(2*R*,3*S*,4*R*,5*S*)-hexane-1,2,3,4,5,6-hexol
Other names : D - Galactitol ; Dulcitol

Molecular formula	$C_6H_{14}O_6$
Molar mass	182 g mol^{-1}

Sorbitol



Contents

1 - Introduction

Sorbitol, also known as glucitol, is a sugar alcohol, which the human body metabolizes slowly. It can be obtained by reduction of glucose, changing the aldehyde group to a hydroxyl group. Sorbitol is found in apples, pears, peaches, and prunes. It is synthesized by sorbitol-6-phosphate dehydrogenase, and converted to fructose by succinate dehydrogenase and sorbitol dehydrogenase. Succinate dehydrogenase is an enzyme complex that participates in the citric acid cycle.

IUPAC name :
(2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol
Other names :
D - glucitol ; D - Sorbitol ; Sorbogem ; Sorbo

Molecular formula	$C_6 H_{14} O_6$
Molar mass	182 g mol $^{-1}$
Density	1.489 g / cm³
Melting point	95 °C
Boiling point	296 °C

Flash point	100°C
Auto ignition temperature	150°C

2 - Uses

2 - 1 - Sweetener

Sorbitol is a sugar substitute. It may be listed under the inactive ingredients listed for some foods and products. Its INS number and E number is 420.

Sorbitol is referred to as a nutritive sweetener because it provides dietary energy: 2.6 kilocalories (11 kilojoules) per gram versus the average 4 kilocalories (17 kilojoules) for carbohydrates. It is often used in diet foods (including diet drinks and ice cream), mints, cough syrups, and sugar-free chewing gum.

It also occurs naturally in many stone fruits and berries from trees of the genus *Sorbus*.

2 - 2 - Laxative

Sorbitol can be used as a non - stimulant laxative via an oral suspension or enema. As with other sugar alcohols, gastrointestinal distress may result when food products that contain sorbitol are consumed. Sorbitol exerts its laxative effect by drawing water into the large intestine, thereby stimulating bowel movements.[3] Sorbitol has been determined safe for use by the elderly, although it is not recommended without consultation with a clinician.[4] Sorbitol is found in some dried fruits and may contribute to the laxative effects of prunes.

2 - 3 - Medical applications

Sorbitol is used in bacterial culture media to distinguish the pathogenic *Escherichia coli* O157:H7 from most other strains of *E. coli*, as it is usually incapable of fermenting sorbitol, but 93% of known *E. coli* strains are capable of doing so.

Sorbitol, combined with kayexalate, helps the body rid itself of excess potassium ions in a hyperkalaemic state.[7] The kayexalate exchanges sodium ions for potassium ions in the bowel, while sorbitol helps to eliminate it. The FDA has discouraged this combination when in 2010 it issued a warning of increased risk for GI necrosis.

2 - 4 - Health care, food, and cosmetic uses

Sorbitol often is used in modern cosmetics as a humectant and thickener . Sorbitol often is used in mouthwash and tooth paste. Some transparent gels can be made only with sorbitol, as it has a refractive index sufficiently high for transparent formulations. It is also used frequently in "sugar free" chewing gum.

Sorbitol is used as a cryoprotectant additive (mixed with sucrose and sodium polyphosphates) in the manufacture of surimi, a highly refined fish paste most commonly produced from Alaska pollock (*Theragra chalcogramma*). It is also used as a humectant in some cigarettes.

Sorbitol sometimes is used as a sweetener and humectant in cookies and other foods that are not identified as "dietary" items.

2 - 5 - Miscellaneous uses

A mixture of sorbitol and potassium nitrate has found some success as an amateur solid rocket fuel.

Sorbitol is identified as a potential key chemical intermediate[11] from biomass resources. Complete reduction of sorbitol opens the way to alkanes, such as hexane, which can be used as a biofuel. Sorbitol itself provides much of the hydrogen required for the transformation.

$$19\ C_6H_{14}O_6 \rightarrow 13\ C_6H_{14} + 36\ CO_2 + 42\ H_2O$$

The above chemical reaction is exothermic; 1.5 moles of sorbitol generate approximately 1 mole of hexane. When hydrogen is co-fed, no carbon dioxide is produced.

3 - Medical importance

Aldose reductase is the first enzyme in the sorbitol-aldose reductase pathway responsible for the reduction of glucose to sorbitol, as well as the reduction of galactose to galactitol. Too much sorbitol trapped in retinal cells, the cells of the lens, and the Schwann cells that myelinate peripheral nerves can damage these cells, leading to retinopathy, cataracts and peripheral neuropathy, respectively. Aldose reductase inhibitors, which are substances that prevent or slow the action of aldose reductase, are currently being investigated as a way to prevent or delay these complications, which frequently occur in the setting of long-term hyperglycemia that accompanies poorly-controlled diabetes. It is thought that these agents may help to prevent the accumulation of intracellular sorbitol that leads to cellular damage in diabetics.

4 - Adverse medical effects

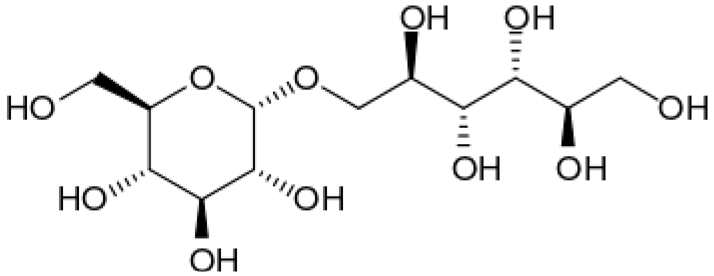
Sorbitol also may aggravate irritable bowel syndrome,[14] and similar gastrointestinal conditions, resulting in severe abdominal pain for those affected, even from small amounts ingested.

It has been noted that the sorbitol added to SPS (Sodium Polystyrene Sulfonate, used in the treatment of hyperkalemia) can cause complications in the GI tract, including bleeding, perforated colonic ulcers, ischemic colitis and colonic necrosis, particularly in patients with uremia. The authors of the paper in question cite a study on rats (both non-uremic and uremic) in which all uremic rats died on a sorbitol enema regimen, whilst uremic rats on non-sorbitol regimens - even with SPS included - showed no signs of colonic damage. In humans, it is suggested that the risk factors for sorbitol-induced damage include "... immunosuppression, hypovolemia, postoperative setting, hypotension after hemodialysis, and peripheral vascular disease." They conclude that SPS-sorbitol should be used with caution, and that "Physicians need to be aware of SPS-sorbitol GI side effects while managing hyperkalemia."

5 - Over dose effects

Ingesting large amounts of sorbitol can lead to abdominal pain, flatulence, and mild to severe diarrhea . Sorbitol ingestion of 20 grams (0.7 oz) per day as sugar-free gum has led to severe diarrhea leading to unintended weight loss of 11 kilograms (24 lb) in eight months, in a woman originally weighing 52 kilograms (110 lb); another patient required hospitalization after habitually consuming 30 grams per day.

Isomalt



IUPAC name :
(2R,3R,4R,5R)-6-[[(2S,3R,4S,5S,6R)- 3,4,5-trihydroxy-6- (hydroxy methyl) - 2-tetrahydropyranyl]oxy]hexane- 1,2,3,4,5-pentol
Other names :
1-O-alpha-D-Glucopyranosyl-D-mannitol

Molecular formula	$C_{12} H_{24} O_{11}$
Molar mass	344.

Isomalt is a sugar substitute, a type of sugar alcohol, used primarily for its sugar-like physical properties. It has only a small impact on blood sugar levels and does not promote tooth decay. It has 2 kilocalories/g, half the calories of sugars.[1] However, like most sugar alcohols (with the exception of erythritol), it carries a risk of gastric distress, including flatulence and diarrhea, when consumed in large quantities. Therefore, isomalt is advised to not be consumed in quantities larger than about 50 g per day for adults and 25 g for children. Isomalt may prove upsetting to the stomach because the body treats it as a dietary fiber instead of as a simple carbohydrate. Therefore, like most fibers, it can increase bowel movements, passing through the bowel in virtually undigested form. As with other dietary fibers, regular consumption of isomalt might eventually lead one to become desensitized to it, decreasing the risk of stomach upset. Isomalt is typically blended with a high-intensity sweetener such as sucralose, so that the mixture has approximately the sweetness of sugar.

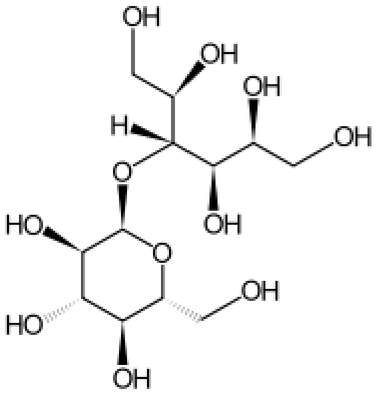
Isomalt is an equimolar mixture of two disaccharides, each composed of two sugars: glucose and mannitol (alpha-D-glucopyranosido-1,6-mannitol) and also glucose and sorbitol (alpha-D-glucopyranosido -1,6-sorbitol). Complete hydrolysis of isomalt yields glucose (50 %), sorbitol (25 %), and mannitol (25%) .[2] It is an odorless, white, crystalline substance containing about 5% water of crystallisation. Isomalt has a minimal cooling effect (positive heat of solution[3]), lower than many other sugar alcohols, in particular, xylitol and erythritol. Isomalt is unusual in that it is a natural sugar alcohol that is produced from beets.

Isomalt is manufactured in a two-stage process in which sugar is first transformed into isomaltulose, a reducing disaccharide (6-O-α-D-glucopyranosido-D-fructose). The isomaltulose is then hydrogenated, using a Raney nickel catalytic converter. The final product — isomalt — is an equimolar composition of 6-O-α-D-glucopyranosido-D-sorbitol (1,6-GPS) and 1-O-α-D-gluco pyranosido-D-mannitol-dihydrate (1,1-GPM-dihydrate).

Isomalt has been approved for use in the United States since 1990. It is also permitted for use in Australia, New Zealand, Switzerland, Canada, Norway, Mexico, Iran and the Netherlands. (note: List of countries is not exhaustive).

Isomalt can be used in sugar sculpture and is preferred by some because it will not crystallise as quickly as sugar.

Maltitol



Contents

1 - Introduction

Maltitol is a sugar alcohol (a polyol) used as a sugar substitute. It has 75 - 90 % of the sweetness of sucrose (table sugar) and nearly identical properties, except for browning. It is used to replace table sugar because it has fewer calories, does not promote tooth decay, and has a somewhat lesser effect on blood glucose. In chemical terms, maltitol is known as 4-O-α-glucopyranosyl-D-sorbitol. It is known under trade names such as Lesys, Maltisweet and SweetPearl®.

IUPAC name :
4-*O*-α-D-Glucopyranosyl-D-glucitol
Other names :
Amalty
Lesys
Maltisweet
SweetPearl

Molecular formula	$C_{12} H_{24} O_{11}$
Molar mass	344 $g\ mol^{-1}$
Melting point	145 °C

2 - Production and uses

Maltitol is a disaccharide produced by Corn Products Specialty Ingredients (formerly SPI Polyols), Cargill, Roquette, and Mitsubishi Shoji Foodtech, among other companies. Maltitol is made by hydrogenation of maltose obtained from starch. Its high sweetness allows it to be used without being mixed with other sweeteners, and exhibits negligible cooling effect (positive heat of solution) in comparison with other sugar alcohols, and is very similar to the subtle cooling effect of sucrose. It is used especially in production of sweets: sugarless hard candies, chewing gum, chocolates, baked goods, and ice cream. The pharmaceutical industry uses maltitol as an excipient, where it is used as a low-calorie sweetening agent. Its similarity to sucrose allows it to be used in syrups with the advantage that crystallization (which may cause bottle caps to stick) is less likely. Maltitol may also be used as a plasticizer in gelatin capsules, as an emollient, and as a humectant.

3 - Chemical properties

Maltitol in its crystallized form measures the same (bulk) as table sugar and browns and caramelizes in a manner very similar to that of sucrose after liquifying by exposure to intense heat. The crystallized form is readily dissolved in warm liquids (120°F/48.9°C and above); the powdered form is preferred if room temperature or cold liquids are used. Due to its sucrose-like structure, maltitol is easy to produce and made commercially available in crystallized, powdered, and syrup forms.

It is not metabolized by oral bacteria, so it does not promote tooth decay. It is somewhat more slowly absorbed than sucrose, which makes it somewhat more suitable for people with diabetes than sucrose. Its food energy value is 2.1 kilocalories (Cal) per gram (8.8 kJ/g); (sucrose is 4.0 Cal / g (16.7 kJ / g)).

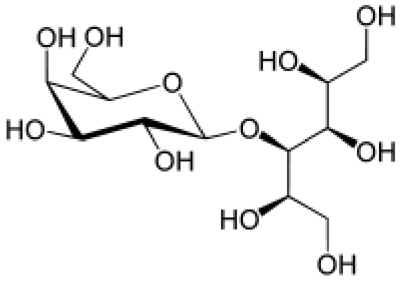
4 - Laxative effect

Like other sugar alcohols (with the exception of erythritol), large quantities of maltitol can have a laxative effect.

5 - Government warnings

In countries such as Australia, Canada, Norway, Mexico and New Zealand, maltitol carries a mandatory warning such as "Excessive consumption may have a laxative effect." In the United States, it is a generally recognized as safe (GRAS) substance, with a recommendation of a warning about its laxative potential when consumed at levels above 100 grams per day.

Lactitol



Contents

1 - Introduction

Lactitol is a sugar alcohol used as a replacement bulk sweetener for low calorie foods with approximately 40 % of the sweetness of sugar. It is also used medically as a laxative. Lactitol is produced by two manufacturers, Danisco and Purac Biochem.

IUPAC name :
4-O-α-D-Galactopyranosyl-D-glucitol
Other names :
Lactitol
Lacty

Molecular formula	$C_{12} H_{24} O_{11}$
Molar mass	344. $g\ mol^{-1}$
Melting point	146 °C

2 Applications

Lactitol is used in a variety of low food energy or low fat foods. High stability makes it popular for baking. It is used in sugar-free candies, cookies (biscuits), chocolate, and ice cream. Lactitol also promotes colon health as a prebiotic. Because of poor absorption, lactitol only has 2.4 Calories (9 kilojoules) per gram, compared to 4 Calories (17 kJ) per gram for typical carbohydrates.

Lactitol is listed as an excipient in some prescription drugs, such as Adderall.

Lactitol is a laxative and is used to prevent or treat constipation, e.g. under the trade name Importal.

Lactitol in combination with Ispaghula husk is an approved combination for idiopathic constipation as a laxative and is used to prevent or treat constipation.

3 - Safety and health

Lactitol, erythritol, sorbitol, xylitol, mannitol, and maltitol are all sugar alcohols. The United States Food and Drug Administration (FDA) classifies sugar alcohols as "generally recognized as safe" (GRAS). They are approved as food additives, and are recognized as not contributing to tooth decay or causing increases in blood glucose. Lactitol is also approved for use in foods in most countries around the world.

Like most other sugar alcohols (with the exception of erythritol), lactitol can cause cramping, flatulence, and diarrhea in some individuals. This is because humans lack a suitable beta-galactosidase in the upper gastrointestinal (GI) tract, and a majority of ingested lactitol reaches the large intestine, where it then becomes fermentable to gut microbes (prebiotic) and can pull water into the gut by osmosis. In a human study with sweetened chocolate, consumption of 5 g per day or less resulted in no GI changes, and 10 g per day caused few changes. Those with other health conditions should consult their GP or dietician prior to consumption.

Polyol

Contents

1 - troduction

A polyol is an alcohol containing multiple hydroxyl groups. In two technological disciplines the term "polyol" has a special meaning: food science and polymer chemistry.

2 - Polyols in food science (Sugar alcohol)

Sugar alcohols, a class of polyols, are commonly added to foods because of their lower calorific content than sugars; however, they are also, in general, less sweet, and are often combined with high-intensity sweeteners. They are also added to chewing gum because they are not broken down by bacteria in the mouth or metabolized to acids, and thus do not contribute to tooth decay.[1] Maltitol, sorbitol, xylitol, erythritol, and isomalt are some of the more common types. Sugar alcohols may be formed under mild reducing conditions from their analogue sugars.

3 - Polyols in polymer chemistry

In polymer chemistry, polyols are compounds with multiple hydroxyl functional groups available for organic reactions. A molecule with two hydroxyl groups is a diol, one with three is a triol, one with four is a tetrol and so on.

Monomeric polyols such as glycerin, pentaerythritol, ethylene glycol and sucrose often serve as the starting point for polymeric polyols. These materials are often referred to as the "initiators" and reacted with propylene oxide or ethylene oxide to produce polymeric polyols. However, they should not be confused with free radical "initiators" used to promote other polymerization reactions. The functional group used as the starting point for a polymeric polyol need not be a hydroxyl group; there are a number of important polyols which are built up from amines. A primary amino group ($-NH_2$) often functions as the starting point for two polymeric chains, especially in the case of polyether polyols.

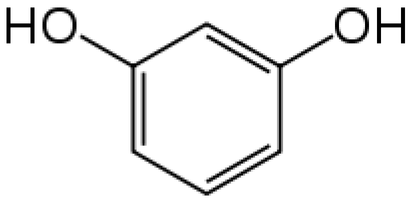
Polymeric polyols are generally used to produce other polymers. They are reacted with isocyanates to make polyurethanes used to make mattresses, foam insulation for appliances (refrigerators and freezers), home and automotive seats, elastomeric shoe soles, fibers (e.g. Spandex), and adhesives.

Polymeric polyols are usually polyethers or polyesters. Polyether polyols are made by reacting epoxides like ethylene oxide or propylene oxide with the multifunctional initiator in the presence of a catalyst, often a strong base such as potassium hydroxide or a double metal cyanide catalyst such as zinc hexacyanocobaltate-t-butanol complex. Common polyether diols are polyethylene glycol, polypropylene glycol, and poly(tetramethylene ether) glycol. The examples shown below are fairly low molecular weight triols based on glycerin (a triol) being reacted with propylene oxide, ethylene oxide or a combination of the two. In reality, the chains would not be of equal length in any one molecule and there would be a distribution of molecular weight polyols within the material. Polyether polyols account for about 90 % of the polymeric polyols used industrially; the balance is polyester polyols.

Another class of polymeric polyols is the polyesters. Polyesters are formed by condensation or step - growth polymerization of diols and dicarboxylic acids (or their derivatives), for example diethylene glycol reacting with phthalic acid. Alternatively, the hydroxyl group and the carboxylic acid (or their derivatives) may be within the same molecule, as in the case of caprolactone. The example below is an idealized structure that could be obtained by reacting pentaerythritol (a tetrol) with gamma-butyrolactone.

Hydroxyl-terminated polybutadiene is a polyol used to produce polyurethane. Polyester polyols from vegetable oils, known as natural oil polyols or NOPs, are replacing some epoxide-based polyols.

Diol

	
Resorcinol	*Ethylene glycol, a simple diol*

Contents

1 - Introduction

A diol is a chemical compound containing two hydroxyl groups (- OH groups). This pairing of functional groups is pervasive and many subcategories have been identified. The most common diols in nature are sugars and their polymers, cellulose. The most common industrial diol is ethylene glycol. Examples of diols in which the hydroxyl functional groups are more widely separated include 1,4-butanediol $HO - (CH_2)_4 - OH$ and bisphenol A, and propylene-1,3-diol or beta propylene glycol, $HO - CH_2 - CH_2 - CH_2 - OH$.

2 - Classification

2 – 1 - Geminal diols

A geminal diol has two hydroxyl groups bonded to the same atom. Examples include methanediol $H_2C(OH)_2$, the hydrated form of formaldehyde. Another example is $(F_3C)_2C(OH)_2$, the hydrated form of hexafluoroacetone.

2 – 2 - Vicinal diols

In a vicinal diol, the two hydroxyl groups occupy vicinal positions, that is, they are attached to adjacent atoms. These compounds are called glycols. Examples include 1,2-ethanediol or ethylene glycol HO - $(CH_2)_2$ - OH, a common ingredient of antifreeze products. Another example is propane-1,2-diol or alpha propylene glycol, HO - CH_2 - CH(OH) - CH_3 used in the food and medicine industry as well as a relatively non-poisonous antifreeze product.

2 – 3 - Bis(phenol)s

Bisphenol A is an important compound that contains two phenol groups.

2 – 4 - Examples of aliphatic diols

Linearity of the diol	Hydroxyls on adjacent carbons (vicinal diols)	Hydroxyls on non-adjacent carbons
Linear	Ethylene glycol	1,3-Propanediol, 1,4-Butanediol, 1,5-Pentanediol, 1,8-octanediol,
Branched	1,2 - Propanediol, 1,2 - Butanediol, 2,3 - Butanediol	1,3-Butanediol, 1,2-pentanediol, Etohexadiol, p-Menthane-3,8-diol, 2-Methyl-2,4-pentanediol

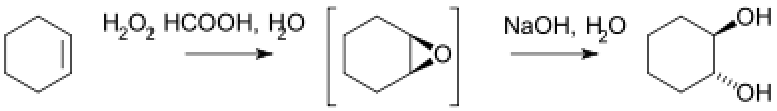
3 - Synthesis

Because diols are a common functional group arrangement, numerous methods of preparation have been developed.

Vicinal diols can be produced from the oxidation of alkenes, usually with dilute acidic potassium permanganate, also known as potassium manganate(VII). Using alkaline potassium manganate(VII) produces a colour change from clear deep purple to clear green; acidic potassium manganate(VII) turns clear colourless.

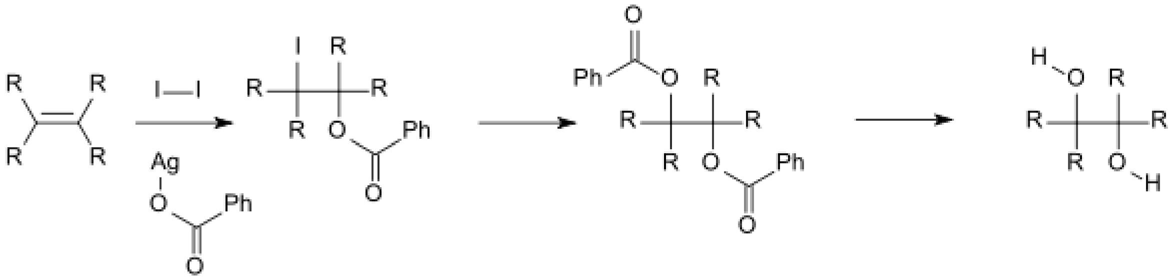
Osmium tetroxide can similarly be used to oxidize alkenes to vicinal diols.

Hydrogen peroxide reacts with an alkene to the epoxide and then by saponification to the diol for example in the synthesis of *trans-cyclohexanediol* batch or by microreactor :



A chemical reaction called Sharpless asymmetric dihydroxylation can be used to produce chiral diols from alkenes using an osmate reagent and a chiral catalyst.

Another method is the Woodward cis-hydroxylation (cis diol) and the related Prévost reaction (anti diol), depicted below, which both use iodine and the silver salt of a carboxylic acid.



In the Prins reaction 1,3- diols can be formed in a reaction between an alkene and formaldehyde.

Geminal diols can be formed by the hydration of ketones.

1,3-diols can be produced diastereoselectively from the corresponding β-hydroxy ketones using the Evans–Saksena or Narasaka–Prasad reduction protocols

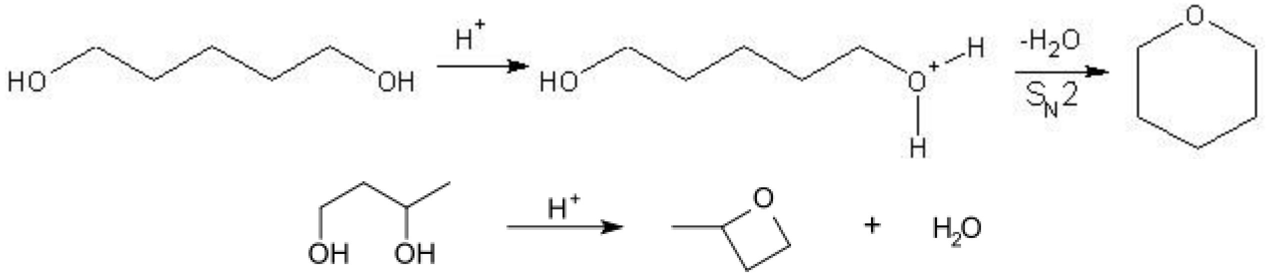
4 - Reactions

4 – 1 - General diols

Diols react as alcohols, by esterification and ether formation.

Diols such as ethylene glycol are used as co-monomers in polymerization reactions forming polymers including some polyesters and polyurethanes. A different monomer with two identical functional groups, such as a dioyl dichloride or dioic acid is required to continue the process of polymerization through repeated esterification processes.

A diol can be converted to cyclic ether by using an acid catalyst, this is diol cyclization. Firstly, it involves protonation of the hydroxyl group. Then, followed by intramolecular nucleophilic substitution, the second hydroxyl group attacks the electron deficient carbon. Provided that there are enough carbon atoms that the angle strain is not too much, a cyclic ether can be formed.



4 – 2 - Vicinal diols

In glycol cleavage, the C-C bond in a vicinal diol is cleaved with formation of ketone or aldehyde functional groups. See Diol oxidation.

4 – 3 - Geminal diols

In general, organic geminal diols readily dehydrate to form a carbonyl group. For example, carbonic acid ($(HO)_2C = O$) is unstable and has a tendency to convert to carbon dioxide (CO_2) and water (H_2O). Nevertheless, in rare situations the chemical equilibrium is in favor of the geminal diol. For example, when formaldehyde ($H_2C= O$) is dissolved in water the geminal diol ($H_2C(OH)_2$), methanediol, is favored. Other examples are the cyclic geminal diols decahydroxy cyclopentane ($C_5(OH)_{10}$) and dodecahydroxy cyclohexane ($C_6(OH)_{12}$), which are stable, whereas the corresponding oxocarbons (C_5O_5 and C_6O_6) do not seem to be.

Ethylene Glycol

Contents

1 - Introduction

Ethylene glycol (IUPAC name: ethane-1,2-diol) is an organic compound widely used as an automotive antifreeze and a precursor to polymers. In its pure form, it is an odorless, colorless, syrupy, sweet-tasting liquid. Ethylene glycol is toxic, and ingestion can result in death.

IUPAC name ; Ethane -1,2 - diol

Other names :

1,2-Ethanediol , Glycol , Ethylene Alcohol , Hypodicarbonous acid , Monoethylene glycol

Molecular formula	$C_2\ H_6\ O_2$
Molar mass	62 g mol^{-1}
Density	1.1132 g/cm³
Melting point	− 12.9 °C
Boiling point	197.3 °C
Solubility in water	Miscible with water

	in all proportions.
Viscosity	1.61×10^{-2} N*s / m^2
Main hazards	It is extremely harmful to pets and children. If ingested, get medical help immediately.
Flash point	111 °C (closed cup)
Auto ignition temperature	410 °C
Structure and properties	n, ε_r, etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

2 - Production

2 – 1 - Historical aspects and natural occurrence

Although almost all sources state that French chemist Charles-Adolphe Wurtz (1817-1884) first prepared ethylene glycol in 1859, he actually first prepared it in 1856. He first treated "ethylene iodide" ($C_2H_4I_2$) with silver acetate and then hydrolyzed the resultant "ethylene diacetate" with potassium hydroxide. Wurtz named his new compound "glycol" because it was intermediate to ethyl alcohol (with one hydroxyl group) and glycerin (with three hydroxyl groups).[3] In 1860, Wurtz prepared ethylene glycol from the hydration of ethylene oxide. There appears to have been no commercial manufacture or application of ethylene glycol prior to World War I, when it was synthesized from ethylene dichloride in Germany and used as a substitute for glycerol in the explosives industry.

In the United States, semicommercial production of ethylene glycol via ethylene chlorohydrin started in 1917. The first large-scale commercial glycol plant was erected in 1925 at South Charleston, West Virginia, by Carbide and Carbon Chemicals Co. (now Union Carbide Corp.). By 1929, ethylene glycol was being used by almost all dynamite manufacturers.

In 1937, Carbide started up the first plant based on Lefort's process for vapor-phase oxidation of ethylene to ethylene oxide.

Carbide maintained a monopoly on the direct oxidation process until 1953, when the Scientific Design process was commercialized and offered for licenses.

This molecule has been observed in outer space.

2 – 2 - Current methods

Ethylene glycol is produced from ethylene (ethene), via the intermediate ethylene oxide. Ethylene oxide reacts with water to produce ethylene glycol according to the chemical equation:

$$C_2H_4O + H_2O \rightarrow HO–CH_2CH_2–OH$$

This reaction can be catalyzed by either acids or bases, or can occur at neutral pH under elevated temperatures. The highest yields of ethylene glycol occur at acidic or neutral pH with a large excess of water. Under these conditions, ethylene glycol yields of 90% can be achieved. The major byproducts are the ethylene glycol oligomers diethylene glycol, triethylene glycol, and tetraethylene glycol. About 6.7 billion kilograms are produced annually.

A higher selectivity is achieved by use of the Shell's OMEGA process. In the OMEGA process, the ethylene oxide is first converted with carbon dioxide (CO_2) to ethylene carbonate to then react with water in a second step to selectively produce mono-ethylene glycol. The carbon dioxide is released in this step again and can be fed back into the process circuit. The carbon dioxide comes in part from the ethylene oxide production, where a part of the ethylene is completely oxidized.

3 - Uses

The major end uses of ethylene glycol are as an antifreeze, which accounts for over 50% of ethylene glycol's commercial uses, and as raw material in the production of polyester fibers, mainly PET, which accounts for 40% of total ethylene glycol consumption. Because this material is cheaply available, it finds many niche applications.

3 – 1 - Coolant and heat transfer agent

The major use of ethylene glycol is as a medium for convective heat transfer in, for example, automobiles and liquid cooled computers. Ethylene glycol is also commonly used in chilled water air conditioning systems that place either the chiller or air handlers outside, or systems that must cool below the freezing temperature of water. In geothermal heating/cooling systems, ethylene glycol is the fluid that transports heat through the use of a geothermal heat pump. The ethylene glycol either gains energy from the source (lake, ocean, water well) or dissipates heat to the source, depending if the system is being used for heating or cooling.

Pure ethylene glycol has a specific heat capacity about one half that of water. So, while providing freeze protection and an increased boiling point, ethylene glycol lowers the specific heat capacity of water mixtures relative to pure water. A 50/50 mix by mass has a specific heat capacity of about 3140 J / Kg C three quarters that of pure water, thus requiring increased flow rates in same system comparisons with water. Additionally, the increase in boiling point over pure water inhibits nucleate boiling on heat transfer surfaces thus reducing heat transfer efficiency in some cases, such as gasoline engine cylinder walls. Therefore, pure ethylene glycol should not be used as an engine coolant in most cases.

3 – 3 - Antifreeze

Due to its low freezing point ethylene glycol resists freezing. A mixture of 60 % ethylene glycol and 40 % water freezes at − 45 °C . Diethylene glycol behaves similarly. It is used as a de-icing fluid for windshields and aircraft. The antifreeze capabilities of ethylene glycol have made it an important component of vitrification (anti crystallization) mixtures for low - temperature preservation of biological tissues and organs.

Ethylene glycol disrupts hydrogen bonding when dissolved in water. Pure ethylene glycol freezes at about −12 °C , when mixed with water molecules, neither can readily form a solid crystal structure, and therefore the freezing point of the mixture is depressed significantly. The minimum freezing point is observed when the ethylene glycol percent in water is about 70%, as shown below. This is the reason pure ethylene glycol is not used as an antifreeze—water is a necessary component as well.

Ethylene glycol freezing point vs. concentration in water	
Weight Percent EG (%)	***Freezing Point (°C)***
0	0
10	- 4
20	- 7
30	- 15
40	- 23
50	- 34
60	- 48
70	- 51
80	- 45
90	- 29
100	- 12

However, the boiling point for aqueous ethylene glycol increases monotonically with increasing ethylene glycol percentage. Thus, the use of ethylene glycol not only depresses the freezing point, but also elevates the boiling point such that the operating range for the heat transfer fluid is broadened on both ends of the temperature scale. The increase in boiling temperature is due to pure ethylene glycol having a much higher boiling point and lower vapor pressure than pure water; there is no chemical stabilization against boiling of the liquid phase at intermediate compositions, as there is against freezing.

Ethylene glycol boiling point vs. concentration in water	
Weight Percent EG (%)	***Boiling Point (°C)***
0	100
10	102

20	102
30	104
40	104
50	107
60	110
70	116
80	124
90	140
100	197

3 – 3 - Precursor to polymers

In the plastics industry, ethylene glycol is important precursor to polyester fibers and resins. Polyethylene terephthalate, used to make plastic bottles for soft drinks, is prepared from ethylene glycol.

3 – 4 - Hydrate inhibition

Because of its high boiling point and affinity for water, ethylene glycol is a useful desiccant. Ethylene glycol is widely used to inhibit the formation of natural gas clathrates (hydrates) in long multiphase pipelines that convey natural gas from remote gas fields to an onshore processing facility. Ethylene glycol can be recovered from the natural gas and reused as an inhibitor after purification treatment that removes water and inorganic salts.

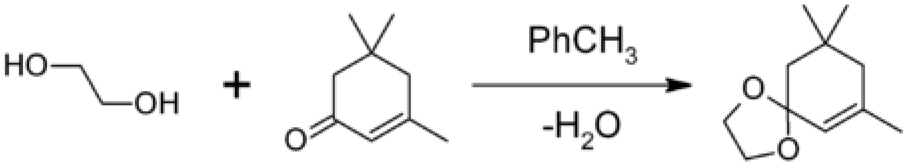
Natural gas is dehydrated by ethylene glycol. In this application, ethylene glycol flows down from the top of a tower and meets a rising mixture of water vapor and hydrocarbon gases. Dry gas exits from the top of the tower. The glycol and water are separated, and the glycol recycled. Instead of removing water, ethylene glycol can also be used to depress the temperature at which hydrates are formed. The purity of glycol used for hydrate suppression (monoethylene glycol) is typically around 80 %, whereas the purity of glycol used for dehydration (triethylene glycol) is typically 95 to more than 99%. Moreover, the injection rate for hydrate suppression is much lower than the circulation rate in a glycol dehydration tower.

3 – 5 - Niche applications

Minor uses of ethylene glycol include the manufacture of capacitors, as a chemical intermediate in the manufacture of 1,4-dioxane, and as an additive to prevent corrosion in liquid cooling systems for personal computers. Ethylene glycol is also used in the manufacture of some vaccines, but it is not itself present in these injections. It is used as a minor (1 – 2 %) ingredient in shoe polish and also in some inks and dyes. Ethylene glycol has seen some use as a rot and fungal treatment for wood, both as a preventative and a treatment after the fact. It has been used in a few cases to treat partially rotted wooden objects to be displayed in museums. It is one of only a few treatments that are successful in dealing with rot in wooden boats, and is relatively cheap. Ethylene glycol may also be one of the minor ingredients in screen cleaning solutions, along with the main ingredient isopropyl alcohol. Ethylene glycol is commonly used as a preservative for biological specimens, especially in secondary schools during dissection as a safer alternative to formaldehyde. It can also be used in killing jars. It is also used as part of the water-based fluid used to control subsea oil and gas production equipment.

4 - Chemical reactions

Ethylene glycol is used as a protecting group for carbonyl groups in organic synthesis. Treating a ketone or aldehyde with ethylene glycol in the presence of an acid catalyst (e.g., p-toluenesulfonic acid; BF_3•Et_2O) gives the corresponding a 1,3-dioxolane, which is resistant to bases and other nucleophiles. The 1,3-dioxolane protecting group can thereafter be removed by further acid hydrolysis.[6] In this example, isophorone was protected using ethylene glycol with p-toluenesulfonic acid in moderate yield. Water was removed by azeotropic distillation to shift the equilibrium to the right .



5 - Toxicity

Ethylene glycol is moderately toxic with an oral LDLO = 786 mg/kg for humans. The major danger is due to its sweet taste. Because of that, children and animals are more inclined to consume large quantities of it than of other poisons. Upon ingestion, ethylene glycol is oxidized to glycolic acid which is, in turn, oxidized to oxalic acid, which is toxic. It and its toxic byproducts first affect the central nervous system, then the heart, and finally the kidneys. Ingestion of sufficient amounts can be fatal if untreated.

According to the annual report of the American Association of Poison Control Centers' National Poison Data System in 2007, there were about 1000 total cases resulting in 16 deaths. The 2008 American Association of Poison Control Centers' National Poison Data System annual report lists 7 deaths.(Toxicity, Ethylene Glycol)

Antifreeze products for automotive use containing propylene glycol in place of ethylene glycol are available, and are generally considered safer to use, as it possesses an unpleasant taste in contrast to the perceived "sweet" taste of toxic ethylene glycol-based coolants, and only produces lactic acid in an animal's body, as their muscles do when exercised.

Australia, the U.K., and seventeen U.S. states (as of 2012) require the addition of a bitter flavoring (denatonium benzoate) to antifreeze; in 2012, U.S. antifreeze manufacturers agreed voluntarily to add a bitter flavoring to all antifreeze that's sold in the consumer market of the U.S.

6 - In the environment

Ethylene glycol breaks down in air in about ten days, and in water or soil in a few weeks. It enters the environment through the disposal of ethylene glycol-containing products, especially at airports where it is used in deicing agents for runways and airplanes.

Ethylene Glycol Dinitrate

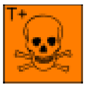
Contents

1 - Introduction

Ethylene glycol dinitrate (EGDN,NGc), also known as nitroglycol, is a chemical compound a yellowish, oily explosive liquid obtained by nitrating ethylene glycol. It is similar to nitro glycerin in both manufacture and properties, though it is more volatile and less viscous.

IUPAC name : 1,2 - dinitroxyethane
Other names :
Ethylene glycol dinitrate , Glycol dinitrate ,
Ethylene dinitrate , Ethylene nitrate ,
1,2-Bis(nitrooxy)ethane , Nitroglycol (NGc) ,
1,2-Ethanediol dinitrate , Dinitroglycol ,
EGDN , Ethane -1,2- diyl dinitrate

Molecular formula	$C_2 H_4 N_2 O_6$
Molar mass	152 g / mol
Appearance	Oily, odorless, colorless to light yellow liquid
Density	1.49 g / cm^3
Melting point	- 22.0 °C
Boiling point	Explodes at 114 °C
Solubility in water	5 g / l
Explosive data	

Shock sensitivity	Medium
Friction sensitivity	Medium
Explosive velocity	7300 m / s
Main hazards	 

3 - History and production

Pure EGDN was first produced by L. Henry in 1870 by dropping a small amount of ethylene glycol into a mixture of nitric and sulfuric acids cooled to 0°C. The previous year, August Kekulé had produced pure EGDN by the nitration of ethylene, but this was actually contaminated with beta-nitroethyl nitrate.

EGDN can be produced either through the nitration of ethylene glycol :

$$C_2H_4(OH)_2 + 2\ HNO_3 \rightarrow C_2H_4(ONO_2)_2 + 2\ H_2O$$

or through the reaction of ethylene oxide and dinitrogen pentoxide :

$$C_2H_4O + N_2O_5 \rightarrow C_2H_4(ONO_2)_2$$

3 - Properties

3 – 1 - Physical properties

Ethylene glycol dinitrate is a colorless volatile liquid when in pure state, but is yellowish when impure. It freezes at -22.3°C, and boils at 199°C.

3 – 2 - Chemical properties

When ethylene glycol dinitrate is rapidly heated to 215°C, it explodes; this is preceded by partial decomposition similar to that of nitroglycerin. EGDN has a slightly higher brisance than nitroglycerin.

Ethylene glycol dinitrate reacts violently with potassium hydroxide, yielding ethylene glycol and potassium nitrate :

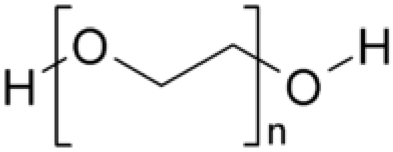
$$C_2H_2(ONO_2)_2 + 2\ KOH \rightarrow C_2H_2(OH)_2 + 2\ KNO_3$$

4 - Other

EGDN was used in manufacturing explosives to lower the freezing point of nitroglycerin, in order to produce dynamite for use in colder weather. Due to its volatility it was used as a detection taggant in some plastic explosives, e.g. Semtex, to allow more reliable explosive detection, until 1995 when it was replaced by Dimethyldinitrobutane. It is considerably more stable than glyceryl trinitrate owing to the lack of secondary hydroxyl groups in the precursor polyol.

Like other organic nitrates, ethylene glycol dinitrate is a vasodilator.

Poly Ethylene Glycol



Contents

1 - Introduction

Polyethylene glycol (PEG) is a polyether compound with many applications from industrial manufacturing to medicine. The structure of PEG is (note the repeated element in parentheses):

$H-(O-CH_2-CH_2)_n-OH$

PEG is also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight.

IUPAC name : poly(oxyethylene) {structure-based}, poly(ethylene oxide) {source-based}	
Other names : Carbowax , GoLYTELY , GlycoLax , Fortrans , TriLyte , Colyte , Halflytely , Macrogol , MiraLAX , MoviPrep	
Molecular formula	$C_{2n} H_{4n+2} O_{n+1}$
Molar mass	variable
Flash point	182 – 287 °C

2 - Available forms and nomenclature

PEG, PEO, or POE refers to an oligomer or polymer of ethylene oxide. The three names are chemically synonymous, but historically PEG has tended to refer to oligomers and polymers with a molecular mass below 20,000 g/mol, PEO to polymers with a molecular mass above 20,000 g/mol, and POE to a polymer of any molecular mass.[2] PEG and PEO are liquids or low-melting solids, depending on their molecular weights. PEGs are prepared by polymerization of ethylene oxide and are commercially available over a wide range of molecular weights from 300 g/mol to 10,000,000 g/mol. While PEG and PEO with different molecular weights find use in different applications, and have different physical properties (e.g. viscosity) due to chain length effects, their chemical properties are nearly identical. Different forms of PEG are also available, depending on the initiator used for the polymerization process – the most common initiator is a monofunctional methyl ether PEG, or methoxypoly(ethylene glycol), abbreviated mPEG. Lower-molecular-weight PEGs are also available as purer oligomers, referred to as monodisperse, uniform, or discrete. Very high purity PEG has recently been shown to be crystalline, allowing determination of a crystal structure by x-ray diffraction.[3] Since purification and separation of pure oligomers is difficult, the price for this type of quality is often 10-1000 fold that of polydisperse PEG.

PEGs are also available with different geometries.

Branched PEGs have three to ten PEG chains emanating from a central core group.

Star PEGs have 10 to 100 PEG chains emanating from a central core group.

Comb PEGs have multiple PEG chains normally grafted onto a polymer backbone.

The numbers that are often included in the names of PEGs indicate their average molecular weights (e.g. a PEG with n = 9 would have an average molecular weight of approximately 400 daltons, and would be labeled PEG 400. Most PEGs include molecules with a distribution of molecular weights (i.e. they are polydisperse). The size distribution can be characterized statistically by its weight average molecular weight (Mw) and its number average molecular weight (Mn), the ratio of which is called the polydispersity index (Mw/Mn). MW and Mn can be measured by mass spectrometry.

PEGylation is the act of covalently coupling a PEG structure to another larger molecule, for example, a therapeutic protein, which is then referred to as a PEGylated protein. PEGylated interferon alfa-2a or −2b are commonly used injectable treatments for Hepatitis C infection.

PEG is soluble in water, methanol, benzene, and dichloromethane, and is insoluble in diethyl ether and hexane. It is coupled to hydrophobic molecules to produce non-ionic surfactants.

PEGs contain potential toxic impurities, such as ethylene oxide and 1,4 - dioxane. Ethylene Glycol is nephrotoxic if applied to damaged skin.

PEGs and methoxypolyethylene glycols are manufactured by Dow Chemical under the tradename *Carbowax* for industrial use, and *Carbowax Sentry* for food and pharmaceutical use. They vary in consistency from liquid to solid, depending on the molecular weight, as indicated by a number following the name. They are used commercially in numerous applications, including as surfactants, in foods, in cosmetics, in pharmaceutics, in biomedicine, as dispersing agents, as solvents, in ointments, in suppository bases, as tablet excipients, and as laxatives. Some specific groups are lauromacrogols, nonoxynols, octoxynols, and poloxamers.

Macrogol, used as a laxative, is a form of polyethylene glycol. The name may be followed by a number which represents the average molecular weight (e.g. macrogol 4000, macrogol 3350 or macrogol 6000).

3 - Production

Polyethylene glycol is produced by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers. The reaction is catalyzed by acidic or basic catalysts. Ethylene glycol and its oligomers are preferable as a starting material instead of water, because they allow the creation of polymers with a low polydispersity (narrow molecular weight distribution). Polymer chain length depends on the ratio of reactants.

$$HOCH_2CH_2OH + n(CH_2CH_2O) \rightarrow HO(CH_2CH_2O)_{n+1}H$$

Depending on the catalyst type, the mechanism of polymerization can be cationic or anionic. The anionic mechanism is preferable because it allows one to obtain PEG with a low polydispersity. Polymerization of ethylene oxide is an exothermic process. Overheating or contaminating ethylene oxide with catalysts such as alkalis or metal oxides can lead to runaway polymerization, which can end in an explosion after a few hours.

Polyethylene oxide, or high-molecular weight polyethylene glycol, is synthesized by suspension polymerization. It is necessary to hold the growing polymer chain in solution in the course of the polycondensation process. The reaction is catalyzed by magnesium-, aluminium-, or calcium-organoelement compounds. To prevent coagulation of polymer chains from solution, chelating additives such as dimethylglyoxime are used.

Alkali catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), or sodium carbonate (Na_2CO_3) are used to prepare low-molecular-weight polyethylene glycol.

4 - Medical uses

PEG is the basis of a number of laxatives (e.g., macrogol-containing products, such as Movicol and polyethylene glycol 3350, or SoftLax, MiraLAX, or GlycoLax). Whole bowel irrigation with polyethylene glycol and added electrolytes is used for bowel preparation before surgery or colonoscopy. The preparation is sold under the brand names GoLYTELY, GaviLyte C, NuLytely, GlycoLax, Fortrans, TriLyte, Colyte, Halflytely, Softlax, Lax-a-Day, ClearLax and MoviPrep. In the United States, MiraLAX and Dulcolax

Balance are sold without prescription for short-term relief of chronic constipation. Miralax is currently FDA approved for adults for a period of seven days, and is not approved for children.[6] A 2007 comparison showed that patients suffering from constipation had a better response to these two medications than to tegaserod.[7] These medications soften the fecal mass by osmotically drawing water into the GI tract. It is generally well tolerated, however, side effects are possible bloating, nausea, gas, and diarrhea (with excessive use).

When attached to various protein medications, polyethylene glycol allows a slowed clearance of the carried protein from the blood. This makes for a longer-acting medicinal effect and reduces toxicity, and allows longer dosing intervals. Examples include PEG-interferon alpha, which is used to treat hepatitis C, and PEGfilgrastim (Neulasta), which is used to treat neutropenia. It has been shown that polyethylene glycol can improve healing of spinal injuries in dogs.[8] One of the earlier findings, that polyethylene glycol can aid in nerve repair, came from the University of Texas (Krause and Bittner).[9] Polyethylene glycol is also commonly used to fuse B-cells with myeloma cells in monoclonal antibody production.

PEG is used as an excipient in many pharmaceutical products. Lower-molecular-weight variants are used as solvents in oral liquids and soft capsules, whereas solid variants are used as ointment bases, tablet binders, film coatings, and lubricants.

PEG is also used in lubricating eye drops.

4 – 1 - Research for new clinical uses

PEG, when labeled with a near-infrared fluorophore, has been used in preclinical work as a vascular agent, lymphatic agent, and general tumor-imaging agent by exploiting the Enhanced permeability and retention effect (EPR) of tumors.

High-molecular-weight PEG (e.g. PEG 8000) has been shown to be a dietary preventive agent against colorectal cancer in animal models.

The Chemoprevention Database shows PEG is the most effective known agent for the suppression of chemical carcinogenesis in rats. Cancer prevention applications in humans, however, have not yet been tested in clinical trials.

The injection of PEG 2000 into the bloodstream of guinea pigs after spinal cord injury leads to rapid recovery through molecular repair of nerve membranes. The effectiveness of this treatment to prevent paraplegia in humans after an accident is not known yet.

Research is being done in the use of PEG to mask antigens on red blood cells. Various research institutes have reported that using PEG can mask antigens without damaging the function and shape of the cell.

Research is also being done on the use of PEG in the field of gene therapy.

PEG is being used in the repair of motor neurons damaged in crush or laceration incidents *in vivo* and *in vitro*. When coupled with melatonin, 75% of damaged sciatic nerves were rendered viable.

5 - Other uses

5 – 1 - Chemical uses

Polyethylene glycol has a low toxicity and is used in a variety of products. The polymer is used as a lubricating coating for various surfaces in aqueous and non-aqueous environments.

Since PEG is a flexible, water - soluble polymer, it can be used to create very high osmotic pressures (on the order of tens of atmospheres). It also is unlikely to have specific interactions with biological chemicals. These properties make PEG one of the most useful molecules for applying osmotic pressure in biochemistry and biomembranes experiments, in particular when using the osmotic stress technique.

Polyethylene glycol is also commonly used as a polar stationary phase for gas chromatography, as well as a heat transfer fluid in electronic testers.

PEO (polyethylene oxide) can serve as the separator and electrolyte solvent in lithium polymer cells. Its low diffusivity often requires high temperatures of operation, but its high viscosity – even near its melting point – allows very thin electrolyte layers to be created. While crystallization of the polymer can degrade performance, many of the salts used to carry charge can also serve as a kinetic barrier to the formation of crystals. Such batteries carry greater energy for their weight than other lithium ion battery technologies.

PEG has also been used to preserve objects that have been salvaged from underwater, as was the case with the warship *Vasa* in Stockholm,[18] the Mary Rose in England and the Ma'agan Michael Ship in Israel.[19] It replaces water in wooden objects, making the wood dimensionally stable and preventing warping or shrinking of the wood when it dries. In addition, PEG is used when working with green wood as a stabilizer, and to prevent shrinkage.

PEG is often used (as an internal calibration compound) in mass spectrometry experiments, with its characteristic fragmentation pattern allowing accurate and reproducible tuning.

PEG derivatives, such as narrow range ethoxylates, are used as surfactants.

PEG has been used as the hydrophilic block of amphiphilic block copolymers used to create some polymersomes.

5 – 2 - Biological uses

PEG is commonly used as a precipitant for plasmid DNA isolation and protein crystallization. X - ray diffraction of protein crystals can reveal the atomic structure of the proteins.

Polymer segments derived from PEG polyols impart flexibility to polyurethanes for applications such as elastomeric fibers (spandex) and foam cushions.

In microbiology, PEG precipitation is used to concentrate viruses. PEG is also used to induce complete fusion (mixing of both inner and outer leaflets) in liposomes reconstituted *in vitro*.

Gene therapy vectors (such as viruses) can be PEG-coated to shield them from inactivation by the immune system and to de-target them from organs where they may build up and have a toxic effect.[22] The size of the PEG polymer has been shown to be important, with larger polymers achieving the best immune protection.

PEG is a component of stable nucleic acid lipid particles (SNALPs) used to package siRNA for use *in vivo*.

In blood banking, PEG is used as a potentiator to enhance detection of antigens and antibodies.

When working with phenol in a laboratory situation, PEG 300 can be used on phenol skin burns to deactivate any residual phenol.

5 – 3 - Commercial uses

PEG is the basis of many skin creams (as *cetomacrogol*) and sexual lubricants (frequently combined with glycerin).

PEG is used in a number of toothpastes as a dispersant. In this application, it binds water and helps keep xanthan gum uniformly distributed throughout the toothpaste.

PEG is also under investigation for use in body armor, and in tattoos to monitor diabetes.

In low - molecular - weight formulations (i.e PEG 400), it is used in Hewlett - Packard designjet printers as an ink solvent and lubricant for the print heads.

PEG is also one of the main ingredients in paintball fills, due to its thickness and flexibility. However, as early as 2006, some Paintball manufacturers began substituting cheaper oil-based alternatives for PEG .

PEG is a major ingredient in e-liquid, used in electronic cigarettes. It is generally used as a 30%–50% proportion of the liquid that is vaporized. Its use is designed to give a smoother effect to the vaporizing action .

PEG is also used as an anti-foaming agent in food[28] – its INS number is 1521 or E1521 in the EU.

5 – 4 - Industrial uses

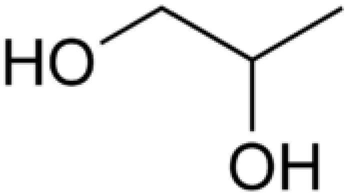
Nitrate ester-plasticized polyethylene glycol is used in Trident II ballistic missile solid rocket fuel.

Dimethyl ethers of PEG are the key ingredient of Selexol, a solvent used by coal - burning, integrated gasification combined cycle (IGCC) power plants to remove carbon dioxide and hydrogen sulfide from the gas waste stream.

PEG has been used as the gate insulator in an electric double-layer transistor to induce superconductivity in an insulator.

PEG is also used as a polymer host for solid polymer electrolytes. Although not yet in commercial production, many groups around the globe are engaged in research on solid polymer electrolytes involving PEG, with the aim of improving their properties, and in permitting their use in batteries, electro-chromic display systems, and other products in the future.

Propylene Glycol



Contents

1 - Introduction

Propylene glycol, also called 1,2-propanediol or propane-1,2-diol, is an organic compound (a diol or double alcohol) with formula $C_3H_8O_2$ or $HO\text{-}CH_2\text{-}CHOH\text{-}CH_3$. It is a colorless, nearly odorless, clear, viscous liquid with a faintly sweet taste, hygroscopic and miscible with water, acetone, and chloroform.

The compound is sometimes called α-propylene glycol to distinguish it from the isomer propane-1,3-diol $HO\text{-}(CH_2)_3\text{-}OH$, also called β-propylene glycol.

IUPAC name : propane -1,2-diol

Other names :
propylene glycol , α-propylene glycol,
1,2-propanediol , 1,2-Dihydroxypropane ,
methyl ethyl glycol (MEG) , methylethylene glycol, PG,
Sirlene , Dowfrost

Molecular formula	$C_3H_8O_2$
Molar mass	76.09 g/mol
Density	1.036 g/cm³
Melting point	− 59 °C
Boiling point	188.2 °C
Solubility in : water , ethanol , diethyl ether , acetone , chloroform	fully miscible

2 - Structure and properties

Propylene glycol is a clear, colorless and hygroscopic liquid. Propylene glycol contains an asymmetrical carbon atom, so it exists in two stereoisomers. The commercial product is a racemic mixture. Pure optical isomers can be obtained by hydration of optically pure propylene oxide.

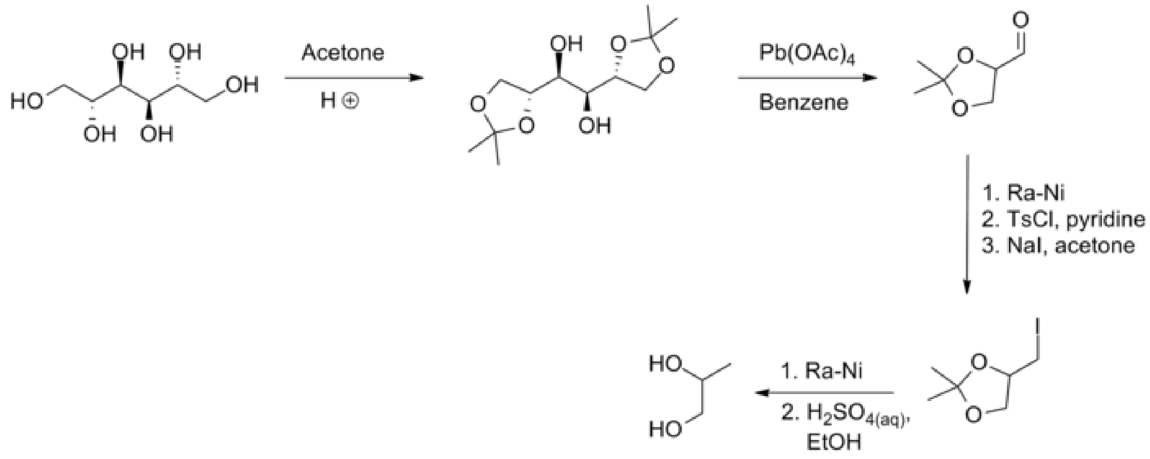
Propylene glycol is a component in newer automotive antifreezes and de-icers used at airports. Like ethylene glycol, the freezing point of water is depressed when mixed with propylene glycol owing to the effects of dissolution of a solute in a solvent (freezing-point depression); glycols are good for this purpose as they are cheap, non-corrosive and have very low volatility.

3 - Production

Industrially, propylene glycol is produced from propylene oxide,[3] and global capacity in 1990 was 900,000 tones per year. Different manufacturers use either non-catalytic high-temperature process at 200 °C to 220 °C , or a catalytic method, which proceeds at 150 °C to 180 °C in the presence of ion exchange resin or a small amount of sulfuric acid or alkali.

Final products contain 20 % 1,2-propanediol, 1.5 % of dipropylene glycol and small amounts of other polypropylene glycols.[5] Further purification produces finished industrial grade or USP/JP/EP/BP grade propylene glycol that is typically 99.5 % or greater. Propylene glycol can also be converted from glycerol, a biodiesel by product.

(S)-Propanediol may be synthesized from D-mannitol, through the following scheme :



45 % of propylene glycol produced is used as chemical feedstock for the production of unsaturated polyester resins. In this regard, propylene glycol reacts with a mixture of unsaturated maleic anhydride and isophthalic acid to give a copolymer. This partially unsaturated polymer undergoes further crosslinking to yield thermoset plastics. Related to this application, propylene glycol reacts with propylene oxide to give oligomers and polymers that are used to produce polyurethanes.

Propylene glycol is considered Generally Recognized As Safe by the U.S. Food and Drug Administration, and it is used as an humectant (E1520), solvent, and preservative in food and for tobacco products, as well as being the major ingredient in the liquid used in electronic cigarettes (along with vegetable glycerine and, more rarely, PEG 400). It is also used in pharmaceutical and personal care products.[4] Propylene glycol is a solvent in many pharmaceuticals, including oral, injectable and topical formulations, such as for diazepam and lorazepam that are insoluble in water, use propylene glycol as a solvent in their clinical, injectable forms.

Like ethylene glycol, propylene glycol is able to lower the melting point of water, and so it is used as aircraft de-icing fluid.[4][8] It is similarly used as automotive antifreeze.

Propylene glycol is a minor ingredient in the oil dispersant Corexit, used in great quantities during the Deepwater Horizon oil spill

5 - Safety

5 – 1 - Humans

The acute oral toxicity of propylene glycol is very low, and large quantities are required to cause perceptible health damage in humans; propylene glycol is metabolized in the human body into pyruvic acid (a normal part of the glucose-metabolism process, readily converted to energy), acetic acid (handled by ethanol-metabolism), lactic acid (a normal acid generally abundant during digestion)m, and propionaldehyde (a potentially hazardous substance).

Serious toxicity generally occurs only at plasma concentrations over 1 g/L, which requires extremely high intake over a relatively short period of time. It would be nearly impossible to reach toxic levels by consuming foods or supplements, which contain at most 1 g/kg of PG. Cases of propylene glycol poisoning are usually related to either inappropriate intravenous administration or accidental ingestion of large quantities by children. The potential for long-term oral toxicity is also low. In one study, in 1972, 12 rats were provided with feed containing as much as 5 % PG in feed over a period of 104 weeks and they showed no apparent ill effects; no data on offspring was offered . Because of its low chronic oral toxicity, propylene glycol was classified by the U. S. Food and Drug Administration as "generally recognized as safe" (GRAS) for use as a direct food additive.

Prolonged contact with propylene glycol is essentially non-irritating to the skin . Undiluted propylene glycol is minimally irritating to the eye, and can produce slight transient conjunctivitis (the eye recovers after the exposure is removed). Exposure to mists may cause eye irritation, as well as upper respiratory tract irritation. Inhalation of the propylene glycol vapors appears to present no significant hazard in ordinary applications. However, limited human experience indicates that inhalation of propylene glycol mists could be irritating to some individuals . It is therefore recommended that propylene glycol not be used in applications where inhalation exposure or human eye contact with the spray mists of these materials is likely, such as fogs for theatrical productions or antifreeze solutions for emergency eye wash stations

Propylene glycol does not cause sensitization and it shows no evidence of being a carcinogen or of being genotoxic.

Adverse responses to intravenous administration of drugs which use PG as an excipient have been seen in a number of people, particularly with large dosages thereof. Responses may include "hypotension, bradycardia... QRS and T abnormalities on the ECG, arrhythmia, cardiac arrest, serum hyperosmolality, lactic acidosis, and haemolysis". A high percentage (12% to 42%) of directly-injected propylene glycol is eliminated / secreted in urine unaltered depending on dosage, with the remainder appearing in its glucuronide-form. The speed of renal filtration decreases as dosage increases , which may be due to propylene glycol's mild anesthetic / CNS-depressant - properties as an alcohol. In one case, intravenous administration of propylene glycol-suspended nitroglycerin to an elderly man may have induced coma and acidosis.

According to a 2010 study by Karlstad University, the concentrations of PGEs, propylene glycol and glycol ethers in indoor air, particularly bedroom air, has been linked to increased risk of developing numerous respiratory and immune disorders in children, including asthma, hay fever, eczema, and allergies, with increased risk ranging from 50 % to 180 %. This concentration has been linked to use of water-based paints and water-based system cleansers.

5 – 2 - Animals

Propylene glycol is an approved food additive for dog food under the category of animal feed and is generally recognized as safe for dogs, with LD_{50} = 9 mL / kg. That said, the figure is higher for most laboratory animals (LD_{50} at levels of 20mL/kg).[32] Similarly, propylene glycol is an approved food additive for human food as well.[33] The exception is that it is prohibited for use in food for cats due to links to Heinz body anemia.

5 – 3 - Allergic reaction

Research has suggested that individuals who cannot tolerate propylene glycol probably experience a special form of irritation, but that they only rarely develop allergic contact dermatitis. Other investigators believe that the incidence of allergic contact dermatitis to propylene glycol may be greater than 2 % in patients with eczema.

Patients with vulvodynia and interstitial cystitis may be especially sensitive to propylene glycol. Women struggling with yeast infections may also notice that some OTC creams can cause intense burning . Post menopausal women who require the use of an estrogen cream may notice that brand name creams made with propylene glycol often create extreme, uncomfortable burning along the vulva and perianal area.

A Swedish study published in 2010 strongly suggests a connection between airborne concentrations of propylene glycol in houses and development of asthma and allergic reactions, such as rhinitis, in children.

5 – 4 - Environmental

Propylene glycol is known to exert high levels of biochemical oxygen demand (BOD) during degradation in surface waters. This process can adversely affect aquatic life by consuming oxygen aquatic organisms need to survive. Large quantities of dissolved oxygen (DO) in the water column are consumed when microbial populations decompose propylene glycol.

The oxygen depletion potential of airport deicing operation discharges is many times greater than that of raw sewage . For example, before application, Type I propylene glycol - based deicing fluid is generally diluted to a mixture containing approximately 50% propylene glycol. Pure propylene glycol has a five - day biochemical oxygen demand (BOD5) concentration of approximately 1,000,000 mg / L . A typical diluted propylene-based deicing fluid could therefore have a BOD5 concentration of approximately 500,000 mg / L . In comparison, raw sewage typically has a BOD5 concentration of approximately 200 mg/L. The amount of fluid used to deice a single jet depends on the nature of the precipitation event and the size of the aircraft but can range from several hundred to several thousand gallons. Therefore, deicing a single jet can generate a BOD5 load greater than that of one million gallons of raw sewage. A large hub airport often has several hundred flights each day.

Sufficient dissolved oxygen levels in surface waters are critical for the survival of fish , macroinvertebrates, and other aquatic organisms. If oxygen concentrations drop below a minimum level, organisms emigrate, if able and possible, to areas with higher oxygen levels or eventually die. This effect can drastically reduce the amount of usable aquatic habitat. Reductions in DO levels can reduce or eliminate bottom-feeder populations, create conditions that favor a change in a community's species profile, or alter critical food-web interactions.

5 – 5 - Corexit implications

The chemical makes up 1 - 5 % of the oil dispersant Corexit, used in great quantities during the Deepwater Horizon oil spill. Corexit has come under scrutiny for probable adverse effects on marine life and humans that are exposed to it. Propylene glycol has also come under scrutiny, as it is the chemical that disperses Corexit and the oil to subsurface depths .

Poly Propylene Glycol

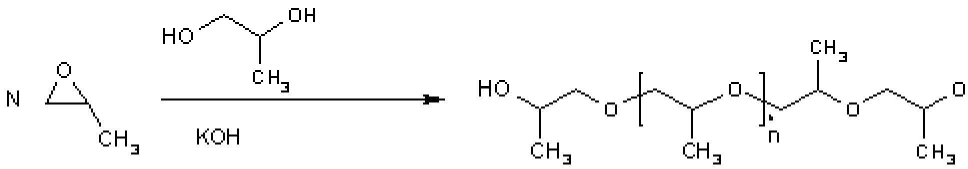
Contents

1 Introduction

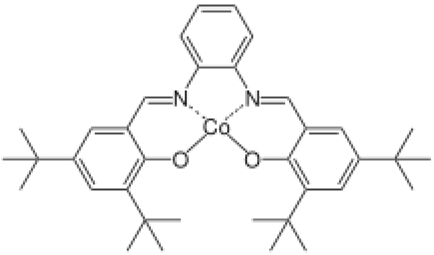
Polypropylene glycol or polypropylene oxide is the polymer of propylene glycol. Chemically it is a polyether. The term poly propylene glycol or PPG is reserved for low to medium range molar mass polymer when the nature of the end - group, which is usually a hydroxyl group, still matters. The term "oxide" is used for high molar mass polymer when end-groups no longer affect polymer properties. In 2003, 60% of the annual production of propylene oxide of 6.6×10^6 tonnes was converted into the polymer.

2 - Polymerization

Polypropylene glycol is produced by ring - opening poly merization of propylene oxide. The initiator is an alcohol and the catalyst a base, usually potassium hydroxide. When the initiator is ethylene glycol or water the polymer is linear. With a multifunctional initiator like glycerine, pentaerythritol or sorbitol the polymer branches out.



Conventional polymerization of propylene oxide results in an atactic polymer. The isotactic polymer can be produced from optically active propylene oxide, but at a high cost. A salen cobalt catalyst has recently been reported to provide isotactic polymerization of the racemic propylene oxide [\].



Cobalt catalyst for isotactic polypropylene oxide

3 - Properties

PPG has many properties in common with polyethylene glycol. The polymer is a liquid at room temperature. Solubility in water decreases rapidly with increasing molar mass. Secondary hydroxyl groups in PPG are less reactive than primary hydroxyl groups in polyethylene glycol. PPG is less toxic than PEG, so biotechnologicals are now produced in PPG.

(copied from IPCS Chemical Safety Information from Intergovernmental Organizations from www.inchem.org: Polypropylene glycol: Hazardous characteristics:)

Combustible and in the form of vapour explosive when exposed to heat or flame. When heated to decomposition it produces acrid and irritating fumes (Sax, 1989).

The toxicity of polypropylene glycol is mainly due to the parent compound and not to its metabolites. Polypropylene glycol has an irritatant effect on direct contact with eyes, mucous membranes and possibly after prolonged contact with skin.

Propylene glycol causes CNS depression similar to that caused by ethanol but it is only one-third as potent. Cardiotoxic effects include arrhythmias and cardiac arrest. Renal and hepatic damage has been reported (Seidenfeld & Hanzlik, 1932).

4 - Uses

PPG is used in many formulations for polyurethanes. It is used as a rheology modifier.

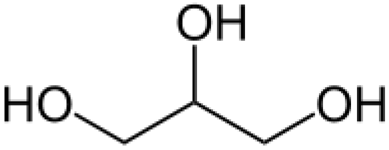
PPG is used as a surfactant, wetting agent, dispersant in leather finishing.

PPG is also employed as a tuning reference in mass spectrometry.

PPG is used as a primary ingredient in the manufacture of paintballs.

PPG is used to administer the drug Melarsoprol in patients suffering from second stage trypanosomiasis since the drug is insoluble in water. This mixture must be injected intravenously. [1]

Glycerol



Contents

1 - Introduction

Glycerol (or glycerine, glycerin) is a simple polyol compound. It is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol backbone is central to all lipids known as triglycerides. Glycerol is sweet-tasting and of low toxicity.

IUPAC name : propane-1,2,3-triol
Other names :
glycerin
glycerine
propanetriol

Molecular formula	$C_3H_8O_3$
Molar mass	92 g mol^{-1}
Appearance	colorless liquid hygroscopic
Odor	odorless

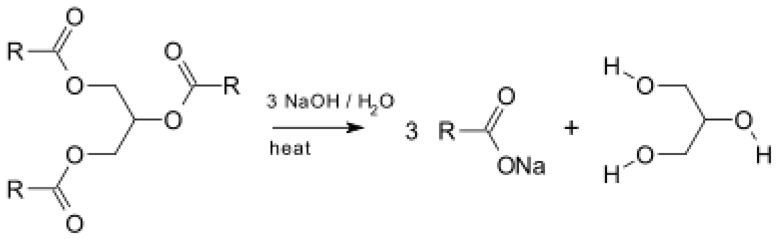
Density	1.261 g / cm^3
Melting point	17.8 °C
Boiling point	290 °C
Refractive index (n_D)	1.4746
Viscosity	1.412 Pa·s
Flash point	160 °C (closed cup) 176 °C (open cup)
Structure and properties	n, ε_r, etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

2 - Production

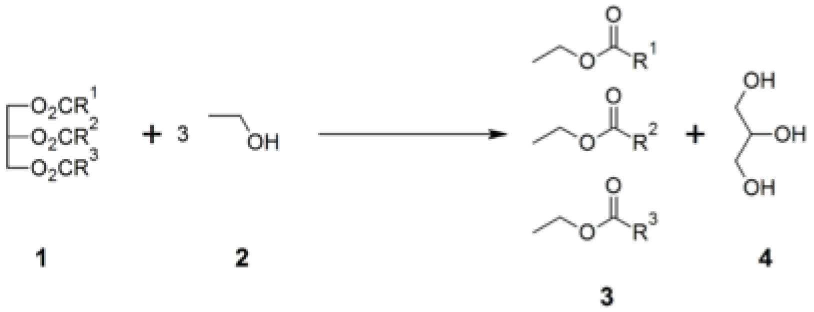
Approximately 950,000 tons per annum are produced in the USA and Europe; 350,000 tons of glycerol were produced per year in the United States alone from 2000 – 2004. Production will increase as the EU directive 2003 / 30 / EC is implemented, which requires the replacement of 5.75 % of petroleum fuels with biofuel across all Member States by 2010, as glycerol is a byproduct in the production of biodiesel. It is projected that by the year 2020, production will be six times more than demand.

2 – 1 - From fats and oils

Triglycerides found in fats and oils are by definition esters of glycerol with long-chain carboxylic acids; the hydrolysis (saponification) or transesterification of these triglycerides produces stoichiometric quantities of glycerol. In this scheme, glycerol is produced as a co-product in the production of long - chain carboxylate salts used as soaps :



It is also a byproduct of the production of biodiesel via transesterification. This form of crude glycerin is often dark in appearance with a thick, syrup-like consistency. Triglycerides (1) are treated with an alcohol such as ethanol (2) with catalytic base to give ethyl esters of fatty acids (3) and glycerol (4) :



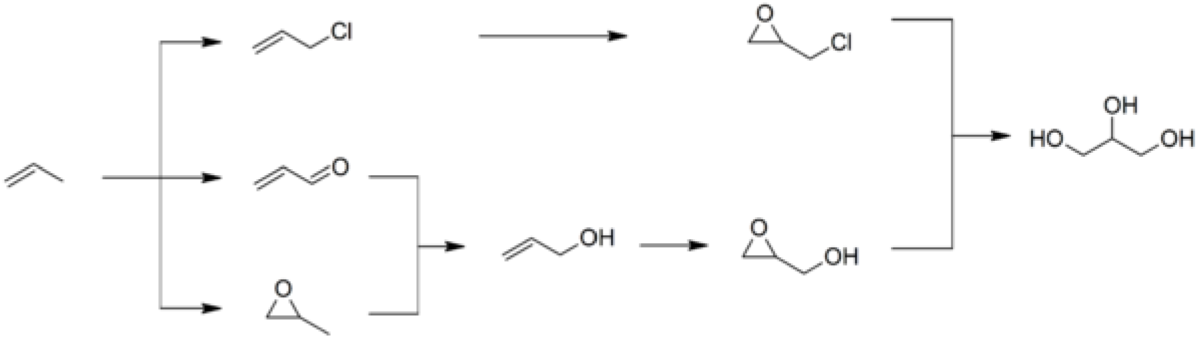
Glycerol from triglycerides is produced on a large scale, but the crude product is of variable quality, with a low selling price of as low as 1-8 U.S. cents per pound in 2011. It can be purified, but the process is expensive. As a result, a good fraction of crude glycerol is disposed of as waste. Some glycerol is burned for energy, but the heat value is low.

Crude glycerol from the hydrolysis of triglycerides can be purified by treatment with activated carbon to remove organic impurities, alkali to remove unreacted glycerol esters, and ion exchange to remove salts. High purity glycerol (> 99.5%) is obtained by multi-step distillation; vacuum is helpful due to the high boiling point of glycerol (290 °C).

2 – 2 - Synthetic glycerol

Synthetic glycerol refers to material obtained from non-triglyceride sources. Glycerol may also be produced by various routes from propylene. The epichlorohydrin process is the most important; it involves the chlorination of propylene to give allyl chloride, which is oxidized with hypochlorite to dichlorohydrins, which reacts with a strong base to give epichlorohydrin. Epichlorohydrin is then hydrolyzed to give glycerol. Chlorine - free processes from propylene include the synthesis of glycerol from acrolein and propylene oxide.

Because of the emphasis on biodiesel, where glycerol is a waste product, the market for glycerol is depressed, and these old processes are no longer economical on a large scale. Due to the glycerol glut, efforts are being made to convert glycerol to its precursors, such as acrolein and epichlorohydrin .



3 - Applications

3 - 1 - Food industry

In foods and beverages, glycerol serves as a humectant, solvent, and sweetener, and may help preserve foods. It is also used as filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liqueurs. Glycerol and water are used to preserve certain types of leaves. As a sugar substitute, it has approximately 27 kilocalories per teaspoon (sugar has 20) and is 60% as sweet as sucrose. It does not feed the bacteria that form plaques and cause dental cavities. As a food additive, glycerol is labeled as E number E422. It is added to icing (frosting) to prevent it setting too hard.

As used in foods, glycerol is categorized by the American Dietetic Association as a carbohydrate. The U.S. Food and Drug Administration (FDA) carbohydrate designation includes all caloric macronutrients excluding protein and fat. Glycerol has a caloric density similar to table sugar, but a lower glycemic index and different metabolic pathway within the body, so some dietary advocates accept glycerol as a sweetener compatible with low carbohydrate diets.

3 – 2 - Pharmaceutical and personal care applications

Glycerol is used in medical and pharmaceutical and personal care preparations, mainly as a means of improving smoothness, providing lubrication and as a humectant. It is found in allergen immunotherapies, cough syrups, elixirs and expectorants, toothpaste, mouthwashes, skin care products, shaving cream, hair care products, soaps and water-based personal lubricants. In solid dosage forms like tablets, glycerol is used as a tablet holding agent. For human consumption, glycerol is classified by the U.S. FDA among the sugar alcohols as a caloric macronutrient.

Glycerol is a component of glycerin soap. Essential oils are added for fragrance. This kind of soap is used by people with sensitive, easily-irritated skin because it prevents skin dryness with its moisturizing properties. It draws moisture up through skin layers and slows or prevents excessive drying and evaporation . With similar benefits, glycerin is a common ingredient in many bath salts recipes. However, some assert that due to glycerin's moisture absorbing properties, it can be more of a hindrance than a benefit .

Glycerol can be used as a laxative when introduced into the rectum in suppository or small-volume (2–10 ml) (enema) form; it irritates the anal mucosa and induces a hyperosmotic effect.

Taken orally (often mixed with fruit juice to reduce its sweet taste), glycerol can cause a rapid, temporary decrease in the internal pressure of the eye. This can be a useful initial emergency treatment of severely elevated eye pressure.

3 – 3 - Botanical extracts

When utilized in 'tincture' method extractions, specifically as a 10% solution, glycerol prevents tannins from precipitating in ethanol extracts of plants (tinctures). It is also used as an 'alcohol-free' alternative to ethanol as a solvent in preparing herbal extractions. It is less extractive when utilized in a standard tincture methodology. Glycerol is approximately 30 % more slowly absorbed by the body resulting in a much lower glycemic load. Alcohol-based tinctures can also have the alcohol removed and replaced with glycerol for its preserving properties. Such products are not 'alcohol-free' in either a scientific or consumable sense, but should in all instances more accurately be referred to as "Alcohol-Removed" products. Fluid extract manufacturers often extract herbs in hot water before adding glycerin to make glycerites.

When used as a primary 'true' alcohol-free (e.g. no alcohol (i.e. ethanol) ever being used) botanical extraction solvent in innovative non-tincture based 'dynamic' methodologies, glycerol has been shown to possess a high degree of extractive versatility for botanicals including removal of numerous constituents and complex compounds, with an extractive power that can rival that of alcohol and water/alcohol solutions. That glycerol possess such high extractive power assumes that glycerol, with its tri-atomic structure, is utilized with dynamic methodologies as opposed to standard passive 'tincturing' methodologies that are better suited to alcohol's di-atomic structure. Glycerol possesses the intrinsic property of not denaturing or rendering a botanical's constituents inert (as di-atomic alcohols – i.e. ethanolic (grain) alcohol, methanolic (wood) alcohol, etc., do). Glycerol is a stable preserving agent for botanical extracts that, when utilized in proper concentrations in an extraction solvent base, does not allow inverting or reduction-oxidation of a finished extract's constituents, even over several years. Both glycerol and ethanol are viable preserving agents. Glycerol is bacteriostatic in its action, and ethanol is bactericidal in its action.

3 – 4 - Antifreeze

Like ethylene glycol and propylene glycol, glycerol is a non-ionic kosmotrope that forms strong hydrogen bonds with water molecules, competing with water-water hydrogen bonds. This disrupts the crystal lattice formation of ice unless the temperature is significantly lowered. The minimum freezing point temperature is at about −37.8 °C corresponding to 70 % glycerol in water.

Glycerol was historically used as an anti-freeze for automotive applications before being replaced by ethylene glycol, which has a lower freezing point. While the minimum freezing point of a glycerol-water mixture is higher than an ethylene glycol-water mixture, glycerol is not toxic and is being re-examined for use in automotive applications.

In the laboratory, glycerol is a common component of solvents for enzymatic reagents stored at temperatures below 0 °C due to the depression of the freezing temperature. It is also used as a cryoprotectant where the glycerol is dissolved in water to reduce damage by ice crystals to laboratory organisms that are stored in frozen solutions, such as bacteria, nematodes, and mammalian embryos.

3 – 5 - Chemical intermediate

Glycerol is used to produce nitroglycerin, which is an essential ingredient of various explosives such as dynamite, gelignite, and propellants like cordite. Reliance on soap-making to supply co-product glycerine made it difficult to increase production to meet wartime demand. Hence, synthetic glycerin processes were national defense priorities in the days leading up to World War II. Nitroglycerin, also known as glyceryl trinitrate (GTN) is commonly used to relieve *angina pectoris*, taken in the form of sub-lingual tablets, or as an aerosol spray.

A great deal of research is being conducted to try to make value-added products from crude glycerol (typically containing 20% water and residual esterification catalyst) obtained from biodiesel production. The use of crude glycerin as an additive to biomass for a renewable energy source when combusted or gasified is also being explored.

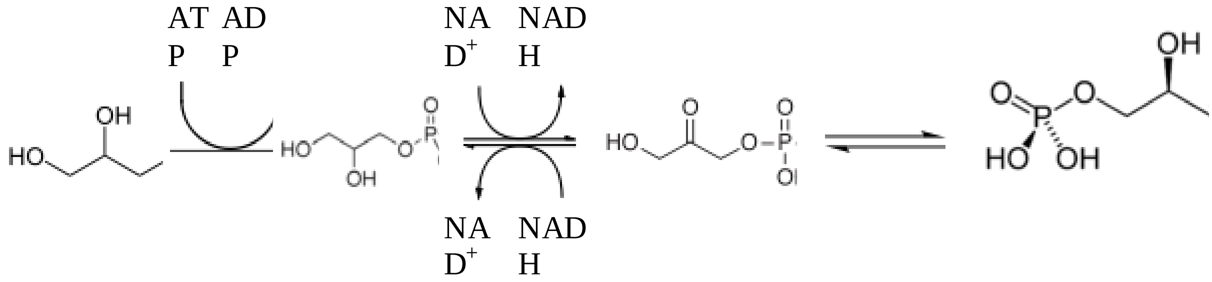
Hydrogen gas production unit
Glycerine acetate (as a potential fuel additive)
Conversion to propylene glycol
Conversion to acrolein
Conversion to ethanol
Conversion to epichlorohydrin, a raw material for epoxy resins

4 - Metabolism

Glycerol is a precursor for synthesis of triacylglycerols and of phospholipids in the liver and adipose tissue. When the body uses stored fat as a source of energy, glycerol and fatty acids are released into the bloodstream. In some organisms, the glycerol component can be converted into glucose by the liver and, thus, provide energy for cellular metabolism.

Before glycerol can enter the pathway of glycolysis or gluconeogenesis (depending on physiological conditions), it must be converted to their intermediate glyceraldehyde 3-phosphate in the following steps :

Glycerol	Glycerol kinase	Glycerol-3-phosphate	Glycerol-3-phosphate dehydrogenase	Dihydroxyacetone phosphate	Triosephosphate isomerase	Glyceraldehyde 3-phosphate



The enzyme glycerol kinase is present only in the liver. In adipose tissue, glycerol 3-phosphate is obtained from dihydroxyacetone phosphate (DHAP) with the enzyme glycerol-3-phosphate dehydrogenase.

Glycerol has very low toxicity when ingested; its LD_{50} oral dose for rats is 12600 mg/kg and 8700 mg/kg for mice.

5 - Historical cases of contamination with diethylene glycol

Glycerine and diethylene glycol are similar in appearance, smell, and taste. The US Federal Food, Drug, and Cosmetic Act was passed following the 1937 "Elixir sulfanilamide" incident of poisoning caused by diethylene glycol contamination of medicine.

On May 4, 2007, the US Food and Drug Administration advised all US makers of medicines to test all batches of glycerine for the toxic diethylene glycol.[26] This followed an occurrence of hundreds of fatal poisonings in Panama resulting from a Chinese factory deliberately falsifying records in order to export the cheaper diethylene glycol as the more expensive glycerol.

Mono Glyceride

Monoacylglycerol can be broadly divided into two groups; 1-monoacylglycerols and 2-monoacylglycerols, depending on the position of the ester bond on the glycerol moiety.

Monoacylglycerols can be formed by both industrial chemical and biological processes. They are formed biochemically via release of a fatty acid from diacylglycerol by diacylglycerol lipase. Monoacylglycerols are broken down by monoacylglycerol lipase.

Mono- and diglycerides are commonly added to commercial food products in small quantities. They act as emulsifiers, helping to mix ingredients such as oil and water that would not otherwise blend well.[1] The values given in the nutritional labels for total fat, saturated fat, and *trans* fat do not include those present in mono- and diglycerides.

The commercial source may be either animal (cow- or hog-derived) or vegetable, and they may be synthetically made as well. They are often found in bakery products, beverages, ice cream, chewing gum, shortening, whipped toppings, margarine, and confections. When used in bakery products, monoglycerides improve loaf volume, and create a smooth, soft crumb.

One special mono acyl glycerol, 2-arachidonoyl glycerol, is a full agonist of the cannabinoid receptors. Another important monoacylglycerol is 2-oleoylglycerol, which is a GPR119 agonist.

Di Glyceride

Contents

1 - Introduction

A diglyceride, or a diacylglycerol (DAG), is a glyceride consisting of two fatty acid chains covalently bonded to a glycerol molecule through ester linkages. One example, shown on the right, is 1-palmitoyl-2-oleoyl-glycerol, which contains side-chains derived from palmitic acid and oleic acid. Diacylglycerols can also have many different combinations of fatty acids attached at both the C-1 and C-2 positions.

2 - Food additive

Mono- and diglycerides are common food additives used to blend together certain ingredients, such as oil and water, which would not otherwise blend well. The values given in the nutritional labels for total fat, saturated fat, and *trans* fat do not include those present in mono- and diglycerides.

The commercial source may be either animal (cow- or hog-derived) or vegetable, derived primarily from partially hydrogenated soy bean and canola oil . They may also be synthetically produced. They are often found in bakery products, beverages, ice cream, peanut butter, chewing gum, shortening, whipped toppings, margarine, confections, and candies.

3 - Biological functions

3 – 1 - Protein kinase C activation

In biochemical signaling, diacylglycerol functions as a second messenger signaling lipid, and is a product of the hydrolysis of the phospholipid phosphatidylinositol 4,5- bisphosphate (PIP2) by the enzyme phospholipase C (PLC) (a membrane-bound enzyme) that, through the same reaction, produces inositol trisphosphate (IP_3). Although inositol trisphosphate diffuses into the cytosol, diacylglycerol remains within the plasma membrane, due to its hydrophobic properties. IP_3 stimulates the release of calcium ions from the smooth endoplasmic reticulum, whereas DAG is a physiological activator of protein kinase C (PKC). The production of DAG in the membrane facilitates translocation of PKC from the cytosol to the plasma membrane.

Diacylglycerol can be mimicked by the tumor-promoting compounds phorbol esters.

3 – 2 - Other

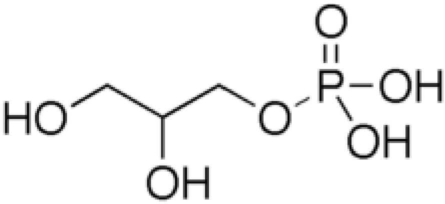
In addition to activating PKC, diacylglycerol has a number of other functions in the cell :

a source for prostaglandins

a precursor of the endocannabinoid 2-arachidonoylglycerol

an activator of a subfamily of transient receptor potential canonical (TRPC) cation channels, TRPC3/6/7.

4 - Metabolism



glycerol-3-phosphate

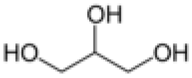
Synthesis of diacylglycerol begins with glycerol-3-phosphate, which is derived primarily from dihydroxyacetone phosphate, a product of glycolysis (usually in the cytoplasm of liver or adipose tissue cells). Glycerol-3-phosphate is first acylated with acyl-coenzyme A (acyl-CoA) to form lysophosphatidic acid, which is then acylated with another molecule of acyl - CoA to yield phosphatidic acid. Phosphatidic acid is then de-phosphorylated to form diacylglycerol.

Diacylglycerol is a precursor to triacylglycerol (triglyceride), which is formed in the addition of a third fatty acid to the diacylglycerol under the catalysis of diglyceride acyltransferase.

Since diacylglycerol is synthesized via phosphatidic acid, it will usually contain a saturated fatty acid at the C-1 position on the glycerol moiety and an unsaturated fatty acid at the C-2 position.

Glycerine Acetate

Glycerine acetate is the ester produced from the esterification of glycerol (1) with acetic acid. Multiple products can be produced from this reaction; these include the monoacetylglycerols (MAG, 2 and 3), diacetylglycerols (DAG, 4 and 5), and triacetalglycerol (TAG, 6) (also known as triacetin).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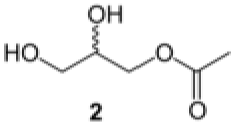
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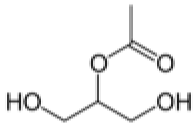
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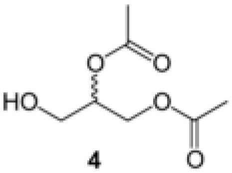
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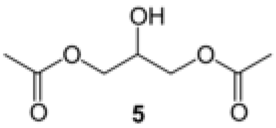
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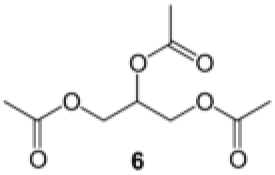
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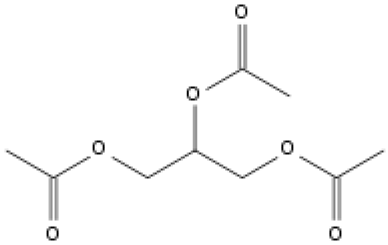
MAG and TAG can be used as fuel additive improving the cold and viscosity properties of biodiesel or the antiknocking properties of gasoline.

Triacetin



IUPAC name : 1,3-di acetyl oxy propan-2-yl acetate	
Molecular formula	$C_9 H_{14} O_6$
Molar mass	218 g/mol
Density	1.1562 g / cm^3
Melting point	+ 3 °C
Boiling point	258 – 260 °C

The triglyceride 1,2,3-triacetoxypropane is more generally known as triacetin and glycerin triacetate. It is the triester of glycerol and acetic acid, and is the second simplest fat after triformin.

It is an artificial chemical compound, commonly used as a food additive, for instance as a solvent in flavourings, and for its humectant function, with E number E1518 and Australian approval code A1518. Triacetin is also a component of casting liquor with TG and as an excipient in pharmaceutical products where it is used as a humectant, a plasticizer, and as a solvent.

Triacetin can also be used as a fuel additive as an antiknock agent which can reduce engine knocking in gasoline, and to improve cold and viscosity properties of biodiesel.

In a 1994 report released by five top cigarette companies, triacetin was listed as one of the 599 cigarette additives. [1] The triacetin is applied to the filter as a plasticizer.

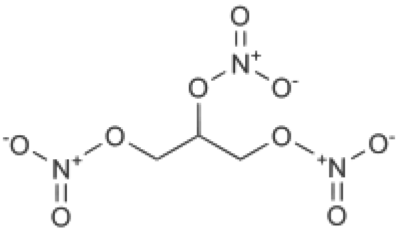
It has been considered as a possible source of food energy in artificial food regeneration systems on long space missions. It is believed to be safe to get over half of one's dietary energy from triacetin.

US Food and Drug Administration has approved it as Generally Regarded as Safe (GRAS) food additive and included it in the database according to the opinion from the Select Committee On GRAS submission (SCOGS). "

Three types of acetostearins have been found to be without toxic effects in long-term feeding tests in rats at levels up to 5 g per kg per day. This contrasts with an estimated human consumption of a fraction of a milligram per kg per day. It is recognized that at an even higher feeding level (10 g per kg per day) male rats developed testicular atrophy and female rats, uterine discoloration. However, such a level which would amount to 50 g or more for an infant and 600 g for an adult per day, is vastly higher than would be possible in the consumption of foods to which acetostearins are added for functional purposes.

Triacetin is included in the SCOGS database since 1975.

Nitro Glycerin



ontents

1 - Introduction

Nitroglycerin (NG), also known as nitroglycerine, tri nitro glycerin , tri nitro glycerine, or nitro, is more correctly known as glyceryl trinitrate or more formally: 1,2,3 – tri nitroxy propane. It is a heavy, colorless, oily, explosive liquid most commonly produced by treating glycerol with white fuming nitric acid under conditions appropriate to the formation of the nitric acid ester. Chemically, the substance is an organic nitrate compound rather than a nitro compound, but the traditional name is often retained. Since the 1860s, nitroglycerin has been used as an active ingredient in the manufacture of explosives, mostly dynamite, and as such it is employed in the construction, demolition, and mining industries. Similarly, since the 1880s, it has been used by the military as an active ingredient, and a gelatinizer for nitrocellulose, in some solid propellants, such as Cordite and Ballistite.

Nitroglycerin is also a major component in double-based smokeless gunpowders used by reloaders. Combined with nitrocellulose, there are hundreds of (powder) combinations used by rifle, pistol, and shotgun reloaders.

Nitroglycerin is also used medically as a vasodilator to treat heart conditions, such as angina and chronic heart failure. Having been used for over 130 years, nitroglycerin is one of the oldest and most useful drugs for treating and preventing attacks of angina pectoris. Though it was previously known that these effects arise because nitroglycerin is converted to nitric oxide, a potent vasodilator, it was not until 2002 that the enzyme for this conversion was discovered to be mitochondrial aldehyde dehydrogenase.[2] Nitroglycerin comes in forms of tablets, sprays or patches.[3] It has been suggested for other uses also, such as an adjunct therapy in prostate cancer.

IUPAC name : 1,2,3-Tri nitroxy propane	
Systematic name : 2,3-Bis (nitro oxy) propyl nitrate	
Other names : 1,3-Di nitro oxy propan-2-yl nitrate , Propane-1,2,3- triyl trinitrate	
Molecular formula	$C_3 H_5 N_3 O_9$
Molar mass	227 g mol^{-1}
Appearance	Colorless liquid
Density	1.6 g cm^{-3} (at 15 °C)
Melting point	14 °C
Boiling point	50 °C (explodes)
Solubility in water	slightly
Solubility	Acetone , ether , benzene , alcohol
Bioavailability	< 1 %
Elimination half-life	3 min
Explosive data	
Shock sensitivity	High

Friction sensitivity	High
Explosive velocity	7700 m s^{-1}
RE factor	1.50
EU classification	E T + N

2 - History

Nitroglycerin was the first practical explosive ever produced that was stronger than black powder. Nitroglycerin was synthesized by the Italian chemist Ascanio Sobrero in 1847, working under Théophile-Jules Pelouze at the University of Turin. Sobrero initially called his discovery pyroglycerine, and warned vigorously against its use as an explosive. It was later adopted as a commercially useful explosive by Alfred Nobel. Nobel experimented with several safer ways to handle the dangerous nitroglycerin after his younger brother Emil Oskar Nobel and several factory workers were killed in a nitroglycerin explosion at the Nobel's armaments factory in 1864 in Heleneborg, Sweden.

One year later, Alfred Nobel founded Alfred Nobel & Company in Germany and built an isolated factory in the Krümmel hills of Geesthacht near Hamburg. This business exported a liquid combination of nitroglycerin and gunpowder called "Blasting Oil", but this was extremely unstable and difficult to handle, as shown in numerous catastrophes. The buildings of the Krümmel factory were destroyed twice.

In April 1866, three crates of nitroglycerin were shipped to California for the Central Pacific Railroad, which planned to experiment with it as a blasting explosive to expedite the construction of the 1,659-foot (506 m)-long Summit Tunnel through the Sierra Nevada Mountains. One of these crates exploded, destroying a Wells Fargo company office in San Francisco and killing 15 people. This led to a complete ban on the transportation of liquid nitroglycerin in California. The on-site manufacture of nitroglycerin was thus required for the remaining hard-rock drilling and blasting required for the completion of the First Transcontinental Railroad in North America.

Liquid nitroglycerin was widely banned elsewhere as well, and these legal problems led to Alfred Nobel and his company's developing dynamite in 1867. This was made by mixing nitroglycerin with diatomaceous earth (called *"kieselgur"* in German) found in the Krümmel hills. Similar mixtures, such as "dualine" (1867), "lithofracteur" (1869), and "gelignite" (1875), were formed by mixing nitroglycerin with other inert absorbents, and many combinations were tried by other companies in attempts to get around Nobel's tightly held patents for dynamite.

Dynamite mixtures containing nitrocellulose, which increases the viscosity of the mix, are commonly known as "gelatins".

Following the discovery that amyl nitrite helped alleviate chest pain, Dr. William Murrell experimented with the use of nitroglycerin to alleviate angina pectoris and to reduce the blood pressure. He began treating his patients with small diluted doses of nitroglycerin in 1878, and this treatment was soon adopted into widespread use after Murrell published his results in the journal *The Lancet* in 1879.[8] A few months before his death in 1896, Alfred Nobel was prescribed nitroglycerine for this heart condition, writing to a friend: "Isn't it the irony of fate that I have been prescribed nitro-glycerin, to be taken internally! They call it Trinitrin, so as not to scare the chemist and the public." The medical establishment also used the name "glyceryl trinitrate" for the same reason.

2 – 1 - Wartime production rates

Large quantities of nitroglycerin were manufactured during World War I and World War II for use as military propellants and in military engineering work. During World War I, HM Factory, Gretna, the largest propellant factory in the Great Britain, produced about 800 long tons (812 tonnes) of Cordite RDB per week. This amount took at least 336 tons of nitroglycerin per week (assuming no losses in production). The Royal Navy had its own factory at Royal Navy Cordite Factory, Holton Heath in Dorset, England. A large cordite factory was also built in Canada during World War I. The Canadian Explosives Limited cordite factory at Nobel, Ontario, was designed to produce 1,500,000 lb (680 t) of cordite per month. This required about 286 tonnes of nitroglycerin per month.

3 - Instability and desensitization

In its pure form, nitroglycerin is a primary contact explosive, with physical shock causing it to explode, and it degrades over time to even more unstable forms. This makes nitroglycerin highly dangerous to transport or use. In this undiluted form, it is one of the world's most powerful explosives, comparable to the more recently-developed RDX and PETN, as well as the plastic explosive C- 4 — which contains 90 to 92 percent of RDX as its active ingredient.

Early in the history of nitroglycerin, it was discovered that liquid nitroglycerin can be "desensitized" by cooling it to about 5 to 10 °C (40 to 50 °F). At this temperature nitroglycerin freezes, contracting upon solidification. However, thawing it out can be extremely sensitizing, especially if impurities are present or if the warming is too rapid.[10] It is possible to chemically "desensitize" nitroglycerin to a point where it can be considered approximately as "safe" as modern high explosives, such as by the addition of approximately 10 to 30 percent ethanol, acetone,[11] or dinitrotoluene. (The percentage varies with the desensitizing agent used.) Desensitization requires extra effort to reconstitute the "pure" product. Failing this, it must be assumed that desensitized nitroglycerin is substantially more difficult to detonate, possibly rendering it useless as an explosive for practical application.

A serious problem in the use of nitroglycerin results from its high freezing point 13 °C . Solid nitroglycerin is much less sensitive to shock than the liquid, a feature that is common in explosives. In the past, nitroglycerin was often shipped in the frozen state, but this resulted in a high number of accidents during the thawing process just before its use. This disadvantage is overcome by using mixtures of nitroglycerin with other polynitrates. For example, a mixture of nitroglycerin and ethylene glycol dinitrate freezes at −29 °C

4 - Detonation

Nitroglycerin and any dilutents can certainly deflagrate, i.e. burn. However, the explosive power of nitroglycerin is derived from detonation: energy from the initial decomposition causes a pressure wave or gradient that detonates the surrounding fuel. This is a self-sustained shock wave that propagates through the explosive medium at some 30 times the speed of sound as a near-instantaneous pressure-induced decomposition of the fuel into a white hot gas. Detonation of nitroglycerin generates gases that would occupy more than 1,200 times the original volume at ordinary room temperature and pressure. Moreover, the heat liberated raises the temperature to about 5,000 °C . This is entirely different from deflagration, which depends solely upon available fuel regardless of pressure or shock. The decomposition results in much higher ratio of energy to gas moles released compared to other explosives, making it one of the hottest detonating high explosives.

5 - Manufacturing

The industrial manufacturing process often uses a nearly 1:1 mixture of concentrated sulfuric acid and concentrated nitric acid. This can be produced by mixing white fuming nitric acid — a quite expensive pure nitric acid in which the oxides of nitrogen have been removed, as opposed to red fuming nitric acid, which contains nitrogen oxides — and concentrated sulfuric acid. More often, this mixture is attained by the cheaper method of mixing fuming sulfuric acid, also known as oleum — sulfuric acid containing excess sulfur trioxide — and azeotropic nitric acid (consisting of about 70 percent nitric acid, with the rest being water).

The sulfuric acid produces protonated nitric acid species, which are attacked by glycerin's nucleophilic oxygen atoms. The nitro group is thus added as an ester $C- O - NO_2$ and water is produced. This is different from an aromatic nitration reaction in which nitronium ions are the active species in an electrophilic attack on the molecule's ring system.

The addition of glycerin results in an exothermic reaction (i.e., heat is produced), as usual for mixed-acid nitrations. However, if the mixture becomes too hot, it results in "runaway", a state of accelerated nitration accompanied by the destructive oxidation of organic materials by the hot nitric acid and the release of poisonous nitrogen dioxide gas at high risk of an explosion. Thus, the glycerin mixture is added slowly to the reaction vessel containing the mixed acid (not acid to glycerin). The nitrator is cooled with cold water or some other coolant mixture and maintained throughout the glycerin addition at about 22 °C . much below which the esterification occurs too slowly to be useful. The nitrator vessel, often constructed of iron or lead and generally stirred with compressed air, has an emergency trap door at its base, which hangs over a large pool of very cold water and into which the whole reaction mixture (called the charge) can be dumped to prevent an explosion, a process referred to as drowning. If the temperature of the charge exceeds about 30 °C (86 °F) (actual value varying by country) or brown fumes are seen in the nitrator's vent, then it is immediately drowned.

6 - Use as an explosive and a propellant

The main use of nitroglycerin, by tonnage, is in explosives such as dynamite and in propellants.

Nitroglycerin is an oily liquid that may explode when subjected to heat, shock or flame. It is dangerously sensitive and dropping or bumping a container may cause it to explode.

Alfred Nobel developed the use of nitroglycerin as a blasting explosive by mixing the nitroglycerin with inert absorbents, particularly *"kieselguhr,"* or diatomaceous earth. He named this explosive dynamite and patented it in 1867. It was supplied ready for use in the form of *sticks*, individually wrapped in greased water-proof paper. Dynamite and similar explosives were widely adopted for civil engineering tasks, such as in drilling highway and railroad tunnels, for mining, for clearing farmland of stumps, in quarrying, and in demolition work. Likewise, military engineers have used dynamite for construction and demolition work.

Nitroglycerin was also used as an ingredient in military propellants for use in firearms.

Nitroglycerin is a high explosive which is so sensitive that a slight jolt, friction, or impact may cause it to detonate. The molecule contains oxygen, nitrogen, and carbon with chemical bonds that are far less powerful than bonds that exist in a number of smaller molecules, particularly certain diatomic gases. Hence, when it explodes, great energy is released as the atoms rearrange to form new diatomic gas molecules with very strong bonds such as N_2, H_2O, and CO. It is the speed of the decomposition reaction which makes it such a violent explosive. A supersonic wave passing through the material causes it to decompose almost instantly. This instantaneous destruction of all molecules is called a detonation, and the destructive blast results from the rapid expansion of hot gases. Nitroglycerin has an advantage over some other high explosives, that practically no visible smoke is produced, therefore it acts as a "smokeless powder".

Because of its extreme sensitivity, nitroglycerin was rendered obsolete as a military explosive, and was replaced by less sensitive explosives such as TNT, RDX, and HMX. Combat engineers still use dynamite.

Alfred Nobel then developed ballistite, by combining nitroglycerin and guncotton. He patented it in 1887. Ballistite was adopted by a number of European governments, as a military propellant. Italy was the first to adopt it. However, it was not adopted by the British Government. This government and the Commonwealth governments, adopted cordite, which had been developed by Sir Frederick Abel and Sir James Dewar of the United Kingdom in 1889. The original Cordite Mk I consisted of 58 % nitroglycerin, 37% guncotton, and 5.0% petroleum jelly. Ballistite and cordite were both manufactured in the forms of *cords*.

Smokeless powders were originally developed using nitrocellulose as the sole explosive ingredient. Therefore they were known as *single base* propellants. A range of smokeless powders that contain both nitrocellulose and nitroglycerin, known as *double base* propellants, were also developed. Smokeless powders were originally supplied only for military use, but they were also soon developed for civilian use and were quickly adopted for sports. Some are known as sporting powders. *Triple base* propellants contain nitrocellulose, nitroglycerin, and nitroguanidine, but are reserved mainly for extremely high caliber ammunition rounds such as those used in tank cannons and naval artillery.

Blasting gelatin, also known as gelignite, was invented by Nobel in 1875, using nitroglycerin, wood pulp, and sodium or potassium nitrates. This was an early low-cost, flexible explosive.

6 – 1 - Dynamite

Alfred Nobel discovered that mixing nitroglycerin with diatomaceous earth would turn the liquid into a paste, called dynamite. An advantage of dynamite was that it could be cylinder-shaped for insertion into the drilling holes used for mining and tunneling. Nobel received the American patent number 78,317 for his dynamite in 1867.

7 - Medical use

Nitroglycerin was first used by William Murrell to treat anginal attacks in 1878, with the discovery published in 1878.

Nitroglycerin belongs to a group of drugs called nitrates, which includes many other nitrates like isosorbide dinitrate (Isordil) and isosorbide mononitrate (Imdur, Ismo, Monoket).[18] These agents all exert their effect by being converted to nitric oxide in the body by mitochondrial aldehyde dehydrogenase , and nitric oxide is a potent natural vasodilator.

In medicine, where it is generally called glyceryl trinitrate, nitroglycerin is used as a heart medication. It is used as a medicine for angina pectoris (ischemic heart disease) in tablets, ointment, solution for intravenous use, transdermal patches, or sprays administered sublingually. Patients who experience angina when doing certain physical activities can often prevent symptoms by taking nitroglycerin 5 to 10 minutes before the activity. Some forms of nitroglycerin last much longer in the body than others. These may come in the form of a pill taken one, two, or three times per day, or even as a patch. It has been shown that round - the - clock exposure to nitrates can cause the body to stop responding normally to this medicine. Experts recommend that the patches be removed at night, allowing the body a few hours to restore its responsiveness to nitrates. Shorter-acting preparations can be used several times a day with less risk of the body getting used to this drug.

Angina pectoris is due to an inadequate flow of blood and oxygen to the heart. It is believed that nitroglycerin corrects the imbalance between the flow of oxygen and blood to the heart.[20] The principal action of nitroglycerin is vasodilation—widening of the blood vessels. At low doses, nitroglycerin will dilate veins more than arteries, but at higher doses it also dilates arteries and is a potent antihypertensive agent. In cardiac treatment the lowering of pressure in the arteries reduces the pressure against which the heart must pump, thereby decreasing afterload.[18] Dilating the veins decreases cardiac preload and leads to the following therapeutic effects during episodes of angina pectoris: subsiding of chest pain, decrease of blood pressure, increase of heart rate, and orthostatic hypotension.

8 - Industrial exposure

Infrequent exposure to high doses of nitroglycerin can cause severe headaches known as "NG head" or "bang head". These headaches can be severe enough to incapacitate some people; however, humans develop a tolerance to and dependence on nitroglycerin after long-term exposure. Withdrawal can (rarely) be fatal; withdrawal symptoms include headaches and heart problems; with re-exposure to nitroglycerin, these symptoms may disappear.

For workers in nitroglycerin (NTG) manufacturing facilities, this can result in a "Monday morning headache" phenomenon for those who experience regular nitroglycerin exposure in the workplace leading to the development of NTG tolerance for the vasodilating effects. Over the weekend the workers lose the tolerance to NTG and when they are reexposed on Monday the prominent vasodilation produces tachycardia, dizziness, and a headache.

Glyceryl Tri Nitrate (Pharmacology)

Contents

1 - Introduction

Glyceryl trinitrate (GTN) is an alternative name for the chemical nitroglycerin, which has been used to treat angina and heart failure since the experiments of William Murrell were widely reported in 1879. Despite this, the mechanism of nitric oxide (NO) generation from GTN and the metabolic consequences of this bioactivation are still not entirely understood.

Systematic (IUPAC) name : 1,3-dinitrooxypropan-2-yl nitrate ; [3-(nitrooxy)-2- [(nitrooxy)methyl]propyl] nitrate	
Bioavailability	< 1 %
Metabolism	Hepatic (rapid)
Half-life	3 minutes
Formula	$C_3H_5N_3O_9$
Mol. mass	227 g / mol

2 - Medical uses

Nitroglycerin is used for the treatment of angina , acute myocardial infarction, severe hypertension ’ and coronary artery spasms due to cocaine .

It is useful in decreasing angina attacks, perhaps more so than reversing angina once started, by supplementing blood concentrations of nitric oxide, also called endothelium-derived relaxing factor, before the structure of NO as the responsible agent was known. This led to the development of transdermal patches of glyceryl trinitrate, providing 24-hour release . However the effectiveness of glyceryl trinitrate is limited by development of tolerance/tachyphylaxis within 2–3 weeks of sustained use. Continuous administration and absorption (such as provided by daily pills and especially skin patches) accelerate onset of tolerance and limit the usefulness of the agent. Thus glyceryl trinitrate works best when used only short term, pulse dosing. Glyceryl trinitrate is useful for AMI and pulmonary edema , again working best if used quickly, within a few minutes of symptom onset, as a pulse dose . It may also be given as a sublingual or buccal dose in the form of a tablet placed under the tongue or a spray into the mouth for the treatment of an angina attack.

Glyceryl trinitrate is also used in the treatment of anal fissures, though usually at a much lower concentration than that used for angina treatment.

3 - Adverse effects

After long-term use for chronic conditions, tolerance may develop in a patient, reducing its effectiveness. Nitrate tolerance was first described soon after the introduction of GTN in cardiovascular therapy as the loss of symptomatic and hemodynamic effects of GTN and/or the need for higher doses of the drug to achieve the same effects. The mechanisms of nitrate tolerance have been thoroughly investigated in the last 30 years and several hypotheses have been proposed. These include :

Impaired biotransformation of GTN to its active principle - NO (or a NO-related species)

Neurohormonal activation, causing sympathetic activation and release of vasoconstrictors such as endothelin and angiotensin II, which counteract the vasodilation induced by GTN

Plasma volume expansion

The oxidative stress hypothesis .

Recent evidence suggests that the latter hypothesis might represent a unifying hypothesis, and a GTN-induced inappropriate production of oxygen free radicals might induce a number of abnormalities which include those described above. Furthermore, studies have shown that nitrate tolerance is associated with vascular abnormalities which have the potential to worsen patients' prognosis (Nakamura et al.). These include endothelial and autonomic dysfunction (Gori et al.). In the short run, glyceryl trinitrate can cause severe headaches, necessitating analgesic (very rarely up to morphine) administration for relief of pain, severe hypotension, and, in certain cases, bradycardia. This makes some physicians nervous and should prompt caution when starting nitrate administration. The painful nature of these adverse effects has a marked negative impact on patient compliance.

GTN must not be used together with vasodilators that combat erectile dysfunction, such as Viagra, Cialis, or Levitra. The combination of the two can lead to severe hypotension, circulatory collapse and death.

3 – 1 - Dangers

It is often recommended that GTN transdermal patches should be removed before defibrillation due to the risk of explosion, but careful investigations have concluded that reports of apparent GTN patch explosions during defibrillation are due to voltage breakdown involving the metal mesh in some patches.

4 - Mechanism of action

GTN is a prodrug which must first be denitrated to produce the active metabolite nitric oxide (NO). Nitrates which undergo denitration within the body to produce NO are called nitrovasodilators and their denitration occurs via a variety of mechanisms. The mechanism by which nitrates produce NO is widely disputed. Some believe that nitrates produce NO by reacting with sulfhydryl groups, while others believe that enzymes such as glutathione S-transferases, cytochrome P450 (CYP), and xanthine oxidoreductase are the primary source of GTN bioactivation. In recent years a great deal of evidence has been produced that supports the belief that clinically relevant denitration of GTN to produce 1,2-glyceryl dinitrate (GDN) and NO is catalysed by mitochondrial aldehyde dehydrogenase (mtALDH).

NO is a potent activator of guanylyl cyclase (GC) by heme-dependent mechanisms; this activation results in cGMP formation from cyclic guanosine triphosphate (cGTP). Thus, NO increases the level of cGMP within the cell. cGMP then activates myosin light chain phosphatase via a cGMP-dependent protein kinase.

5 - History

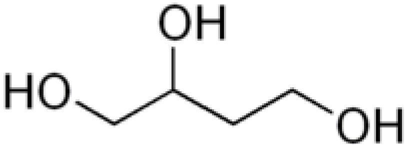
It was known almost from the time of its discovery by Ascanio Sobrero in 1846-7 that the tasting or close handling of nitroglycerin could cause sudden intense headaches, which indicated some form of vasodilation effect. This was reported by Sobrero. Constantin Hering developed a sublinguial dose form of nitroglycerin in 1847 and advocated for it as a treatment of a number of diseases. However, it was not known to be a specific treatment for blood pressure and chest pain.

Following Doctor Thomas Brunton's discovery that amyl nitrite could be used to treat chest pain, Doctor William Murrellexperimented with the use of nitroglycerin to alleviate angina pectoris and reduce blood pressure, and proved that the headaches occurred due to overdose. He began treating patients with small doses in 1878, and the substance was soon adopted into widespread use after he published his results in *The Lancet* in 1879. The medical establishment used the name "glyceryl trinitrate" or "trinitrin" to avoid alarming patients who associated nitroglycerin with explosions.

6 - Research

A recent medical development will include a small amount of nitroglycerin (trademark as Zanifil Gel) in the tip of a new Durex condom to stimulate erection during intercourse. "The CSD500 condom contains a chemical in its teat, called glyceryl trinitrate (GTN), which is absorbed by the skin and causes blood vessels to dilate."

1 , 2 , 4 - Butanetriol



1,2,4-Butanetriol is a clear or slightly yellow, odorless, hygroscopic, flammable, viscous liquid. It is an alcohol with three hydrophilic alcoholic hydroxyl groups. It is similar to glycerol and erythritol. It is chiral, with two possible enantiomers.

1,2,4-Butanetriol is used in the manufacture of butanetriol trinitrate (BTTN), an important military propellant.

1,2,4-Butanetriol can be prepared synthetically by several different methods such as hydroformylation of glycidol and subsequent reduction of the product, sodium borohydride reduction of esterified malic acid, or catalytic hydrogenation of malic acid. However, of an increasing importance is the biotechnological synthesis using genetically engineered *Escherichia coli* and *Pseudomonas fragi* bacteria.

IUPAC name : Butane-1,2,4-triol
Other names :
1,2,4-Butanetriol
1,2,4-Trihydroxybutane
Triol 124
2-Deoxyerthritol

Molecular formula	$C_4 H_{10} O_3$
Molar mass	106 g mol^{-1}
Density	1.19
Boiling point	190 – 191 °C
Flash point	112 °C

Natural Oil Polyols

Contents

1 - Introduction

Natural oil polyols, also known as NOPs or biopolyols, are polyols derived from vegetable oils by several different techniques. The primary use for these materials is in the production of polyurethanes. Most NOPs qualify as biobased products, as defined by the United States Secretary of Agriculture in the Farm Security and Rural Investment Act of 2002.

NOPs all have similar sources and applications, but the materials themselves can be quite different, depending on how they are made. All are clear liquids, ranging from colorless to medium yellow. Their viscosity is also variable and is usually a function of the molecular weight and the average number of hydroxyl groups per molecule (higher mw and higher hydroxyl content both giving higher viscosity.) Odor is a significant property which is different from NOP to NOP. Most NOPs are still quite similar chemically to their parent vegetable oils and as such are prone to becoming rancid. This involves autoxidation of fatty acid chains containing carbon-carbon double bonds and ultimately the formation of odoriferous, low molecular weight aldehydes, ketones and carboxylic acids. Odor is undesirable in the NOPs themselves, but more importantly, in the materials made from them.

There are a limited number of naturally occurring vegetable oils (triglycerides) which contain the unreacted hydroxyl groups that account for both the name and important reactivity of these polyols. Castor oil is the only commercially-available natural oil polyol that is produced directly from a plant source: all other NOPs require chemical modification of the oils directly available from plants.

The hope is that using renewable resources as feedstocks for chemical processes will reduce the environmental footprint[1] by reducing the demand on non-renewable fossil fuels currently used in the chemical industry and reduce the overall production of carbon dioxide, the most notable greenhouse gas. One NOP producer, Cargill, estimates that its BiOH(TM)polyol manufacturing process produces 36 % less global warming emissions (carbon dioxide) , a 61 % reduction in non-renewable energy use (burning fossil fuels), and a 23 % reduction in the total energy demand, all relative to polyols produced from petrochemicals.

2 - Sources of natural oil polyols

Ninety percent of the fatty acids that make up castor oil is ricinoleic acid, which has a hydroxyl group on C-12 and a carbon-carbon double bond. The structure below shows the major component of castor oil which is composed of the tri-ester of rincinoleic acid and glycerin:

Other vegetable oils - such as soy bean oil,[3] peanut oil, and canola oil - contain carbon-carbon double bonds, but no hydroxyl groups. There are several processes used to introduce hydroxyl groups onto the carbon chain of the fatty acids, and most of these involve oxidation of the C-C double bond. Treatment of the vegetal oils with ozone cleaves the double bond, and esters or alcohols can be made, depending on the conditions used to process the ozonolysis product.[4] The example below shows the reaction of triolein with ozone and ethylene glycol.

Air oxidation, (autoxidation), the chemistry involved in the "drying" of drying oils, gives increased molecular weight and introduces hydroxyl groups. The radical reactions involved in autoxidation can produce a complex mixture of crosslinked and oxidized triglycerides. Treatment of vegetable oils with peroxy acids gives epoxides which can be reacted with nucleophiles to give hydroxyl groups. This can be done as a one - step process . Note that in the example shown below only one of the three fatty acid chains is drawn fully, the other part of the molecule is represented by "R_1" and the nucleophile is unspecified. Earlier examples also include acid catalyzed ring opening of epoxidized soybean oil to make oleochemical polyols for polyurethane foams [6] and acid catalyzed ring opening of soy fatty acid methyl esters with multifunctional polyols to form new polyols for casting resins.

Triglycerides of unsaturated (containing carbon-carbon double bonds) fatty acids or methyl esters of these acids, can be treated with carbon monoxide and hydrogen in the presence of a metal catalyst to add a -CHO (formyl) groups to the chain (hydroformylation reaction) followed by hydrogenation to give the needed hydroxyl groups.[8] In this case R_1 can be the rest of the triglyceride, or a smaller group such as methyl (in which case the substrate would be similar to biodiesel). If R=Me then additional reactions like transesterification are needed to build up a polyol.

3 - Uses

Castor oil has found numerous applications, many of them due to the presence of the hydroxyl group that allows chemical derivatization of the oil or modifies the properties of castor oil relative to vegetable oils which do not have the hydroxyl group. Castor oil undergoes most of the reactions that alcohols do, but the most industrially important one is reaction with diisocyanates to make polyurethanes.

Castor oil by itself has been used in making a variety of polyurethane products, ranging from coatings to foams, and the use of castor oil derivatives continues to be an area of active development. Castor oil derivatized with propylene oxide[9] makes polyurethane foam for mattresses and yet another new derivative is used in coatings

Apart from castor oil, which is a relatively expensive vegetable oil and is not produced domestically in many industrialized countries, the use of polyols derived from vegetable oils to make polyurethane products began attracting attention beginning around 2004. The rising costs of petrochemical feedstocks and an enhanced public desire for environmentally friendly green products have created a demand for these materials.[11] One of the most vocal supporters of these polyurethanes made using natural oil polyols is the Ford Motor Company, which first debuted polyurethane foam made using soy oil in the seats of its 2008 Ford Mustang. Ford has since placed soy foam seating in all its North American vehicle platforms. The interest of automakers is responsible for much of the work being done on the use of NOPs in polyurethane products for use in cars, for example is seats, and headrests, armrests, soundproofing, and even body panels.

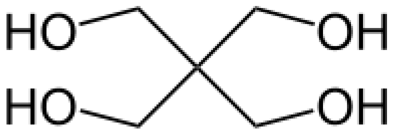
One of the first uses for NOPs (other than castor oil) was to make spray-on polyurethane foam insulation for buildings.

NOPs are also finding use in polyurethane slab foam used to make conventional mattresses as well as memory foam mattresses.

The characteristics of NOPs can be varied over a very wide range. This can be done by selection of the base Natural Oil (or oils) used to make up the NOP. Also, using known and increasingly novel (Garrett & Du) chemical techniques, it is possible to graft additional groups onto the triglyceride chains of the NOP and change its processing characteristics and this in turn will change and modify in a controlled manner, the physical properties of the final article which the NOP is being used to produce. Differences and modifications in the process regime and reaction conditions used to make a given NOP also generally lead to different chemical architectures and therefore different end use performance of that NOP; so that even though two NOPs may have been made from the same Natural Oil root, they may be surprisingly different when used and, will produce a detectably different end product too. Commercially, (AD 2012) NOPs are available and made from; sawgrass oil, soybean oil, castor oil (as an grafted NOP), rapeseed oil, palm oil (kernel and mesocarp), and coconut oil. There is also some work being done on NOPs made from Natural Animal oils.

Initially in the USA, and since early 2010, it has been routinely possible to replace over 50% of petrochemical based polyols with NOPs for use in slab foams sold into the mass market, furniture and bedding industries. The commercialised technology . also eliminates or greatly reduces the odour problem, mentioned above, normally associated with the use of NOPs. This is particularly important when the NOP is to be used at ever higher percentage levels, to try to reduce dependency on petrochemical materials, and to produce materials for use in the domestic and contract furniture segments which are historically very sensitive to "chemical" odours in the final foam product in people's homes and places of work.

Penta Erythritol



IUPAC name : 2,2-Bis(hydroxymethyl)1,3- propanediol

Other names :

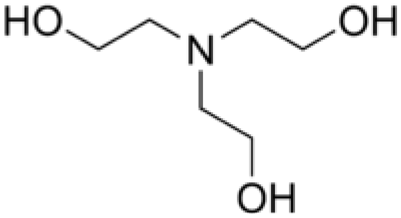
Hercules P 6, mono pentaerythritol , tetramethylolmethane , THME , PETP , penta erythrite , Pentek , Hercules Aqualon

Molecular formula	$C_5 H_{12} O_4$
Molar mass	136
Appearance	white solid
Density	1.396 g / cm^3
Melting point	260.5 °C
Boiling point	276 °C at 30 mm Hg
Solubility in water	5.6 g / 100 mL at 15 °C
Flash point	200.1 °C

Pentaerythritol is an organic compound with the formula $C_5H_{12}O_4$. This white, crystalline polyol with the neopentane backbone is a versatile building block for the preparation of many polyfunctionalized compounds such as the explosive PETN and pentaerythritol tetraacrylate . Derivatives of pentaerythritol are components of alkyd resins, varnishes, PVC stabilizers, tall oil esters, and olefin antioxidants.

Halogen - free pentaerythritol esters are also environmentally friendly alternative to conventional electrical transformer fluids, being both readily biodegradable and non-hazardous in water. They advantageously replace poly chloro biphenyl (PCB), and even silicone-based or fluorinated hydrocarbons, as dielectric fluid in transformers. Their low volatility and high flash point give them an excellent resistance to ignition in case of major electrical failure and transformer rupture.

Tri Ethanol Amine



Contents

1 - Introduction

Triethanolamine, often abbreviated as TEA, is a viscous organic compound that is both a tertiary amine and a triol. A triol is a molecule with three alcohol groups. Like other amines, triethanolamine is a weak base. Triethanolamine can also be abbreviated as TEOA, which can help to distinguish it from triethylamine. Approximately 150000 metric tons were produced in 1999. It is a colourless compound although samples may appear yellow because of impurities.

IUPAC name : Tris (2-hydroxyethyl)amine
Other names :
Triethylolamine
2,2',2''-Trihydroxy-triethylamine
Tris(2-hydroxyethyl)amine
Trolamine
TEA

TEOA	
Molecular formula	$C_6\ H_{15}\ N\ O_3$
Molar mass	149 g mol^{-1}
Appearance	Colourless liquid
Odor	Ammoniacal
Density	1.124 g mL^{-1}
Melting point	22 °C
Boiling point	335 °C
Solubility in water	149 g L^{-1} (at 20 °C)
Vapor pressure	1 Pa (at 20 °C)
Refractive index (n_D)	1.485
Specific heat capacity, C	389 J K^{-1} mol^{-1}
GHS signal word	WARNING
Flash point	179 °C
Autoignition temperature	325 °C
Explosive limits	1.3 – 8.5 %
LD_{50}	2.2 g kg^{-1} (oral, guinea pig) 2.2 g kg^{-1} (oral, rabbit) 5.53 g kg^{-1} (oral, rat) 5.846 g kg^{-1} (oral, mouse) 22.5 g kg^{-1} (dermal, rabbit)

2 - Production

Triethanolamine is produced from the reaction of ethylene oxide with aqueous ammonia, also produced are ethanolamine and diethanolamine. The ratio of the products can be controlled by changing the stoichiometry of the reactants.

3 - Applications

Triethanolamine is used primarily as an emulsifier and surfactant. It is a common ingredient in formulations used for both industrial and consumer products. The triethanolamine neutralizes fatty acids, adjusts and buffers the pH, and solubilises oils and other ingredients that are not completely soluble in water. Some common products in which triethanolamine is found are liquid laundry detergents, dishwashing liquids, general cleaners, hand cleaners, polishes, metalworking fluids, paints, shaving cream and printing inks.

3 – 1 - Cement production

Triethanolamine is also used as organic additive (0.1 wt. %) in the grinding of cement clinker. It facilitates the grinding process by preventing agglomeration and coating of the powder at the surface of balls and mill wall.

3 – 2 - Cosmetics and medicine

Various ear diseases and infections are treated with eardrops containing triethanolamine polypeptide oleate-condensate, such as Cerumenex in the United States. In pharmaceutics, triethanolamine is the active ingredient of some ear drops used to treat impacted earwax. It also serves as a pH balancer in many different cosmetic products - ranging from cleansing creams and milks, skin lotions, eye gels, moisturizers, shampoos, shaving foams etc. TEA is a fairly strong base: a 1% solution has a pH of approximately 10, whereas the pH of skin is below pH 7, more or less 5.5-6.0. Cleansing milk / cream emulsions based on TEA are particularly good at removing makeup.

3 – 3 - In the laboratory and in amateur photography

Another common use of TEA is as a complexing agent for aluminium ions in aqueous solutions. This reaction is often used to mask such ions before complexometric titrations with another chelating agent such as EDTA. TEA has also been used in photographic (silver halide) processing. It has been promoted as a useful alkali by amateur photographers.

3 – 4 - In Electroless Plating

TEA is now commonly and very effectively used as a complexing agent in Electroless Plating.

4 - Safety and regulation

4 – 1 - Allergic reactions

A 1996 study found that Triethanolamine (TEA) occasionally causes contact allergy . A 2001 study found TEA in a sunscreen caused an allergic contact dermatitis. A 2007 study found TEA in ear drops caused a contact allergy. Systemic and respiratory tract (RT) toxicity was analyzed for 28 days in a nose specific inhalation 2008 study in Wistar rats; TEA seems to be less potent in regard to systemic toxicity and RT irritancy than diethanolamine (DEA). Exposure to TEA resulted in focal inflammation, starting in single male animals from 20 mg / m3 concentrations. A 2009 study stated patch test reactions reveal a slight irritant potential instead of a true allergic response in several cases and also indicated the risk of skin sensitization to TEA seems to be very low.

4 – 2 - Tumors

Reports indicated that TEA causes an increased incidence of tumor growth in the liver in female B6C3F1 mice, but not in male mice or in Fischer 344 rats. A 2004 study concluded "TEA may cause liver tumors in mice via a choline-depletion mode of action and that this effect is likely caused by the inhibition of choline uptake by cells."

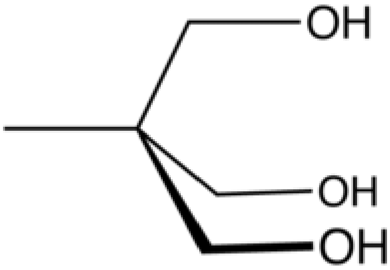
4 – 3 - Environmental toxicity

A 2009 study found that TEA has potential acute, sub-chronic and chronic toxicity properties in respect to aquatic species.

4 – 4 - Regulation

TEA is listed under Schedule 3, part B of the Chemical Weapons Convention as it can be used in the manufacture of nitrogen mustards.

Tri Methylol Ethane



Contents

1 - Introduction

Trimethylolethane (TME) is the organic compound with the formula $CH_3C(CH_2OH)_3$. This colorless solid is a triol, that is it contains three hydroxy functional groups. More specifically, it features three primary alcohol groups in a compact neopentyl structure. Its esters are known for their resistance to heat, light, hydrolysis, and oxidation. More important than TME and closely related is trimethylolpropane (TMP).

IUPAC name :
2-(hydroxymethyl)-2-methylpropane-1,3-diol
Other names :
TME; trimet; metriol; methriol; pentaglycerol ; penta glycerine ; methyl trimethanol methane ; tris(hydroxymethyl) ethane ,

Molecular formula	$C_5 H_{12} O_3$
Molar mass	120 g/mol
Density	1.22 g / mL
Melting point	180 °C
EU classification	Flammable (F)
Flash point	150 °C

2 - Production

Trimethylolethane is produced via a two step process, starting with the condensation reaction of propionaldehyde with formaldehyde:

$CH_3CH_2CHO + 2\ CH_2O \rightarrow CH_3C(CH_2OH)_2CHO$

The second step entails a Cannizaro reaction :

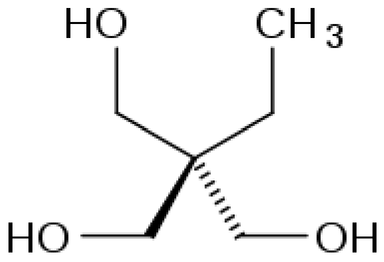
$CH_3C(CH_2OH)_2CHO + CH_2O + NaOH \rightarrow$
$CH_3C(CH_2OH)_3 + NaO_2CH$

A few thousand tons are produced annually in this way.

3 - Applications

TME is an intermediate in the production of alkyd and polyester resins, powder coating resins, synthetic lubricants based on polyol esters, stabilizers for plastics, plasticizers, and pigment coatings based on titanium dioxide. Trimethylolethane based resins have superior weatherability and resistance to alkali and heat. Trimethylolethane is used in some phase change materials. The typical composition is then 63 wt.% TME with 37 wt.% water. The mixture has melting point of 29.8 °C and heat of fusion 218 kJ/kg. Nitration of trimethylolethane gives trimethylolethane trinitrate, an explosive, monopropellant, and energetic plasticizer.

Tri Methylol Propane



Contents

1 - Introduction

Trimethylolpropane (TMP) is the organic compound with the formula $CH_3CH_2C(CH_2OH)_3$. This colorless solid is a triol. Containing three hydroxy functional groups, TMP is a widely used building block in the polymer industry.

IUPAC name :
2-(hydroxymethyl)-2-ethylpropane-1,3-diol
Other names :
TMP , 2-ethyl-2-hydroxymethyl-1,3-propanediol

Molecular formula	$C_6H_{14}O_3$
Molar mass	134 g / mol
Density	1.084 g/mL
Melting point	58 °C
Boiling point	289 °C
EU classification	Flammable (F)
Flash point	172 °C

2 - Production

TMP is produced via a two step process, starting with the condensation of butanal with formaldehyde:

$CH_3CH_2CH_2CHO + 2\ CH_2O \rightarrow CH_3CH_2C(CH_2OH)_2CHO$

The second step entails a Cannizaro reaction:

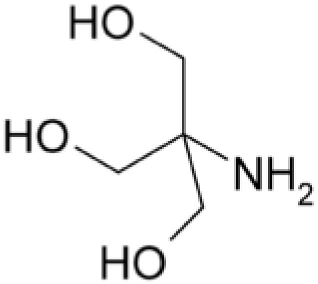
$$CH_3CH_2C(CH_2OH)_2CHO + CH_2O + NaOH \rightarrow CH_3CH_2C(CH_2OH)_3 + NaO_2CH$$

Approximately 200,000 tone are produced annually in this way.

3 - Applications

TMP is mainly consumed as a precursor to alkyd resins. Other wise, acrylated and alkoxylated TMP's are used as multifunctional monomers to produce various coatings, Ethoxylated and propoxylated TMP, derived condensation of from TMP and the epoxides, are used for production of flexible polyurethanes. Allyl ether derivatives of TMP, with the formula $CH_3CH_2C(CH_2OCH_2CH{=}CH_2)_{3-x}(CH_2OH)_x$ are precursors to high-gloss coatings and ion exchange resins. The oxetane "TMPO" is a photoinduceable polymerization initiator.

Tris



Contents

1 - Intoduction

Tris (also known as THAM) is an abbreviation of the organic compound known as tris(hydroxymethyl)aminomethane, with the formula $(HOCH_2)_3CNH_2$. Tris is extensively used in biochemistry and molecular biology . In biochemistry, Tris is widely used as a component of buffer solutions, such as in TAE and TBE buffer, especially for solutions of nucleic acids. It is a primary amine and thus undergoes the reactions associated with typical amines, e.g. condensations with aldehydes.

IUPAC name :
2-Amino-2-hydroxymethyl-propane-1,3-diol
Other names :
TRIS , Tris , Tris base , Tris buffer , Trizma^{TM} , Trisamine , THAM , Tromethamine , Trometamol , Tromethane

Molecular formula	$C_4 H_{11} N O_3$
Molar mass	121 $g\ mol^{-1}$
Appearance	White crystalline powder
Density	1.328 g / cm^3
Melting point	> 175 -176 °C

Boiling point	219 °C
Solubility in water	~ 50 g /100 mL (25 °C)
Acidity (pK_a)	8.07
Main hazards	Irritant
Flash point	Non - flammable

2 - Buffering features

Tris has a pK_a of 8.07 at 25 °C, which implies that the buffer has an effective pH range between 7.1 and 9.0.

2 - 1 - Buffer details

The pK_a declines approximately 0.03 units per degree Celsius rise in temperature.

Silver-containing single-junction pH electrodes (e.g., silver chloride electrode) are incompatible with Tris (Ag-tris precipitation clogs the junction). Double-junction electrodes are resistant to this problem, and non-silver containing electrodes are immune.

When making buffer solutions by neutralizing TrisHCl requires attention to the attendant changes in ionic strength.

2 – 2 - Buffer inhibition

Tris inhibits a number of enzymes , and therefore it should be used with care when studying proteins.

3 - Preparation

Tris is prepared industrially in two steps from nitromethane via the intermediate $(HOCH_2)_3CNO_2$. Reduction of the latter gives tris(hydroxymethyl)aminomethane.

4 - Uses

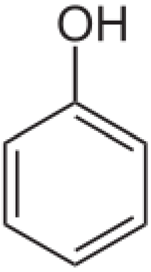
The useful buffer range for tris (7-9) coincides with the physiological pH typical of most living organisms. This, and its low cost, make tris one of the most common buffers in the biology/biochemistry laboratory. Tris is also used as a primary standard to standardize acid solutions for chemical analysis.

4 – 1 - Medical

Tris (usually known as THAM in this context) is used as alternative to sodium bicarbonate in the treatment of metabolic acidosis.

Tris is one of the most widely used buffers in molecular biology and cell culture due to its low toxicity, stability and buffering capacity.

Phenol



Contents

1 - Introduction

Phenol, also known as carbolic acid, is an organic compound with the formula C_6H_5OH. It is a white crystalline solid that is volatile. The molecule consists of a phenyl group ($-C_6H_5$) bonded to a hydroxyl group ($-OH$). It is mildly acidic, but requires careful handling due to its propensity to cause burns.

Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 billion kg/year) from petroleum. It is an important industrial commodity as a precursor to many materials and useful compounds . Its major uses involve its conversion to plastics or related materials. Phenol and its chemical derivatives are key for building polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs.

IUPAC name : Phenol
Other names :
Carbolic acid , benzenol, phenylic acid , hydroxybenzene , phenic acid

Molecular formula	$C_6 H_6 O$
Molar mass	94 g mol^{-1}
Appearance	Transparent crystalline solid
Odor	Sweet and tarry
Density	1.07 g/cm^3
Melting point	40.5 °C
Boiling point	181.7 °C
Solubility in water	8.3 g / 100 mL (20 °C)
Acidity (pK_a)	9.95 (in water), 29.1 (in aceto nitrile)
GHS pictograms	 [
EU classification	Toxic (T) Muta. Cat. 3 Corrosive (C)
Flash point	79 °C

2 - Properties

Phenol is appreciably soluble in water, with about 8.3 g dissolving in 100 mL (0.88 M). Homogeneous mixtures of phenol and water at phenol to water mass ratios of ~2.6 and higher are also possible. The sodium salt of phenol, sodium phenoxide, is far more water soluble.

2 – 1 - Acidity

Phenol is weakly acidic but at high pH's gives the phenolate anion $C_6H_5O^-$ (also called phenoxide) :

$$PhOH \rightleftarrows PhO^- + H^+ \quad K = 10^{-10}$$

Compared to aliphatic alcohols, phenol is about 1 million times more acidic, although it is still considered a weak acid. It reacts completely with aqueous NaOH to lose H^+, whereas most alcohols react only partially. Phenols are less acidic than carboxylic acids, and even carbonic acid.

One explanation for the increased acidity over alcohols is resonance stabilization of the phenoxide anion by the aromatic ring. In this way, the negative charge on oxygen is delocalized on to the ortho and para carbon atoms. In another explanation, increased acidity is the result of orbital overlap between the oxygen's lone pairs and the aromatic system. In a third, the dominant effect is the induction from the sp^2 hybridised carbons; the comparatively more powerful inductive withdrawal of electron density that is provided by the sp^2 system compared to an sp^3 system allows for great stabilization of the oxyanion.

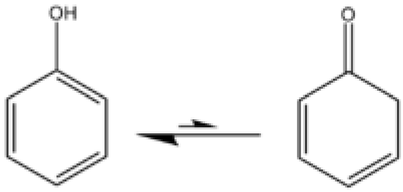
The pK_a of the enol of acetone is 10.9, comparable to that for phenol. The acidities of phenol and acetone enol diverge in the gas phase owing to the effects of solvation. About 1/3 of the increased acidity of phenol is attributable to inductive effects, with resonance accounting for the remaining difference.

2 – 1 - 1 - Phenoxide anion

Resonance structures of the phenoxide anion

The phenoxide anion has a similar nucleophilicity to free amines, with the further advantage that its conjugate acid (neutral phenol) does not become entirely deactivated as a nucleophile even in moderately acidic conditions. Phenols are sometimes used in peptide synthesis to "activate" carboxylic acids or esters to form activated esters. Phenolate esters are more stable toward hydrolysis than acid anhydrides and acyl halides but are sufficiently reactive under mild conditions to facilitate the formation of amide bonds.

2 – 1 - 2 – Tautomerism



Phenol-cyclohexadienone tautomerism

Phenol exhibits keto-enol tautomerism with its unstable keto tautomer cyclohexadienone, but only a tiny fraction of phenol exists as the keto form. The equilibrium constant for enolisation is approximately 10^{-13}, meaning that only one in every ten trillion molecules is in the keto form at any moment. The small amount of stabilisation gained by exchanging a C = C bond for a C=O bond is more than offset by the large destabilisation resulting from the loss of aromaticity. Phenol therefore exists entirely in the enol form.

Phenoxides are enolates stabilised by aromaticity. Under normal circumstances, phenoxide is more reactive at the oxygen position, but the oxygen position is a "hard" nucleophile whereas the alpha-carbon positions tend to be "soft".

2 – 2 - Reactions

Phenol is highly reactive toward electrophilic aromatic substitution as the oxygen atom's pi electrons donate electron density into the ring. By this general approach, many groups can be appended to the ring, via halogenation, acylation, sulfonation, and other processes. However, phenol's ring is so strongly activated — second only to aniline - that bromination or chlorination of phenol leads to substitution on all carbons ortho and para to the hydroxy group, not only on one carbon.

Aqueous solution of phenol is weakly acidic and turns blue litmus slightly to red. Phenol is easily neutralized by sodium hydroxide forming sodium phenate or phenolate, but it being weaker than carbonic acid cannot be neutralized by sodium bicarbonate or sodium carbonate to liberate carbon dioxide

$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

When a mixture of phenol and benzoyl chloride when shaken in presence of dilute sodium hydroxide solution, phenyl benzoate is formed. This is an example of Schotten-Baumann reaction :

$C_6H_5OH + C_6H_5COCl \rightarrow C_6H_5OCOC_6H_5 + HCl$

Phenol is reduced to benzene when it is distilled with zinc dust or its vapour is passed over granules of zinc at 400 °C :

$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$

When phenol is reacted with diazomethane in the presence of boron trifluoride (BF_3), anisole is obtained as the main product and nitrogen gas is released :

$C_6H_5OH + CH_2N_2 \rightarrow C_6H_5OCH_3 + N_2$

3 - Production

Because of phenol's commercial importance, many methods have been developed for its production. The dominant current route, accounting for 95 % of production (2003), involves the partial oxidation of cumene (isopropylbenzene) via the Hock rearrangement :

$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5OH + (CH_3)_2CO$

Compared to most other processes, the cumene-hydroperoxide process uses relatively mild synthesis conditions, and relatively inexpensive raw materials. However, to operate economically, there must be demand for both phenol, and the acetone by-product.

An early commercial route, developed by Bayer and Monsanto in the early 1900s, begins with the reaction of a strong base with benzenesulfonate :

$C_6H_5SO_3H + 2\ NaOH \rightarrow C_6H_5OH + Na_2SO_3 + H_2O$

Other methods under consideration involve :

hydrolysis of chlorobenzene, using base or steam (Raschig-Hooker process) :

$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$

direct oxidation of benzene with nitrous oxide, a potentially "green" process :

$C_6H_6 + N_2O \rightarrow C_6H_5OH + N_2$

oxidation of toluene, as developed by Dow Chemical :

$C_6H_5CH_3 + 2\ O_2 \rightarrow C_6H_5OH + CO_2 + H_2O$

In the Lummus Process, the oxidation of toluene to benzoic acid is conducted separately.

Phenol is also a recoverable byproduct of coal pyrolysis.

4 - Uses

The major uses of phenol, consuming two thirds of its production, involve its conversion to precursors to plastics. Condensation with acetone gives bisphenol - A , a key precursor to polycarbonates and epoxide resins. Condensation of phenol, alkylphenols, or diphenols with formaldehyde gives phenolic resins, a famous example of which is Bakelite. Partial hydrogenation of phenol gives cyclohexanone, a precursor to nylon. Nonionic detergents are produced by alkylation of phenol to give the alkylphenols, e.g., nonylphenol, which are then subjected to ethoxylation.[4]

Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceutical drugs. Phenol is also used as an oral anesthetic/analgesic in products such as Chloraseptic or other brand name and generic equivalents, commonly used to temporarily treat pharyngitis.

4 – 1 - Niche uses

Phenol is so inexpensive that it attracts many small-scale uses. It once was widely used as an antiseptic, especially as Carbolic soap, from the early 1900s through the 1970s. It is a component of industrial paint strippers used in the aviation industry for the removal of epoxy, polyurethane and other chemically resistant coatings.

Phenol derivatives are also used in the preparation of cosmetics including sunscreens , hair dyes, and skin lightening preparations.

5 - History

Phenol was discovered in 1834 by Friedlieb Ferdinand Runge who extracted it (in impure form) from coal tar. Runge called phenol "Karbolsäure" (coal-oil-acid, carbolic acid). Coal tar remained the primary source until the development of the petrochemical industry. In 1841, the French chemist Auguste Laurent obtained phenol in pure form.

In 1836, Auguste Laurent coined the name "phène" for benzene; this is the root of the word "phenol" and "phenyl". In 1843, French chemist Charles Gerhardt coined the name "phénol".

The antiseptic properties of phenol were used by Sir Joseph Lister (1827–1912) in his pioneering technique of antiseptic surgery. Lister decided that the wounds themselves had to be thoroughly cleaned. He then covered the wounds with a piece of rag or lint covered in phenol, or carbolic acid as he called it. The skin irritation caused by continual exposure to phenol eventually led to the substitution of aseptic (germ-free) techniques in surgery.

Phenol is the active ingredient in some oral analgesics such as Chloraseptic spray and Carmex.

Phenol was the main ingredient of the Carbolic Smoke Ball, an ineffective device marketed in London in the 19th century as protecting against influenza and other ailments, and the subject of the famous law case Carlill v Carbolic Smoke Ball Company.

5 – 1 - Second World War

Injections of phenol were used as a means of individual execution by the Nazis during the Second World War.[24] It was originally used by the Nazis in 1939 as part of Action T4.[25] Although Zyklon-B pellets were used in the gas chambers to exterminate large groups of people, the Nazis learned that extermination of smaller groups was more economical via injection of each victim with phenol. Phenol injections were given to thousands of people, especially at Auschwitz-Birkenau. Approximately one gram is sufficient to cause death.[26][27] One of the best known inmates to be executed with a phenol injection in Auschwitz was St. Maximilian Kolbe, a Catholic priest who volunteered to undergo two weeks of starvation and dehydration in the place of another inmate.

6 - Natural occurrences

Temporal glands secretion examination showed the presence of phenol and 4-methyl phenol during musth in male elephants.

6 – 1 - Occurrence in whisky

Phenol is a measurable component in the aroma and taste of the distinctive Islay scotch whisky, generally ~ 30 , but can be over 150[31] ppm in the malted barley used to produce whisky.

7 - Biodegradation

Cryptanaerobacter phenolicus is a bacterium species that produces benzoate from phenol via 4-hydroxybenzoate. *Rhodococcus phenolicus* is a bacterium species able to degrade phenol as sole carbon sources.

8 - Toxicity

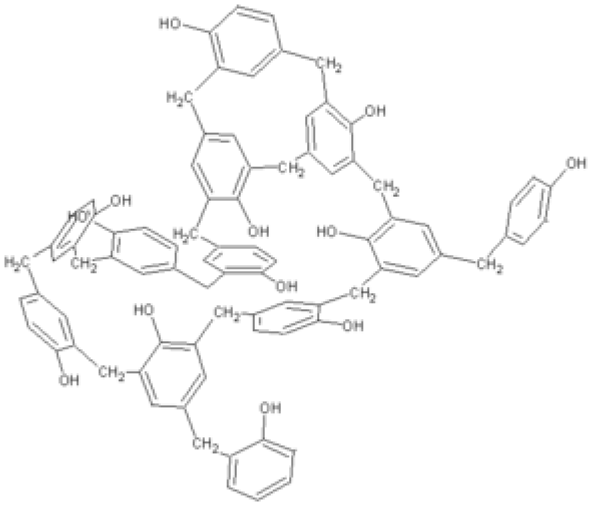
Phenol and its vapors are corrosive to the eyes, the skin, and the respiratory tract. Repeated or prolonged skin contact with phenol may cause dermatitis, or even second and third-degree burns. Inhalation of phenol vapor may cause lung edema.[34] The substance may cause harmful effects on the central nervous system and heart, resulting in dysrhythmia, seizures, and coma.[36] The kidneys may be affected as well. Long-term or repeated exposure of the substance may have harmful effects on the liver and kidneys." There is no evidence that phenol causes cancer in humans. Besides its hydrophobic effects, another mechanism for the toxicity of phenol may be the formation of phenoxyl radicals.

Chemical burns from skin exposures can be decontaminated by washing with polyethylene glycol, isopropyl alcohol,[41] or perhaps even copious amounts of water. Removal of contaminated clothing is required, as well as immediate hospital treatment for large splashes. This is particularly important if the phenol is mixed with chloroform (a commonly-used mixture in molecular biology for DNA & RNA purification).

9 - Phenols

The word *phenol* is also used to refer to any compound that contains a six-membered aromatic ring, bonded directly to a hydroxyl group (- OH). Thus, phenols are a class of organic compounds of which the phenol discussed in this article is the simplest member.

Phenol Formaldehyde Resin



Contents

1 - Introduction

Phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. Phenolic resins are mainly used in the production of circuit boards. They are better known however for the production of molded products including pool balls, laboratory countertops, and as coatings and adhesives. In the form of Bakelite, they are the earliest commercial synthetic resin.

2 - Formation and structure

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol:

$$HOC_6H_5 + CH_2O \rightarrow HOC_6H_4CH_2OH$$

The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge :

$$HOC_6H_4CH_2OH + HOC_6H_5 \rightarrow (HOC_6H_4)_2CH_2 + H_2O$$

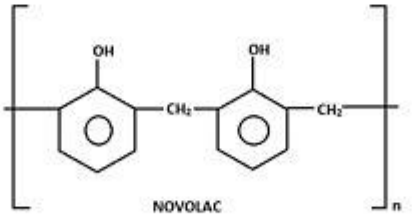
The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is itself an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.

$$2\ HOC_6H_4CH_2OH \rightarrow (HOC_6H_4CH_2)_2O + H_2O$$

3 - Novolacs

Novolacs are phenol-formaldehyde resins with a formaldehyde to phenol molar ratio of less than one. The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids. The phenol units are mainly linked by methylene and/or ether groups. Novolacs are commonly used as photoresists. See also photolithography. The molecular weights are in the low thousands, corresponding to about 10-20 phenol units.

Hexa methylene tetramine or "hexamine" is a hardener added to crosslink novolac. At a temperature > 90 °C, it forms methylene and dimethylene amino bridges.



Novolac

4 - Resoles

Base - catalysed phenol-formaldehyde resins are made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resoles. Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction, at around 70 °C, forms a thick reddish-brown tacky material, which is rich in hydroxymethyl and benzylic ether groups.

The rate of the base-catalysed reaction initially increases with pH, and reaches a maximum at about pH = 10. The reactive species is the phenoxide anion ($C_6H_5O^-$) formed by deprotonation of phenol. The negative charge is delocalised over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde.

Being thermosets, hydroxymethyl phenols will crosslink on heating to around 120 °C to form methylene and methyl ether bridges through eliminating water molecules. At this point the resin is a 3-dimensional network, which is typical of polymerised phenolic resins. The high crosslinking gives this type of phenolic resin its hardness, good thermal stability, and chemical imperviousness. Resols are referred to as "one step" resins as they cure without a cross linker unlike novolacs, a "two step" resin.

Resoles are major polymeric resin materials widely used for gluing and bonding building materials. Exterior plywood, oriented strand boards (OSB), engineered laminated composite lumber (LCL) are typical applications.

5 - Crosslinking and the phenol/formaldehyde ratio

When the molar ratio of formaldehyde:phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely crosslinked. This is why novolacs (F:P <1) don't harden without the addition of a crosslinking agent, and why resoles with the formula F:P >1 will.

6 - Applications

Phenolic resins are found in myriad industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards and household laminates. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control. Snooker balls as well as balls from many table-based ball games are also made from phenol formaldehyde resin. The binding agent in normal (organic) brake pads, brake shoes and clutch disks are phenolic resin.

The Dutch forger Han van Meegeren mixed phenol formaldehyde with his oil paints before baking the finished canvas in order to fake the drying out of the paint over the centuries.

7 - Trade names

Tufnol plate

Bakelaque is a rigid laminate or tube made from phenolic resin on a substrate cotton fabric, paper or glass.

Bakelite is made from phenolic resin and wood flour.

Kooltherm is a rigid closed-cell thermoset insulation

Novotext is cotton fibre-reinforced phenolic, using randomly oriented fibres.

Aquafoam is a phenolic foam developed by Syndicate Sales, Inc. that absorbs and retains water, and is used to grip flowers in the design of floral arrangements.

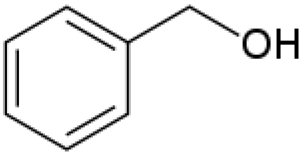
Oasis is "an open-celled phenolic foam that readily absorbs water and is used as a base for flower arrangements."

Paxolin Paperstone and Richlite are made from phenolic resin and paper.

Trymer Green is a rigid cellular phenolic thermal insulation.

Tufnol is made from phenolic resin and woven cotton or linen fabric.

Benzyl Alcohol



Contents

1 - Intoduction

Benzyl alcohol is an organic compound with the formula $C_6H_5CH_2OH$. The benzyl group is often abbreviated "Bn" (not to be confused with "Bz" which is used for benzoyl), thus benzyl alcohol is denoted as BnOH. Benzyl alcohol is a colorless liquid with a mild pleasant aromatic odor. It is a useful solvent due to its polarity, low toxicity, and low vapor pressure. Benzyl alcohol is partially soluble in water (4 g / 100 mL) and completely miscible in alcohols and diethyl ether.

IUPAC name : Phenyl methanol	
Other names : Phenyl carbinol	
Molecular formula	$C_7 H_8 O$
Molar mass	108.14 g mol^{-1}
Appearance	colorless liquid
Odor	slightly aromatic
Density	1.044 g cm^{-3}
Melting point	-15..2 °C
Boiling point	205.3 °C
Solubility in water	4.29 g /100 mL
Solubility	soluble in benzene,

	methanol, chloroform, ethanol, ether, acetone
Refractive index (n_D)	1.5396
Flash point	101 °C
Autoignition temperature	436 °C
LD_{50}	1250 mg / kg (rat , oral)

2 - Occurrence and preparation

Benzyl alcohol is produced naturally by many plants and is commonly found in fruits and teas. It is also found in a variety of essential oils including jasmine, hyacinth, and ylang-ylang.

Benzyl alcohol is prepared by the hydrolysis of benzyl chloride using sodium hydroxide:

$$C_6H_5CH_2Cl + NaOH \rightarrow C_6H_5CH_2OH + NaCl$$

It can also be prepared via a Grignard reaction by reacting phenylmagnesium bromide (C_6H_5MgBr) with formaldehyde, followed by acidification.

3 - Reactions

Like most alcohols, it reacts with carboxylic acids to form esters. In organic synthesis, benzyl esters are popular protecting groups because they can be removed by mild hydrogenolysis.

Benzyl alcohol reacts with acrylonitrile to give *N*-benzylacrylamide. This is an example of a Ritter reaction:

$$C_6H_5CH_2OH + NCCHCH_2 \rightarrow C_6H_5CH_2N(H)C(O)CHCH_2$$

4 - Applications

Benzyl alcohol is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings.[5] It is also a precursor to a variety of esters, used in the soap, perfume, and flavor industries. It is often added to intravenous medication solutions as a preservative due to its bacteriostatic and antipruritic properties. It is also used as a photographic developer.

4 – 1 - Nanotechnological uses

Benzyl alcohol has been used as a dielectric solvent for the dielectrophoretic reconfiguration of nanowires.

4 – 2 - Use in health care

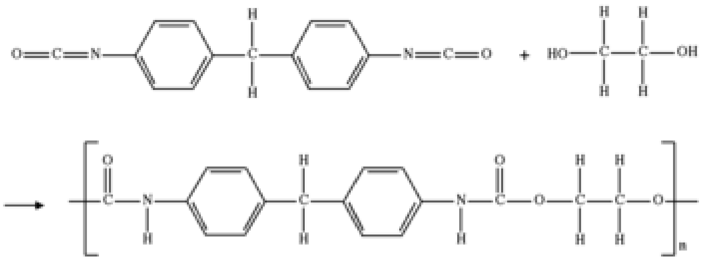
Benzyl alcohol is used as a bacteriostatic preservative at low concentration in intravenous medications. It is oxidized rapidly in healthy individuals to benzoic acid, conjugated with glycine in the liver, and excreted as hippuric acid. High concentrations can result in toxic effects including respiratory failure, vasodilation, hypotension, convulsions, and paralysis. Newborns, especially if critically ill, may not metabolize benzyl alcohol as readily as adults. Reports in the early 1980s of sixteen neonatal deaths associated with the use of saline flush solutions containing benzyl alcohol preservative led to recommendations to avoid its use in neonates.

The use of benzyl alcohol as a 5 % solution has been approved by the U.S. FDA in the treatment of head lice in children older than 6 months and in adults. The product is sold in the United States (prescription-only) as Ulesfia lotion. The benzyl alcohol prevents the lice from closing their respiratory spiracles: the spiracles become blocked with the other products in the lotion, and the lice asphyxiate.[8] The lotion is not effective against louse eggs, and so two applications with an interval of seven days are required to treat a case of louse infestation.

4 – 3 - Other uses

Benzyl alcohol has nearly the same refraction index of quartz and wool fibre. If a clear quartz object is immersed in benzyl alcohol, it becomes almost invisible. This has been used as a method to non-destructively recognize if an object is made of true quartz or not (see crystal skull). Similarly, white wool immersed in benzyl alcohol also becomes almost invisible clearly revealing contaminants such as dark and medullated fibres and vegetable matter.

Poly Urethane



Polyurethane synthesis, wherein the urethane groups — NH-(C=O)-O- link the molecular units.

Contents

1 - Introduction

Polyurethane (**PUR** and **PU**) is a polymer composed of a chain of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available.

Polyurethane polymers are formed by reacting an isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule.

Polyurethane products often are simply called “urethanes”, but should not be confused with ethyl carbamate, which is also called urethane. Polyurethanes neither contain nor are produced from ethyl carbamate.

Polyurethanes are used in the manufacture of flexible, high-resilience foam seating; rigid foam insulation panels; microcellular foam seals and gaskets; durable elastomeric wheels and tires (such as roller coaster wheels); automotive suspension bushings; electrical potting compounds; high performance adhesives; surface coatings and surface sealants; synthetic fibers (e.g., Spandex); carpet underlay; hard-plastic parts (e.g., for electronic instruments); hoses and skateboard wheels.

2 - History

Otto Bayer and his coworkers at I.G. Farben in Leverkusen, Germany, first made polyurethanes in 1937. The new polymers had some advantages over existing plastics that were made by polymerizing olefins, or by polycondensation, and were not covered by patents obtained by Wallace Carothers on polyesters.[2] Early work focused on the production of fibres and flexible foams and PUs were applied on a limited scale as aircraft coating during World War II.[2] Polyisocyanates became commercially available in 1952 and production of flexible polyurethane foam began in 1954 using toluene diisocyanate (TDI) and polyester polyols. These materials were also used to produce rigid foams, gum rubber, and elastomers. Linear fibers were produced from hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO).

In 1956 DuPont introduced polyether polyols, specifically poly(tetramethylene ether) glycol and BASF and Dow Chemical started selling polyalkylene glycols in 1957. Polyether polyols were cheaper, easier to handle and more water resistant than polyester polyols, and became more popular. Union Carbide and Mobay, a U.S. Monsanto/Bayer joint venture, also began making polyurethane chemicals . In 1960 more than 45,000 metric tons of flexible polyurethane foams were produced. The availability of chlorofluoroalkane blowing agents, inexpensive polyether polyols, and methylene diphenyl diisocyanate (MDI) allowed polyurethane rigid foams to be used as high performance insulation materials. In 1967, urethane modified polyisocyanurate rigid foams were introduced, offering even better thermal stability and flammability resistance. During the 1960s, automotive interior safety components such as instrument and door panels were produced by back-filling thermoplastic skins with semi-rigid foam.

In 1969, Bayer exhibited an all plastic car in Düsseldorf, Germany. Parts of this car, such as the fascia and body panels were manufactured using a new process called RIM, Reaction Injection Molding in which the reactants were mixed then injected into a mold. The addition of fillers, such as milled glass, mica, and processed mineral fibres gave rise to reinforced RIM (RRIM), which provided improvements in flexural modulus (stiffness), reduction in coefficient of thermal expansion and thermal stability. This technology was used to make the first plastic-body automobile in the United States, the Pontiac Fiero, in 1983. Further increases in stiffness were obtained by incorporating pre-placed glass mats into the RIM mold cavity, also known broadly as resin injection molding or structural RIM.

Starting in the early 1980s, water-blown microcellular flexible foams were used to mold gaskets for automotive panels and air filter seals, replacing PVC plastisol from automotive applications have greatly increased market share. Polyurethane foams are now used in high temperature oil filter applications.

Polyurethane foam (including foam rubber) is sometimes made using small amounts of blowing agents to give less dense foam, better cushioning/energy absorption or thermal insulation. In the early 1990s, because of their impact on ozone depletion, the Montreal

Protocol restricted the use of many chlorine-containing blowing agents, such as trichlorofluoromethane (CFC-11). By the late 1990s, the use of blowing agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) were widely used in North America and the EU, although chlorinated blowing agents remained in use in many developing countries.

In the 1990s new two-component polyurethane and hybrid polyurethane-polyurea elastomers were used for spray-in-place load bed liners and military marine applications for the U.S. Navy. A one-part polyurethane is specified as high durability deck coatings under MIL-PRF-32171 for the US Navy. This technique for coating creates a durable, abrasion resistant composite with the metal substrate, and eliminates corrosion and brittleness associated with drop-in thermoplastic bed liners.

Rising costs of petrochemical feedstocks and an enhanced public desire for environmentally friendly green products raised interest in polyols derived from vegetable oils.[5] One of the most vocal supporters of these polyurethanes made using natural oil polyols is the Ford Motor Company.

3 - Chemistry

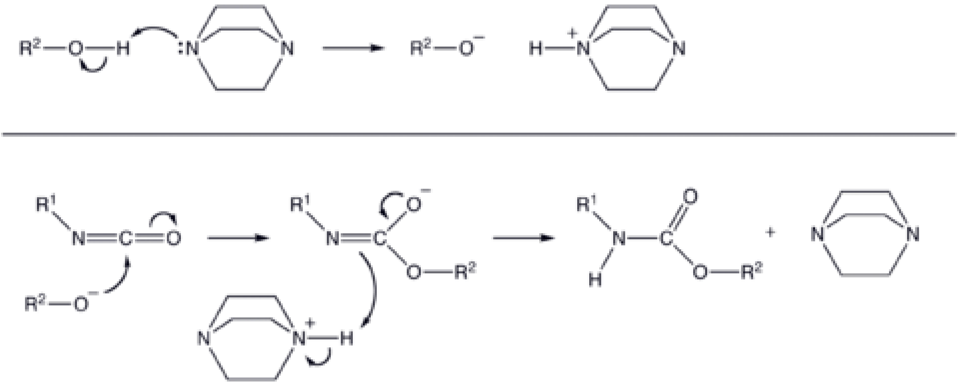
Polyurethanes are in the class of compounds called **reaction polymers**, which include epoxies, unsaturated polyesters, and phenolics . Polyurethanes are produced by reacting an isocyanate containing two or more isocyanates groups per molecule $(R- (N = C= O)_{n \geq 2})$ with a polyol containing on average two or more hydroxy groups per molecule $(R'- (OH)_{n \geq 2})$, in the presence of a catalyst.

The properties of a polyurethane are greatly influenced by the types of isocyanates and polyols used to make it. Long, flexible segments, contributed by the polyol, give soft, elastic polymer. High amounts of crosslinking give tough or rigid polymers. Long chains and low crosslinking give a polymer that is very stretchy, short chains with lots of crosslinks produce a hard polymer while long chains and intermediate crosslinking give a polymer useful for making foam. The crosslinking present in polyurethanes means that the polymer consists of a three-dimensional network and molecular weight is very high. In some respects a piece of polyurethane can be regarded as one giant molecule. One consequence of this is that typical polyurethanes do not soften or melt when they are heated...they are thermosetting polymers. The choices available for the isocyanates and polyols, in addition to other additives and processing conditions allow polyurethanes to have the very wide range of properties that make them such widely used polymers.

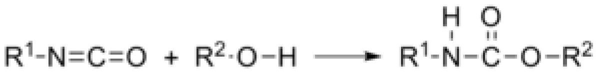
Isocyanates are very reactive materials. This makes them useful in making polymers but also requires special care in handling and use. The aromatic isocyanates, diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) are more reactive than aliphatic isocyanates, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). Most of the isocyanates are difunctional, that is they have exactly two isocyanate groups per molecule. An important exception to this is polymeric diphenylmethane diisocyanate, which is a mixture of molecules with two-, three-, and four- or more isocyanate groups. In cases like this the material has an average functionality greater than two, commonly 2.7. Isocyanates with functionality greater than two act as crosslinking sites as mentioned in the previous paragraph.

Polyols are polymers in their own right and have on average two or more hydroxyl groups per molecule. Polyether polyols are mostly made by polymerizing ethylene oxide and propylene oxide. Polyester polyols are made similarly to polyester polymers. The polyols used to make polyurethanes are not "pure" compounds since they are often mixtures of similar molecules with different molecular weights and mixtures of molecules that contain different numbers of hydroxyl groups, which is why the "average functionality" is often mentioned. Despite them being complex mixtures, industrial grade polyols have their composition sufficiently well controlled to produce polyurethanes having consistent properties. As mentioned earlier, it is the length of the polyol chain and the functionality that contribute much to the properties of the final polymer. Polyols used to make rigid polyurethanes have molecular weights in the hundreds, while those used to make flexible polyurethanes have molecular weights up to ten thousand or more.

PU reaction mechanism catalyzed by a tertiary amine



generalized urethane reaction



$$R^1\text{-N=C=O} + R^2\text{-O-H} \longrightarrow R^1\text{-}\overset{\text{H}}{\text{N}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-}R^2$$

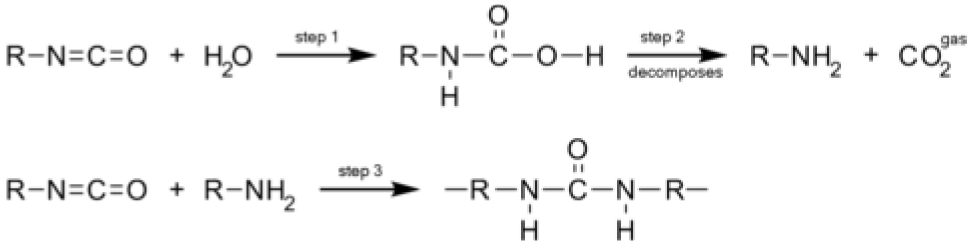
The polymerization reaction makes a polymer containing the urethane linkage, -RNHCOOR'- and is catalyzed by tertiary amines, such as 1,4-diazabicyclo[2.2.2]octane (also called DABCO or TEDA), and metallic compounds, such as dibutyltin dilaurate or bismuth octanoate. This is often referred to as the gellation reaction or simply gelling.

If water is present in the reaction mixture (it is often added intentionally to make foams), the isocyanate reacts with water to form a urea linkage and carbon dioxide gas and the resulting polymer contains both urethane and urea linkages. This reaction is referred to as the blowing reaction and is catalyzed by tertiary amines like bis-(2-dimethylaminoethyl)ether.

A third reaction, particularly important in making insulating rigid foams is the isocyanate trimerization reaction, which is catalyzed by potassium octoate, for example.

One of the most desirable attributes of polyurethanes is their ability to be turned into foam. Making a foam requires the formation of a gas at the same time as the urethane polymerization (gellation) is occurring. The gas can be carbon dioxide, either generated by reacting isocyanate with water. or added as a gas or produced by boiling volatile liquids. In the latter case heat generated by the polymerization causes the liquids to vaporize. The liquids can be HFC-245fa (1,1,1,3,3-penta fluoro propane) and HFC-134a (1,1,1,2-tetra fluoro ethane), and hydrocarbons such as n - pentane.

carbon dioxide gas formed by reacting water and isocyanate



When water is used to produce the gas, care must be taken to use the right combination of catalysts to achieve the proper balance between gellation and blowing. The reaction to generate carbon dioxide involves water molecule reacting with an isocyanate first forming an unstable carbamic acid, which then decomposes into carbon dioxide and an amine. The amine reacts with more isocyanate to give a substituted urea. Water has a very low molecular weight, so even though the weight percent of water may be small, the molar proportion of water may be high and considerable amounts of urea produced. The urea is not very soluble in the reaction mixture and tends to form separate "hard segment" phases consisting mostly of polyurea. The concentration and organization of these polyurea phases can have a significant impact on the properties of the polyurethane foam.

High-density microcellular foams can be formed without the addition of blowing agents by mechanically frothing or nucleating the polyol component prior to use.

Surfactants are used in polyurethane foams to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and surface defects. Rigid foam surfactants are designed to produce very fine cells and a very high closed cell content. Flexible foam surfactants are designed to stabilize the reaction mass while at the same time maximizing open cell content to prevent the foam from shrinking.

An even more rigid foam can be made with the use of specialty trimerization catalysts which create cyclic structures within the foam matrix, giving a harder, more thermally stable structure, designated as polyisocyanurate foams. Such properties are desired in rigid foam products used in the construction sector.

Careful control of viscoelastic properties — by modifying the catalysts and polyols used — can lead to memory foam, which is much softer at skin temperature than at room temperature.

Foams can be either "closed cell", where most of the original bubbles or cells remain intact, or "open cell", where the bubbles have broken but the edges of the bubbles are stiff enough to retain their shape. Open cell foams feel soft and allow air to flow through so they are comfortable when used in seat cushions or mattresses. Closed cell rigid foams are used as thermal insulation, for example in refrigerators.

Microcellular foams are tough elastomeric materials used in coverings of car steering wheels or shoe soles.

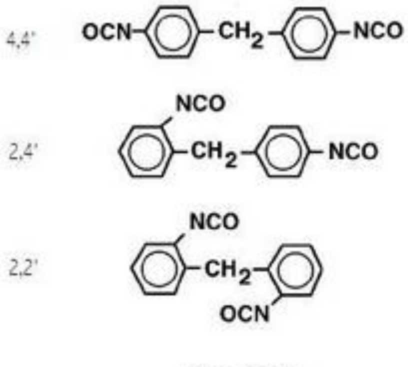
4 - Raw materials

The main ingredients to make a polyurethane are isocyanates and polyols. Other materials are added to help processing the polymer or to change the properties of the polymer.

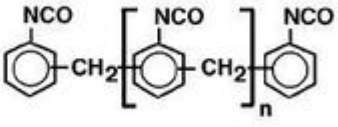
4 – 1 - Isocyanates

Isocyanates used to make polyurethane must have two or more isocyanate groups on each molecule. The most commonly used isocyanates are the aromatic diisocyantes, toluene diisocyanate (TDI) and methylene diphenyl diisocyanate, MDI.

TDI and MDI are generally less expensive and more reactive than other isocyanates. Industrial grade TDI and MDI are mixtures of isomers and MDI often contains polymeric materials. They are used to make flexible foam (for example slabstock foam for mattresses or molded foams for car seats), rigid foam (for example insulating foam in refrigerators) elastomers (shoe soles, for example), and so on. The isocyanates may be modified by partially reacting them with polyols or introducing some other materials to reduce volatility (and hence toxicity) of the isocyanates, decrease their freezing points to make handling easier or to improve the properties of the final polymers.



Pure MDI's



Polymeric MDI's

Aliphatic and cycloaliphatic isocyanates are used in smaller volumes, most often in coatings and other applications where color and transparency are important since polyurethanes made with aromatic isocyanates tend to darken on exposure to light.[14] The most important aliphatic and cycloaliphatic isocyanates are 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate, IPDI), and 4,4'-diisocyanato dicyclohexylmethane, (H_{12}MDI or hydrogenated MDI).

4 – 2 - Polyols

Polyols can be polyether polyols, which are made by the reaction of epoxides with an active hydrogen containing starter compounds, or polyester polyols, which are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. They can be further classified according to their end use. Higher molecular weight polyols (molecular weights from 2,000 to 10,000) are used to make more flexible polyurethanes while lower molecular weight polyols make more rigid products.

Polyols for flexible applications use low functionality initiators such as dipropylene glycol (f = 2), glycerine (f = 3) or a sorbitol/water solution (f = 2.75) . Polyols for rigid applications use high functionality initiators such as sucrose (f = 8) , sorbitol (f = 6), toluenediamine (f = 4) , and Mannich bases (f = 4). Propylene oxide and/or ethylene oxide is added to the initiators until the desired molecular weight is achieved. The order of addition and the amounts of each oxide affect many polyol properties, such as compatibility, water-solubility, and reactivity. Polyols made with only propylene oxide are terminated with secondary hydroxyl groups and are less reactive than polyols capped with ethylene oxide, which contain a higher percentage of primary hydroxyl groups. Graft polyols (also called filled polyols or polymer polyols) contain finely dispersed styrene-acrylonitrile, acrylonitrile, or polyurea (PHD) polymer solids chemically grafted to a high molecular weight polyether backbone. They are used to increase the load-bearing properties of low-density high-resiliency (HR) foam, as well as add toughness to microcellular foams and cast elastomers. Initiators such as ethylenediamine and triethanolamine are used to make low molecular weight rigid foam polyols that have built-in catalytic activity due to the presence of nitrogen atoms in the backbone. A special class of polyether polyols, poly(tetramethylene ether) glycols, which are made by polymerizing tetrahydrofuran, are used in high performance coating, wetting and elastomer applications.

Conventional polyester polyols are based on virgin raw materials and are manufactured by the direct polyesterification of high-purity diacids and glycols, such as adipic acid and 1,4-butanediol. Polyester polyols are usually more expensive and more viscous than polyether polyols, but they make polyurethanes with better solvent, abrasion, and cut resistance. Other polyester polyols are based on reclaimed raw materials. They are manufactured by transesterification (glycolysis) of recycled poly(ethyleneterephthalate) (PET) or dimethylterephthalate (DMT) distillation bottoms with glycols such as diethylene glycol. These low molecular weight, aromatic polyester polyols are used in rigid foam, and bring low cost and excellent flammability characteristics to polyisocyanurate (PIR) boardstock and polyurethane spray foam insulation.

Specialty polyols include polycarbonate polyols, poly capro lactone polyols, poly butadiene polyols, and polysulfide polyols. The materials are used in elastomer, sealant, and adhesive applications that require superior weatherability, and resistance to chemical and environmental attack. Natural oil polyols derived from castor oil and other vegetable oils are used to make elastomers, flexible bunstock, and flexible molded foam. Copolymerizing chlorotrifluoroethylene or tetrafluoroethylene with vinyl ethers containing hydroxyalkyl vinyl ether produces fluorinated (FEVE) polyols. Two component fluorinated polyurethane prepared by reacting FEVE fluorinated polyols with polyisocyanate have been applied for make ambient cure paint/coating. Since fluorinated polyurethanes contain high percentage of fluorine-carbon bond which is the strongest bond among all chemical bonds. Fluorinated polyurethanes have excellent resistance to UV, acids, alkali, salts, chemicals, solvents, weathering, corrosion, fungi and microbial attack. These have become the first choice for high performance coating/paints.

4 – 3 - Chain extenders and cross linkers

Chain extenders ($f = 2$) and cross linkers ($f = 3$ or greater) are low molecular weight hydroxyl and amine terminated compounds that play an important role in the polymer morphology of polyurethane fibers, elastomers, adhesives, and certain integral skin and microcellular foams. The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as cross-links between the amorphous polyether (or polyester) soft segment domains. This phase separation occurs because the mainly non - polar, low melting soft segments are incompatible with the polar, high melting hard segments. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present in coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency. Upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction. This reorientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values . The choice of chain extender also determines flexural, heat, and chemical resistance properties. The most important chain extenders are ethylene glycol, 1,4- butanediol (1,4-BDO or BDO), 1,6-hexanediol, cyclohexane dimethanol and hydroquinone bis(2-hydroxyethyl) ether (HQEE). All of these glycols form polyurethanes that phase separate well and form well defined hard segment domains, and are melt processable. They are all suitable for thermoplastic polyurethanes with the exception of ethylene glycol, since its derived bis-phenyl urethane undergoes unfavorable degradation at high hard segment levels.[7] Diethanolamine and triethanolamine are used in flex molded foams to build firmness and add catalytic activity. Diethyltoluenediamine is used extensively in RIM, and in polyurethane and polyurea elastomer formulations.

table of chain extenders and cross linkers

hydroxyl compounds – difunctional molecules

	MW	**s.g.**	**m.p. °C**	**b.p. °C**
ethylene glycol	62.1	1.110	-13.4	197.4
diethylene glycol	106.1	1.111	-8.7	245.5
triethylene glycol	150.2	1.120	-7.2	287.8
tetraethylene glycol	194.2	1.123	-9.4	325.6

propylene glycol	76.1	1.032	supercools	187.4
dipropylene glycol	134.2	1.022	supercools	232.2
tripropylene glycol	192.3	1.110	supercools	265.1
1,3-propanediol	76.1	1.060	-28	210
1,3-butanediol	92.1	1.005	-	207.5
1,4-butanediol	92.1	1.017	20.1	235
neopentyl glycol	104.2	-	130	206
1,6-hexanediol	118.2	1.017	43	250
1,4-cyclohexanedimethanol	-	-	-	-
HQEE	-	-	-	-
ethanolamine	61.1	1.018	10.3	170
diethanolamine	105.1	1.097	28	271
methyldiethanolamine	119.1	1.043	-21	242
phenyldiethanolamine	181.2	-	58	228
hydroxyl compounds – trifunctional molecules				
	MW	**s.g.**	**f.p. °C**	**b.p. °C**
glycerol	92.1	1.261	18.0	290
trimethylolpropane	-	-	-	-
1,2,6-hexanetriol	-	-	-	-
triethanolamine	149.2	1.124	21	-
hydroxyl compounds – tetrafunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
pentaerythritol	136.2	-	260.5	-
N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine	-	-	-	-
amine compounds – difunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
diethyltoluenediamine	178.3	1.022	-	308
dimethylthiotoluenediamine	214.0	1.208	-	-

4 – 4 - Catalysts

Polyurethane catalysts can be classified into two broad categories, amine compounds and metal complexes. Traditional amine catalysts have been tertiary amines such as triethylenediamine (TEDA, 1,4-diazabicyclo[2.2.2]octane or DABCO), dimethyl cyclo hexylamine (DMCHA), and dimethylethanolamine (DMEA). Tertiary amine catalysts are selected based on whether they drive the urethane (polyol+isocyanate, or gel) reaction, the urea (water+isocyanate, or blow) reaction, or the isocyanate trimerization reaction (e.g., using potassium acetate, to form isocyanurate ring structure). Catalysts that contain a hydroxyl group or secondary amine, which react into the polymer matrix, can replace traditional catalysts thereby reducing the amount of amine that can come out of the polymer.

Metallic compounds based on mercury, lead, tin, bismuth, and zinc are used as polyurethane catalysts. Mercury carboxylates, are particularly effective catalysts for polyurethane elastomer, coating and sealant applications, since they are very highly selective towards the polyol+isocyanate reaction, but they are toxic. Bismuth and zinc carboxylates have been used as alternatives. Alkyl tin carboxylates, oxides and mercaptides oxides are used in all types of polyurethane applications. Tin mercaptides are used in formulations that contain water, as tin carboxylates are susceptible to hydrolysis.

4 – 5 - Surfactants

Surfactants are used to modify the characteristics of both foam and non-foam polyurethane polymers. They take the form of polydimethylsiloxane-polyoxyalkylene block copolymers, silicone oils, nonylphenol ethoxylates, and other organic compounds. In foams, they are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and sub-surface voids. In non-foam applications they are used as air release and anti-foaming agents, as wetting agents, and are used to eliminate surface defects such as pin holes, orange peel, and sink marks.

5 - Production

Polyurethanes are produced by mixing two or more liquid streams. The isocyanate is usually added by itself and the polyol stream is usually more complex, containing catalysts, surfactants, blowing agents and so on. The two components are referred to as a polyurethane system, or simply a system. The isocyanate is commonly referred to in North America as the 'A-side' or just the 'iso'. The blend of polyols and other additives is commonly referred to as the 'B-side' or as the 'poly'. This mixture might also be called a 'resin' or 'resin blend'. In Europe the meanings for 'A-side' and 'B-side' are reversed. Resin blend additives may include chain extenders, cross linkers, surfactants, flame retardants, blowing agents, pigments, and fillers. Polyurethane can be made in a variety of densities and hardnesses by varying the isocyanate, polyol or additives.

6 - Health and safety

Fully reacted polyurethane polymer is chemically inert.[25] No exposure limits have been established by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity. Polyurethane polymer is a combustible solid and can be ignited if exposed to an open flame.[26] Decomposition from fire can produce mainly carbon monoxide, and trace nitrogen oxides and hydrogen cyanide. Firefighters should wear self-contained breathing apparatus in enclosed areas.

Liquid resin blends and isocyanates may contain hazardous or regulated components. They should be handled in accordance with manufacturer recommendations found on product labels, and in MSDS (Material Safety Data Sheet) and product technical literature. Isocyanates are known skin and respiratory sensitizers, and proper engineering controls should be in place to prevent exposure to isocyanate liquid and vapor. Additionally, amines, glycols, and phosphate present in spray polyurethane foams present unknown risks to the individuals exposed to them.[27] Proper hygiene controls and personal protective equipment (PPE), such as gloves, respirators, and protective clothing and eye wear should be used.

In the United States, additional health and safety information can be found through organizations such as the Polyurethane Manufacturers Association (PMA) and the Center for the Polyurethanes Industry (CPI), as well as from polyurethane system and raw material manufacturers. In Europe, health and safety information is available from ISOPA,[28] the European Diisocyanate and Polyol Producers Association. Regulatory information can be found in the Code of Federal Regulations Title 21 (Food and Drugs) and Title 40 (Protection of the Environment).

7 - Fungus

Students at Yale University have noticed a fungus that eats polyurethane . This fact was reported from a trip to the Ecuadorian Amazon and the fungus is called *Pestalotiopsis microspora*.

8 - Manufacturing

The methods of manufacturing polyurethane finished goods range from small, hand pour piece-part operations to large, high-volume bunstock and boardstock production lines. Regardless of the end-product, the manufacturing principle is the same: to meter the liquid isocyanate and resin blend at a specified stoichiometric ratio, mix them together until a homogeneous blend is obtained, dispense the reacting liquid into a mold or on to a surface, wait until it cures, then demold the finished part.

8 – 1 - Dispensing equipment

Although the capital outlay can be high, it is desirable to use a meter-mix or dispense unit for even low-volume production operations that require a steady output of finished parts. Dispense equipment consists of material holding (day) tanks, metering pumps, a mix head, and a control unit. Often, a conditioning or heater-chiller unit is added to control material temperature in order to improve mix efficiency, cure rate, and to reduce process variability. Choice of dispense equipment components depends on shot size, throughput, material characteristics such as viscosity and filler content, and process control. Material day tanks may be single to hundreds of gallons in size, and may be supplied directly from drums, IBCs (intermediate bulk containers, such as totes), or bulk storage tanks. They may incorporate level sensors, conditioning jackets, and mixers. Pumps can be sized to meter in single grams per second up to hundreds of pounds per minute. They can be rotary, gear, or piston pumps, or can be specially hardened lance pumps to meter liquids containing highly abrasive fillers such as wollastonite, chopped or hammer milled glass fibres.

A high pressure mix head, showing material supply and hydraulic actuator lines. Rear view.

The pumps can drive low-pressure (10 to 30 bar, ~1 to 3 MPa) or high-pressure (125 to 250 bar, ~12.5 to 25.0 MPa) dispense systems. Mix heads can be simple static mix tubes, rotary element mixers, low-pressure dynamic mixers, or high-pressure hydraulically actuated direct impingement mixers. Control units may have basic on/off – dispense/stop switches, and analogue pressure and temperature gauges, or may be computer controlled with flow meters to electronically calibrate mix ratio, digital temperature and level sensors, and a full suite of statistical process control software. Add-ons to dispense equipment include nucleation or gas injection units, and third or fourth stream capability for adding pigments or metering in supplemental additive packages.

8 – 2 - Tooling

Distinct from pour - in - place, bun and boardstock, and coating applications, the production of piece parts requires some type of tooling to contain and form the reacting liquid. The choice of mold-making material is dependent on the expected number of uses to end-of-life (EOL), molding pressure, flexibility, and heat transfer characteristics.

RTV silicone is used for tooling that has an EOL in the thousands of parts. It is typically used for molding rigid foam parts, where the ability to stretch and peel the mold around undercuts is needed. The heat transfer characteristic of RTV silicone tooling is poor. High-performance, flexible polyurethane elastomers are also used in this way.

Epoxy, metal-filled epoxy, and metal-coated epoxy is used for tooling that has an EOL in the tens-of-thousands of parts. It is typically used for molding flexible foam cushions and seating, integral skin and microcellular foam padding, and shallow-draft RIM bezels and fascia. The heat transfer characteristic of epoxy tooling is fair; the heat transfer characteristic of metal-filled and metal-coated epoxy is good. Copper tubing can be incorporated into the body of the tool, allowing hot water to circulate and heat the mold surface.

Aluminum is used for tooling that has an EOL in the hundreds-of-thousands of parts. It is typically used for molding microcellular foam gasketing and cast elastomer parts, and is milled or extruded into shape.

Mirror-finish stainless steel is used for tooling that imparts a glossy appearance to the finished part. The heat transfer characteristic of metal tooling is excellent.

Finally, molded or milled polypropylene is used to create low-volume tooling for molded gasket applications. Instead of many expensive metal molds, low-cost plastic tooling can be formed from a single metal master, which also allows greater design flexibility. The heat transfer characteristic of polypropylene tooling is poor, which must be taken into consideration during the formulation process.

9 - Applications

In 2007, the global consumption of polyurethane raw materials was above 12 million metric tons, the average annual growth rate is about 5 %.

10 - Testing

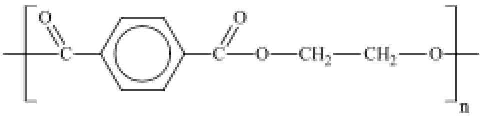
10 – 1 - Effects of visible light

Polyurethanes, especially those made using aromatic isocyanates, contain chromophores which interact with light. This is of particular interest in the area of polyurethane coatings, where light stability is a critical factor and is the main reason that aliphatic isocyanates are used in making polyurethane coatings. When PU foam, which is made using aromatic isocyanates, is exposed to visible light it discolors, turning from off-white to yellow to reddish brown. It has been generally accepted that apart from yellowing, visible light has little effect on foam properties.[31][32] This is especially the case if the yellowing happens on the outer portions of a large foam, as the deterioration of properties in the outer portion has little effect on the overall bulk properties of the foam itself.

It has been reported that exposure to visible light can affect the variability of some physical property test results.[33] Consequently, it was recommended that foam samples should be protected from exposure to light prior to testing.

Higher-energy UV radiation promotes chemical reactions in foam, some of which are detrimental to the foam structure.[34]

Poly Ethylene Terephthalate



Contents

1 - Introduction

Polyethylene terephthalate (sometimes written poly(ethylene terephthalate)), commonly abbreviated **PET**, **PETE**, or the obsolete

PETP or PET-P, is a thermoplastic polymer resin of the polyester family and is used in synthetic fibers; beverage, food and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber. The term *polyethylene terephthalate* is a source of confusion because this substance, PET, does not contain polyethylene. Thus, the alternate form, *poly(ethylene terephthalate)*, is often used in scholarly journals for the sake of accuracy and clarity.

Depending on its processing and thermal history, polyethylene terephthalate may exist both as an amorphous (transparent) and as a semi-crystalline polymer. The semicrystalline material might appear transparent (particle size < 500 nm) or opaque and white (particle size up to a few microns) depending on its crystal structure and particle size. Its monomer (bis-β-hydroxyterephthalate) can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct. Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification / trans esterification) with water as the byproduct.

IUPAC name : poly(ethylene terephthalate)	
Molecular formula	$(C_{10}H_8O_4)_n$
Molar mass	variable
Density	1.38 g/cm^3 (20 °C), amorphous: 1.370 g/cm^3, single crystal: 1.455 g/cm^3
Melting point	> °C250 °C, 260 °C
Boiling point	> °C350 °C (decomposes)
Solubility in water	practically insoluble[3]
Thermal conductivity	0.15 to 0.24 W m^{-1} K^{-1}
Refractive index (n_D)	1.57–1.58, 1.5750
Specific heat capacity, *C*	1.0 kJ/(kg·K)[1]

The majority of the world's PET production is for synthetic fibers (in excess of 60 %), with bottle production accounting for around 30% of global demand. In the context of textile applications, PET is referred to by its common name, "polyester," whereas the acronym "PET" is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the third-most-produced polymer; polyethylene (PE) and polypropylene (PP) are first and second, respectively.

PET consists of polymerized units of the monomer ethylene terephthalate, with repeating $C_{10}H_8O_4$ units. PET is commonly recycled, and has the number "1" as its recycling symbol.

PET

Young's modulus (E)	2800 – 3100 MPa
Tensile strength (σ_t)	55 –75 MPa
Elastic limit	50 –150 %
notch test	3.6 kJ / m^2
Glass transition temperature (Tg)	67 to 81 °C
Vicat B	82 °C
linear expansion coefficient (α)	7×10^{-5}/K
Water absorption (ASTM)	0.16

2 - Uses

Because PET is an excellent barrier material, plastic bottles made from PET are widely used for soft drinks (see carbonation). For certain specialty bottles, PET sandwiches an additional polyvinyl alcohol layer to further reduce its oxygen permeability.

Biaxially oriented PET film (often known by one of its trade names, "Mylar") can be aluminized by evaporating a thin film of metal onto it to reduce its permeability, and to make it reflective and opaque (MPET). These properties are useful in many applications, including flexible food packaging and thermal insulation such as "space blankets". Because of its high mechanical strength, PET film is often used in tape applications, such as the carrier for magnetic tape or backing for pressure sensitive adhesive tapes.

Non-oriented PET sheet can be thermoformed to make packaging trays and blisters. If crystallizable PET is used, the trays can be used for frozen dinners, since they withstand both freezing and oven baking temperatures.

When filled with glass particles or fibers, it becomes significantly stiffer and more durable.

PET is also used as substrate in thin film and solar cell.

3 - History

PET was patented in 1941 by John Rex Whinfield, James Tennant Dickson and their employer the Calico Printers' Association of Manchester. E. I. DuPont de Nemours in Delaware, USA, first used the trademark **Mylar** in June of 1951 and received registration of it in 1952.[5] It is still the most well known name used for polyester film. The current owner of the trademark is Dupont Teijin Films US, a partnership with a Japanese company.

The PET bottle was patented in 1973 by Nathaniel Wyeth.

4 - Physical properties

Sailcloth is typically made from PET fibers also known as polyester or under the brand name Dacron; colorful lightweight spinnakers are usually made of nylon.

PET in its natural state is a colorless, semi-crystalline resin. Based on how it is processed, PET can be semi-rigid to rigid, and it is very lightweight. It makes a good gas and fair moisture barrier, as well as a good barrier to alcohol (requires additional "barrier" treatment) and solvents. It is strong and impact-resistant.

About 60 % crystallization is the upper limit for commercial products, with the exception of polyester fibers. Besides, about 60% crystalline polymer about 40% of the polymer chains remaining amorphous. Clear products can be produced by rapidly cooling molten polymer below T_g glass transition temperature to form an amorphous solid. Like glass, amorphous PET forms when its molecules are not given enough time to arrange themselves in an orderly, crystalline fashion as the melt is cooled. At room temperature the molecules are frozen in place, but, if enough heat energy is put back into them by heating above T_g, they begin to move again, allowing crystals to nucleate and grow. This procedure is known as solid-state crystallization.

When allowed to cool slowly, the molten polymer forms a more crystalline material. This material has spherulites containing many small crystallites when crystallized from an amorphous solid, rather than forming one large single crystal. Light tends to scatter as it crosses the boundaries between crystallites and the amorphous regions between them. This scattering means that crystalline PET is opaque and white in most cases. Fiber drawing is among the few industrial processes that produce a nearly single-crystal product.

4 – 1 - Intrinsic viscosity

One of the most important characteristics of PET is referred to as intrinsic viscosity (IV)

The intrinsic viscosity of the material, found by extrapolating to zero concentration of relative viscosity to concentration which is measured in deciliters per gram (dℓ / g) . Intrinsic viscosity is dependent upon the length of its polymer chains but has no units due to being extrapolated to zero concentration. The longer the polymer chains the more entanglements between chains and therefore the higher the viscosity. The average chain length of a particular batch of resin can be controlled during polycondensation.

The intrinsic viscosity range of PET

Fiber grade
0.40 – 0.70 Textile
0.72 – 0.98 Technical, tire cord
Film grade
0.60 – 0.70 BoPET (biaxially oriented PET film)
0.70 – 1.00 Sheet grade for thermoforming
Bottle grade
0.70 – 0.78 Water bottles (flat)
0.78 – 0.85 Carbonated soft drink grade
Monofilament, engineering plastic
1.00 – 2.00

5 - Drying

PET is hygroscopic, meaning that it absorbs water from its surroundings. However, when this 'damp' PET is then heated, the water hydrolyzes the PET, decreasing its resilience. Thus, before the resin can be processed in a molding machine, it must be dried. Drying is achieved through the use of a desiccant or dryers before the PET is fed into the processing equipment.

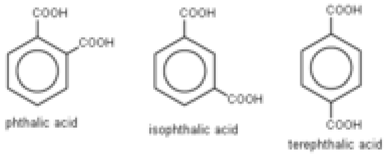
Inside the dryer, hot dry air is pumped into the bottom of the hopper containing the resin so that it flows up through the pellets, removing moisture on its way. The hot wet air leaves the top of the hopper and is first run through an after-cooler, because it is easier to remove moisture from cold air than hot air. The resulting cool wet air is then passed through a desiccant bed. Finally, the cool dry air leaving the desiccant bed is re-heated in a process heater and sent back through the same processes in a closed loop. Typically, residual moisture levels in the resin must be less than 50 parts per million (parts of water per million parts of resin, by weight) before processing. Dryer residence time should not be shorter than about four hours. This is because drying the material in less than 4 hours would require a temperature above 160 °C, at which level hydrolysis would begin inside the pellets before they could be dried out.

PET can also be dried in compressed air resin dryers. Compressed air dryers do not reuse drying air. Dry, heated compressed air is circulated through the PET pellets as in the desiccant dryer, then released to the atmosphere.

6 - Copolymers

In addition to pure (homopolymer) PET, PET modified by copolymerization is also available.

In some cases, the modified properties of copolymer are more desirable for a particular application. For example, cyclohexane dimethanol (CHDM) can be added to the polymer backbone in place of ethylene glycol. Since this building block is much larger (6 additional carbon atoms) than the ethylene glycol unit it replaces, it does not fit in with the neighboring chains the way an ethylene glycol unit would. This interferes with crystallization and lowers the polymer's melting temperature. In general, such PET is known as PETG or PET-G (Polyethylene Terephtalate Glycol-modified; Eastman Chemical, SK Chemicals, and Artenius Italia are some PETG manufacturers). PETG is a clear amorphous thermoplastic that can be injection molded or sheet extruded. It can be colored during processing.



Replacing terephthalic acid (right) with isophthalic acid (center) creates a kink in the PET chain, interfering with crystallization and lowering the polymer's melting point.

Another common modifier is isophthalic acid, replacing some of the 1,4-(*para*-) linked terephthalate units. The 1,2-(*ortho*-) or 1,3-(*meta*-) linkage produces an angle in the chain, which also disturbs crystallinity.

Such copolymers are advantageous for certain molding applications, such as thermoforming, which is used for example to make tray or blister packaging from co-PET film, or amorphous PET sheet (A-PET) or PETG sheet. On the other hand, crystallization is important in other applications where mechanical and dimensional stability are important, such as seat belts. For PET bottles, the use of small amounts of isophthalic acid, CHDM, DEG or other comonomers can be useful: if only small amounts of comonomers are used, crystallization is slowed but not prevented entirely. As a result, bottles are obtainable via stretch blow molding ("SBM"), which are both clear and crystalline enough to be an adequate barrier to aromas and even gases, such as carbon dioxide in carbonated beverages.

7 - Production

Polyethylene terephthalate is produced from ethylene glycol and dimethyl terephthalate ($C_6H_4(CO_2CH_3)_2$) or terephthalic acid.

The former is a transesterification reaction, whereas the latter is an esterification reaction.

7 – 1 - Dimethyl terephthalate process

In dimethyl terephthalate process, this compound and excess ethylene glycol are reacted in the melt at 150–200 °C with a basic catalyst. Methanol (CH_3OH) is removed by distillation to drive the reaction forward. Excess ethylene glycol is distilled off at higher temperature with the aid of vacuum. The second transesterification step proceeds at 270–280 °C, with continuous distillation of ethylene glycol as well.

The reactions are idealized as follows :

First step

$$C_6H_4(CO_2CH_3)_2 + 2\ HOCH_2CH_2OH \rightarrow C_6H_4(CO_2CH_2CH_2OH)_2 + 2\ CH_3OH$$

Second step

$$n\ C_6H_4(CO_2CH_2CH_2OH)_2 \rightarrow [(CO)C_6H_4(CO_2CH_2CH_2O)]_n + n\ HOCH_2CH_2OH$$

7 - 2 - Terephthalic acid process

In the terephthalic acid process, esterification of ethylene glycol and terephthalic acid is conducted directly at moderate pressure (2.7–5.5 bar) and high temperature (220–260 °C). Water is eliminated in the reaction, and it is also continuously removed by distillation:

$$n\ C_6H_4(CO_2H)_2 + n\ HOCH_2CH_2OH \rightarrow [(CO)C_6H_4(CO_2CH_2CH_2O)]_n + 2n\ H_2O$$

8 - Degradation

PET is subjected to various types of degradations during processing. The main degradations that can occur are hydrolytic, thermal and, probably most important, thermal oxidation. When PET degrades, several things happen: discoloration, chain scissions resulting in reduced molecular weight, formation of acetaldehyde, and cross-links ("gel" or "fish-eye" formation). Discoloration is due to the formation of various chromophoric systems following prolonged thermal treatment at elevated temperatures. This becomes a problem when the optical requirements of the polymer are very high, such as in packaging applications. The thermal and thermooxidative degradation results in poor processibility characteristics and performance of the material.

One way to alleviate this is to use a copolymer. Comonomers such as CHDM or isophthalic acid lower the melting temperature and reduce the degree of crystallinity of PET (especially important when the material is used for bottle manufacturing). Thus, the resin can be plastically formed at lower temperatures and/or with lower force. This helps to prevent degradation, reducing the acetaldehyde content of the finished product to an acceptable (that is, unnoticeable) level. See copolymers, above. Another way to improve the stability of the polymer is to use stabilizers, mainly antioxidants such as phosphites. Recently, molecular level stabilization of the material using nanostructured chemicals has also been considered.

8 – 1 - Acetaldehyde

Acetaldehyde is a colorless, volatile substance with a fruity smell. Although it forms naturally in some fruit, it can cause an off-taste in bottled water. Acetaldehyde forms by degradation of PET through the mishandling of the material. High temperatures, (PET decomposes above 300 °C or 570 °F), high pressures, extruder speeds (excessive shear flow raises temperature), and long barrel residence times all contribute to the production of acetaldehyde. When acetaldehyde is produced, some of it remains dissolved in the walls of a container and then diffuses into the product stored inside, altering the taste and aroma. This is not such a problem for non-consumables (such as shampoo), for fruit juices (which already contain acetaldehyde), or for strong-tasting drinks like soft drinks. For bottled water, however, low acetaldehyde content is quite important, because, if nothing masks the aroma, even extremely low concentrations (10–20 parts per billion in the water) of acetaldehyde can produce an off-taste.

8 – 2 - Antimony

Antimony (Sb) is a metalloid element that is used as a catalyst in the form of the compound such as antimony trioxide (Sb_2O_3) or antimony triacetate in the production of PET. After manufacturing, a detectable amount of antimony can be found on the surface of the product. This residue can be removed with washing. Antimony also remains in the material itself and can, thus, migrate out into food and drinks. Exposing PET to boiling or microwaving can increase the levels of antimony significantly, possibly above USEPA maximum contamination levels. The drinking water limit assessed by WHO is 20 parts per billion (WHO, 2003), and the drinking water limit in the USA is 6 parts per billion . Although antimony trioxide is of low toxicity when taken orally , its presence is still of concern. The Swiss Federal Office of Public Health investigated the amount of antimony migration, comparing waters bottled in PET and glass: The antimony concentrations of the water in PET bottles were higher, but still well below the allowed maximum concentration. The Swiss Federal Office of Public Health concluded that small amounts of antimony migrate from the PET into bottled water, but that the health risk of the resulting low concentrations is negligible (1% of the "tolerable daily intake" determined by the WHO). A later (2006) but more widely publicized study found similar amounts of antimony in water in PET bottles . The WHO has published a risk assessment for antimony in drinking water.

Fruit juice concentrates (for which no guidelines are established), however, that were produced and bottled in PET in the UK were found to contain up to 44.7 µg / L of antimony, well above the EU limits for tap water of 5 µg / L.

9 - Safety

Commentary published in Environmental Health Perspectives in April 2010 suggested that PET might yield endocrine disruptors under conditions of common use and recommended[17] research on this topic. Proposed mechanisms include leaching of phthalates as well as leaching of antimony.

10 - Bottle processing equipment

There are two basic molding methods for PET bottles, one-step and two-step. In two-step molding, two separate machines are used. The first machine injection molds the preform, which resembles a test tube, with the bottle-cap threads already molded into place. The body of the tube is significantly thicker, as it will be inflated into its final shape in the second step using stretch blow molding.

In the second step, the preforms are heated rapidly and then inflated against a two-part mold to form them into the final shape of the bottle. Preforms (uninflated bottles) are now also used as robust and unique containers themselves; besides novelty candy, some Red Cross chapters distribute them to homeowners to store medical history for emergency responders.

In one-step machines, the entire process from raw material to finished container is conducted within one machine, making it especially suitable for molding non-standard shapes (custom molding), including jars, flat oval, flask shapes etc. Its greatest merit is the reduction in space, product handling and energy, and far higher visual quality than can be achieved by the two-step system.

11 - Polyester recycling industry

While most thermoplastics can, in principle, be recycled, PET bottle recycling is more practical than many other plastic applications because of the high value of the resin and the almost exclusive use of PET for widely used water and carbonated soft drink bottling. PET has a resin identification code of 1. The prime uses for recycled PET are polyester fiber, strapping, and non-food containers.

Because of the recyclability of PET and the relative abundance of post-consumer waste in the form of bottles, PET is rapidly gaining market share as a carpet fiber. Mohawk Industries released everSTRAND in 1999, a 100% post-consumer recycled content PET fiber. Since that time, more than 17 billion bottles have been recycled into carpet fiber.[20] Pharr Yarns, a supplier to numerous carpet manufacturers including Looptex, Dobbs Mills, and Berkshire Flooring , produces a BCF (bulk continuous filament) PET carpet fiber containing a minimum of 25 % post -consumer recycled content.

PET, as with many plastics, is also an excellent candidate for thermal disposal (incineration), as it is composed of carbon, hydrogen, and oxygen, with only trace amounts of catalyst elements (but no sulfur). PET has the energy content of soft coal.

When recycling polyethylene terephthalate or PET or polyester, in general two ways have to be differentiated:

The chemical recycling back to the initial raw materials purified terephthalic acid (PTA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) where the polymer structure is destroyed completely , or in process intermediates like bis - ß - hydroxy terephthalate

The mechanical recycling where the original polymer properties are being maintained or reconstituted.

Chemical recycling of PET will become cost-efficient only applying high capacity recycling lines of more than 50,000 tons/year. Such lines could only be seen, if at all, within the production sites of very large polyester producers. Several attempts of industrial magnitude to establish such chemical recycling plants have been made in the past but without resounding success. Even the promising chemical recycling in Japan has not become an industrial break through so far. The two reasons for this are: at first, the difficulty of consistent and continuous waste bottles sourcing in such a huge amount at one single site, and, at second, the steadily increased prices and price volatility of collected bottles. The prices of baled bottles increased for instance between the years 2000 and 2008 from about 50 Euro/ton to over 500 Euro/ton in 2008.

Mechanical recycling or direct circulation of PET in the polymeric state is operated in most diverse variants today. These kinds of processes are typical of small and medium-size industry. Cost-efficiency can already be achieved with plant capacities within a range of 5 000 – 20 000 tons/year. In this case, nearly all kinds of recycled-material feedback into the material circulation are possible today. These diverse recycling processes are being discussed hereafter in detail.

Besides chemical contaminants and degradation products generated during first processing and usage, mechanical impurities are representing the main part of quality depreciating impurities in the recycling stream. Recycled materials are increasingly introduced into manufacturing processes, which were originally designed for new materials only. Therefore, efficient sorting, separation and cleaning processes become most important for high quality recycled polyester.

When talking about polyester recycling industry, we are concentrating mainly on recycling of PET bottles, which are meanwhile used for all kinds of liquid packaging like water, carbonated soft drinks, juices, beer, sauces, detergents, household chemicals and so on. Bottles are easy to distinguish because of shape and consistency and separate from waste plastic streams either by automatic or by hand-sorting processes. The established polyester recycling industry consists of three major sections:

PET bottle collection and waste separation — waste logistics
Production of clean bottle flakes — flake production
Conversion of PET flakes to final products — flake processing

Intermediate product from the first section is baled bottle waste with a PET content greater than 90 %. Most common trading form is the bale but also bricked or even loose, pre-cut bottles are common in the market. In the second section, the collected bottles are converted to clean PET bottle flakes. This step can be more or less complex and complicated depending on required final flake quality. During the third step, PET bottle flakes are processed to any kind of products like film, bottles, fiber, filament, strapping or intermediates like pellets for further processing and engineering plastics.

Besides this external (post-consumer) polyester bottle recycling, numbers of internal (pre-consumer) recycling processes exist, where the wasted polymer material does not exit the production site to the free market, and instead is reused in the same production circuit. In this way, fiber waste is directly reused to produce fiber, preform waste is directly reused to produce preforms, and film waste is directly reused to produce film.

11 – 1 - PET bottle recycling

11 – 1 – 1 - Purification and decontamination

The success of any recycling concept is hidden in the efficiency of purification and decontamination at the right place during processing and to the necessary or desired extent.

In general, the following applies: The earlier in the process foreign substances are removed, and the more thoroughly this is done, the more efficient the process is.

The high Plasticizer temperature of PET in the range of 280 °C is the reason why almost all common organic impurities such as PVC, PLA, polyolefin, chemical wood-pulp and paper fibers, polyvinyl acetate, melt adhesive, coloring agents, sugar, and protein residues are transformed into colored degradation products that, in their turn, might release in addition reactive degradation products. Then, the number of defects in the polymer chain increases considerably. The particle size distribution of impurities is very wide, the big particles of 60–1000 µm — which are visible by naked eye and easy to filter — representing the lesser evil, since their total surface is relatively small and the degradation speed is therefore lower. The influence of the microscopic particles, which — because they are many — increase the frequency of defects in the polymer, is comparable bigger.

The motto "What the eye does not see the heart cannot grieve over" is considered to be very important in many recycling processes. Therefore besides efficient sorting the removal of visible impurity particles by melt filtration processes is playing a particular part in this case.

In general, one can say that the processes to make PET bottle flakes from collected bottles are as versatile as the different waste streams are different in their composition and quality. In view of technology there isn't just one way to do it. Meanwhile, there are many engineering companies that are offering flake production plants and components, and it is difficult to decide for one or other plant design. Nevertheless, there are processes that are sharing most of these principles. Depending on composition and impurity level of input material, the general following process steps are applied.

Bale opening, briquette opening
Sorting and selection for different colors, foreign polymers especially PVC, foreign matter, removal of film, paper, glass, sand, soil, stones, and metals

Pre-washing without cutting
Coarse cutting dry or combined to pre-washing
Removal of stones, glass, and metal
Air sifting to remove film, paper, and labels
Grinding, dry and / or wet
Removal of low-density polymers (cups) by density differences
Hot-wash

Caustic wash, and surface etching, maintaining intrinsic viscosity and decontamination

Rinsing

Clean water rinsing

Drying

Air-sifting of flakes

Automatic flake sorting

Water circuit and water treatment technology

Flake quality control

11 – 1 – 2 - Impurities and material defects

The number of possible impurities and material defects that accumulate in the polymeric material is increasing permanently—when processing as well as when using polymers—taking into account a growing service lifetime, growing final applications and repeated recycling. As far as recycled PET bottles are concerned, the defects mentioned can be sorted in the following groups:

Reactive polyester OH- or COOH- end groups are transformed into dead or non-reactive end groups, e.g. formation of vinyl ester end groups through dehydration or decarboxylation of terephthalate acid, reaction of the OH- or COOH- end groups with mono-functional degradation products like mono-carbonic acids or alcohols. Results are decreased reactivity during re-polycondensation or re-SSP and broadening the molecular weight distribution.

The end group proportion shifts toward the direction of the COOH end groups built up through a thermal and oxidative degradation. The results are decrease in reactivity, and increase in the acid autocatalytic decomposition during thermal treatment in presence of humidity.

Number of polyfunctional macromolecules increases. Accumulation of gels and long-chain branching defects.

Number, concentration, and variety of nonpolymer-identical organic and inorganic foreign substances are increasing. With every new thermal stress, the organic foreign substances will react by decomposition. This is causing the liberation of further degradation-supporting substances and coloring substances.

Hydroxide and peroxide groups build up at the surface of the products made of polyester in presence of air (oxygen) and humidity. This process is accelerated by ultraviolet light. During an ulterior treatment process, hydro peroxides are a source of oxygen radicals, which are source of oxidative degradation. Destruction of hydro peroxides is to happen before the first thermal treatment or during plasticization and can be supported by suitable additives like antioxidants.

Taking into consideration the above-mentioned chemical defects and impurities, there is an ongoing modification of the following polymer characteristics during each recycling cycle, which are detectable by chemical and physical laboratory analysis.

In particular:

Increase of COOH end - groups

Increase of color number b

Increase of haze (transparent products)

Increase of oligomer content

Reduction in filterability

Increase of by-products content such as acetaldehyde, formaldehyde

Increase of extractable foreign contaminants

Decrease in color L

Decrease of intrinsic viscosity or dynamic viscosity

Decrease of crystallization temperature and increase of crystallization speed

Decrease of the mechanical properties like tensile strength, elongation at break or elastic modulus

Broadening of molecular weight distribution

The recycling of PET-bottles is meanwhile an industrial standard process that is offered by a wide variety of engineering companies.

11 – 2 - Processing examples for recycled polyester

Recycling processes with polyester are almost as varied as the manufacturing processes based on primary pellets or melt. Depending on purity of the recycled materials, polyester can be used today in most of the polyester manufacturing processes as blend with virgin polymer or increasingly as 100 % recycled polymer. Some exceptions like BOPET-film of low thickness, special applications like optical film or yarns through FDY-spinning at > 6000 m/min, micro filaments, and micro-fibers are produced from virgin polyester only.

11 – 2 – 1 - Simple re-pelletizing of bottle flakes

This process consists in transforming bottle waste into flakes, by drying and crystallizing the flakes, by plasticizing and filtering, as well as by pelletizing. Product is an amorphous re-granulate of an intrinsic viscosity in the range of 0.55 – 0.7 dℓ / g, depending on how complete pre-drying of PET flakes has been done.

Special feature are: Acetaldehyde and oligomers are contained in the pellets at lower level; the viscosity is reduced somehow, the pellets are amorphous and have to be crystallized and dried before further processing.

Processing to:

A-PET film for thermoforming
Addition to PET virgin production
BoPET packaging film
PET Bottle resin by SSP
Carpet yarn
Engineering plastic
Filaments
Non-woven
Packaging stripes
Staple fibre.

Choosing the re-pelletizing way means having an additional conversion process that is, at the one side, energy-intensive and cost-consuming, and causes thermal destruction. At the other side, the pelletizing step is providing the following advantages:

Intensive melt filtration
Intermediate quality control
Modification by additives
Product selection and separation by quality
Processing flexibility increased
Quality uniformization.

11 – 2 – 2 - Manufacture of PET-pellets or flakes for bottles (bottle to bottle) and A-PET

This process is, in principle, similar to the one described above; however, the pellets produced are directly (continuously or discontinuously) crystallized and then subjected to a solid-state polycondensation (SSP) in a tumbling drier or a vertical tube reactor. During this processing step, the corresponding intrinsic viscosity of 0.80 – 0.085 dℓ/g is rebuild again and, at the same time, the acetaldehyde content is reduced to < 1 ppm.

The fact that some machine manufacturers and line builders in Europe and USA make efforts to offer independent recycling processes, e.g. the so-called bottle-to-bottle (B-2-B) process, such as BePET, Starlinger, URRC or BÜHLER, aims at generally furnishing proof of the "existence" of the required extraction residues and of the removal of model contaminants according to FDA applying the so-called challenge test, which is necessary for the application of the treated polyester in the food sector. Besides this process approval it is nevertheless necessary that any user of such processes has to constantly check the FDA-limits for the raw materials manufactured by himself for his process.

11 – 2 – 3 - Direct conversion of bottle flakes

In order to save costs, an increasing number of polyester intermediate producers like spinning mills, strapping mills, or cast film mills are working on the direct use of the PET-flakes, from the treatment of used bottles, with a view to manufacturing an increasing number of polyester intermediates. For the adjustment of the necessary viscosity, besides an efficient drying of the flakes, it is possibly necessary to also reconstitute the viscosity through polycondensation in the melt phase or solid-state polycondensation of the flakes. The latest PET flake conversion processes are applying twin screw extruders, multi-screw extruders or multi-rotation systems and coincidental vacuum degassing to remove moisture and avoid flake pre-drying. These processes allow the conversion of undried PET flakes without substantial viscosity decrease caused by hydrolysis.

With regard to the consumption of PET bottle flakes, the main portion of about 70 % is converted to fibers and filaments. When using directly secondary materials such as bottle flakes in spinning processes, there are a few processing principles to obtain.

High-speed spinning processes for the manufacture of POY normally need a viscosity of 0.62 – 0.64 dℓ / g. Starting from bottle flakes, the viscosity can be set via the degree of drying. The additional use of Ti O_2 is necessary for full dull or semi dull yarn. In order to protect the spinnerets, an efficient filtration of the melt is, in any case is necessary. For the time-being, the amount of POY made of 100% recycling polyester is rather low because this process requires high purity of spinning melt. Most of the time, a blend of virgin and recycled pellets is used.

Staple fibers are spun in an intrinsic viscosity range that lies rather somewhat lower and that should be between 0.58 and 0.62 dℓ/g. In this case, too, the required viscosity can be adjusted via drying or vacuum adjustment in case of vacuum extrusion. For adjusting the viscosity, however, an addition of chain length modifier like ethylene glycol or diethylene glycol can also be used.

Spinning non-woven — in the fine titer field for textile applications as well as heavy spinning non-woven as basic materials, e.g. for roof covers or in road building — can be manufactured by spinning bottle flakes. The spinning viscosity is again within a range of 0.58–0.65 dℓ/g.

One field of increasing interest where recycled materials are used is the manufacture of high-tenacity packaging stripes, and monofilaments. In both cases, the initial raw material is a mainly recycled material of higher intrinsic viscosity. High-tenacity packaging stripes as well as monofilament are then manufactured in the melt spinning process.

11 – 3 - Recycling to the monomers

Polyethylene terephthalate can be depolymerized to yield the constituent monomers. After purification, the monomers can be used to prepare new polyethylene terephthalate. The ester bonds in polyethylene terephthalate may be cleaved by hydrolysis, or by transesterification. The reactions are simply the reverse of those used in production.

11 – 3 – 1 - Partial glycolysis

Partial glycolysis (transesterification with ethylene glycol) converts the rigid polymer into short-chained oligomers that can be melt-filtered at low temperature. Once freed of the impurities, the oligomers can be fed back into the production process for polymerization.

The task consists in feeding 10 – 25 % bottle flakes while maintaining the quality of the bottle pellets that are manufactured on the line. This aim is solved by degrading the PET bottle flakes — already during their first plasticization, which can be carried out in a single- or multi-screw extruder — to an intrinsic viscosity of about 0.30 dℓ/g by adding small quantities of ethylene glycol and by subjecting the low-viscosity melt stream to an efficient filtration directly after plasticization. Furthermore, temperature is brought to the lowest possible limit. In addition, with this way of processing, the possibility of a chemical decomposition of the hydro peroxides is possible by adding a corresponding P-stabilizer directly when plasticizing. The destruction of the hydro peroxide groups is, with other processes, already carried out during the last step of flake treatment for instance by adding H_3PO_3.[24] The partially glycolyzed and finely filtered recycled material is continuously fed to the esterification or prepolycondensation reactor, the dosing quantities of the raw materials are being adjusted accordingly.

11 - 4 - Total glycolysis, methanolysis, and hydrolysis

The treatment of polyester waste through total glycolysis to fully convert the polyester to bis(2-hydroxyethyl) terephthalate ($C_6H_4(CO_2CH_2CH_2OH)_2$). This compound is purified by vacuum distillation, and is one of the intermediates used in polyester manufacture (see production). The reaction involved is as follows:

$$[(CO)C_6H_4(CO_2CH_2CH_2O)]_n + n\ HOCH_2CH_2OH \rightarrow n\ C_6H_4(CO_2CH_2CH_2OH)_2$$

This recycling route has been executed on an industrial scale in Japan as experimental production.

Similar to total glycolysis, methanolysis converts the polyester to dimethyl terephthalate, which can be filtered and vacuum distilled:

$$[(CO)C_6H_4(CO_2CH_2CH_2O)]_n + 2n\ CH_3OH \rightarrow n\ C_6H_4(CO_2CH_3)_2$$

Methanolysis is only rarely carried out in industry today because polyester production based on dimethyl terephthalate has shrunk tremendously, and many dimethyl terephthalate producers have disappeared.

Also as above, polyethylene terephthalate can be hydrolyzed to terephthalic acid and ethylene glycol under high temperature and pressure. The resultant crude terephthalic acid can be purified by recrystallization to yield material suitable for re-polymerization:

$$[(CO)C_6H_4(CO_2CH_2CH_2O)]_n + 2n\ H_2O \rightarrow n\ C_6H_4(CO_2H)_2 + n\ HOCH_2CH_2OH$$

This method does not appear to have been commercialized yet.

Contents

Poly Propylene Glycol	890
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