Consortium for
Educational
Communication

Module
on

Industrial Production Of Alcohols

By

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TEXT

Introduction

Physical properties

Alcohols are colourless liquids with a special faint odour. Aliphatic alcohols burn with blue flame (without smoke) while aromatic alcohols burn with yellow smoky flame. Boiling point of alcohols are considerably high it increases as the molecular weight increases (alcohols have the ability to form H - bond). Alcohols are miscible with water except benzyl alcohol, cyclohexanol, and *sec*-butanol (which are very slightly soluble in water).

Structure

Similar to water, an alcohol can be pictured as having an sp^3 hybridized tetrahedral oxygen atom with nonbonding pairs of electrons occupying two of the four sp^3 hybrid orbitals. Alkyl groups are generally bulkier than hydrogen atoms, however, so the R–O–H bond angle in alcohols is generally larger than the ١٠٤,٥° H–O–H bond angle in water. For example, the ١٠٨,٩° bond angle in methanol shows the effect of the methyl group, which is larger than the hydrogen atom of water.

Classification of alcohols

Alcohols fall into different classes depending on how the OH group is positioned on the chain of carbon atoms. There are some chemical differences between the various types.

➢ Primary alcohols

In a primary (1°) alcohol, the carbon which carries the OH group is only attached to one alkyl group. Example: Ethanol, propan-1-ol, 2-methylpropan-1-ol.

There is an exception to this. Methanol, CH3OH, is counted as a primary alcohol even though there are *no* alkyl groups attached to the carbon with the OH group on it.

➢ Secondary alcohols

In a secondary (2°) alcohol, the carbon with the OH group attached is joined directly to *two* alkyl groups, which may be the same or different. Examples: Propane-2-ol, butan-2-ol, pentan-3-ol.

- **Tertiary alcohols**

In a tertiary (3°) alcohol, the carbon atom holding the OH group is attached directly to *three* alkyl groups, which may be any combination of same or different. Examples: 2-methylpropan-2-ol, 2-methylbutan-2-ol.

Nomenclature

As with other types of organic compounds, alcohols are named by both formal and common systems. The most generally applicable system is that adopted at a meeting of the International Union of Pure and Applied Chemistry (IUPAC) in Paris in ١٩٥٧. Using the IUPAC system, the name for an alcohol uses the -ol suffix with the name of the parent alkane, together with a number to give the location of the hydroxyl group. The rules are summarized in a three-step procedure:

- Name the longest carbon chain that contains the carbon atom bearing the −OH group. Drop the final -e from the alkane name, and add the suffix -ol.
- Number the longest carbon chain starting at the end nearest the −OH group, and use the appropriate number, if necessary, to indicate the position of the −OH group.
- Name the substituents, and give their numbers as for an alkane or alkene

Industrial production of alcohols

One of the most commonly served beverages in the world, ethanol is consumed by millions of adults each years. Ethanol is commercially produced using a process called fermentation; this is the process in which yeasts is used to break down glucose into alcohol and CO_2. Carbon dioxide gas bubbles out of the fermenting solution into the air leaving a mixture of ethanol and water, which is later distilled and then sold to individuals looking to get drunk.

The first four alcohol functional groups (methanol, ethanol, propanol, butanol) can be biological synthesized to be used as an alternative to fossil fuels as they burn very cleanly, producing only CO_2 and water. Ethanol can be made from sources such as corn and sugar making it a useful renewable resource for countries which can't meet their petrol needs.

Ethanol fermentation

Ethanol fermentation, also called **alcoholic fermentation**, is a biological process which converts sugars such as glucose, fructose, and sucrose into cellular energy, producing ethanol and carbon dioxide as a side-effect. Because yeasts perform this conversion in the absence of oxygen, alcoholic fermentation is considered an anaerobic process.

Ethanol fermentation has many uses, including the production of alcoholic beverages, the production of ethanol fuel, and bread baking

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; cider and perry are produced by similar fermentation of natural sugar in apples and pears, respectively; and other fruit wines are produced from the fermentation of the sugars in any other kinds of fruit. Brandy and eaux de vie (e.g. slivovitz) are produced by distillation of these fruit-fermented beverages.
- 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 malted (i.e. germinated). Other sources of starch (e.g. potatoes and unmalted grain) may be added to the mixture, as the amylase will act on those starches as well. Whiskey and vodka are also distilled; gin and related beverages are produced by the addition of flavoring agents to a vodka-like feedstock during distillation.
- Rice wines (including sake) are produced by the fermentation of grain starches converted to sugar by the mold *Aspergillus oryzae*. *Baijiu*, *soju*, and *shōchū* are distilled from the product of such fermentation.
- Rum a ll 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 nd some other beverages are produced by fermentation and distillation

of sugarcane. Rum is usually produced from the sugarcane product molasses.

Alcoholic beverages

These products of alcoholic fermentations originated in spontaneous fermentation processes are of great antiquity. However, it is only in recent years that modern methods of industrial microbiology have been applied to their manufacture. In principle, the production of alcoholic beverages is similar to the production of industrial ethyl alcohol. These fermentation processes do not suffer competition from synthetics products. This is because the character of the beverage is dependent upon interactions between a variety of biological factors that have not yet been denned in chemical or physical terms. In beverage production refinements are introduced with respect to flavour, aroma, colour, and sanitation that are not necessary in the making of industrial alcohol.

Beer: *Beer* is made by the yeast fermentation of grains to ethanol and carbon dioxide. There are five major steps in the manufacture of *beer* or *ale* from grain. These are *malting, mashing, 'fermenting, maturing,* and *finishing. Malting* and *mashing* are concerned with the conversion of starch into fermentable form such as maltose or glucose. The chief raw material is *malt,* which is germinated barley that has been dried and ground. It contains stanch, proteins, and high concentration of amylases and proteinases. Amylases convert the starch into fermentable sugar. Mould amylase derived from *Aspergillus oryzae* is sometimes used for the same purpose. Ground malt is mashed in warm water to bring about the digestion of starch and proteins. The aqueous extract contains dextrins, maltose, and other sugars, protein breakdown products, minerals and various growth factors. This is a rich nutrient medium and is called *beer wort.* The beer wort is filtered and *hops* are added, *Hops* are the flowers of *Humulus lupulus.* They are added for flavour, colour, aroma and for mild antibacterial activity to prevent the growth of spoilage bacteria.

A large inoculum of selected strain of *Saccharomyces cerevisiae* is added to the wort to bring about a vigorous fermentation. Yeasts are classified as *'top yeasts'* or *'bottom yeasts. Top yeasts* float on the surface of a fermenting mixture and are employed in making *ale.* Bottom yeasts settle in the fermentation tank and are used in making *beer.* Beer fermentation takes place at 6 to 12°C, whereas ale fermentation is complete in five to seven days at 14 to 23°C. The alcoholic content of beer is between 3 to 6 % and that of ale is somewhat higher.

The fermented wort is refrigerated at 0°C for two weeks to several months to remove the harsh flavour and other undesirable characteristics. Some of the harshness attributed to higher alcohols disappears as they are oxidized or esterified during *aging*. Finishing process consists of carbonation, cooling, filtering and dispensing into barrels, bottles, and cans. Bottled or canned beer is usually pasteurized at 60°C for 20 minutes to kill yeasts and other microorganisms. As an alternative, the beer may be passed through a filter to remove microorganisms, and then aseptically dispensed into sterile cans.

Brewing process

Work in the brewery is typically divided into 7 steps: Mashing, Lautering, Boiling, Fermenting, Conditioning, Filtering, and Filling.

Mashing: Mashing is the process of mixing milled grain (typically malted grain) with water, and heating this mixture up with rests at certain temperatures to allow enzymes in the malt to break down the starch in the grain into sugars, typically maltose.

Lautering: Lautering is the separation of the extracts won during mashing from the spent grain. It is achieved in either a lauter tun, a wide vessel with a false bottom, or a mash filter, a plate-and-frame filter designed for this kind of separation. Lautering has 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.

Lauter tun: A lauter tun is the traditional vessel used for separation of the extracted wort. While the basic principle of its operation has remained the same since its first use, technological advances have led to better designed lauter tuns capable of quicker and more complete extraction of the sugars from the grain. The false bottom in a lauter tun has thin slits to hold back the solids and allow liquids to pass through. The solids, not the false bottom, form a filtration medium and hold back small solids, allowing the otherwise cloudy mash to run out of the lauter tun as a clear liquid. The false bottom of a lauter tun is today made of wedge wire, which can provide a free-flow surface in the bottom of the tun. In the past the run-off tubes flowed through swan-neck valves into a wort collection grant. While visually stunning, this system led to a lot of oxygen uptake. Such a system has mostly been replaced either by a central wort-collection vessel or the arrangement of outlet ports into concentric zones, with each zone having a ring-shaped collection pipe. Brewhouses in plain public view, particularly those in brewpubs, often maintain the swan-neck valves and grant for their visual effect. A quality lauter tun has rotating rake arms with a central drive unit. Depending on the size of the lauter tun, there can be between two and six rake arms. Cutting blades hang from these arms. The blade is usually wavy and has a plough-like foot. Each blade has its own path around the tun and often the whole rake assembly can be raised and lowered. Attached to each of these arms is a flap which can be raised and lowered for pushing the spend grains out of the tun. The brewer, or better yet an automated system, can raise and lower the rake arms depending on the turbidity (cloudiness) of the run-off, and the tightness of the grain bed, as measured by the pressure difference between the top and bottom of the grain bed.

A system will introduce sparge water into the lauter tun. Most systems have a ring of spray heads that insure an even and gentle introduction of the sparge water. The watering system should not beat down on the grain bed and form a channel. Large breweries have self-closing inlets on the bottom of the tun through which the mash is transferred to the lauter tun, and one outlet, also on the bottom of the tun, into which the spent grains fall after lautering is complete. Craft breweries often have many ways on the side of the mash tun for spent grain removal, which then must be helped along to a large extent by the brewer. Some small breweries use a combination mash/lauter tun, in which the rake system cannot be implemented because the mixing mechanism for mashing is of higher importance. The stirring blades can be used as an ersatz rake, but typically they cannot be moved up and down, and would disturb the bed too much were they used deep in the grain bed.

Mash Filter: A 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 doesn't act like a filtration medium in a mash filter.

Boiling: Boiling the won extracts, called wort, ensures its sterility, and thus prevents a lot of infections. During the boil hops are added, which contribute bitterness, flavor, and aroma compounds to the beer, and, along with the heat of the boil, causes proteins in the wort to coagulate and the pH of the wort to fall. Finally, the vapours produced during the boil volatilize off flavours, including dimethyl sulfide precursors. The boil must be conducted so that is it even and intense. The boil lasts between 50 and 120 minutes, depending on its intensity, the hop addition schedule, and volume of wort the brewer expects to evaporate.

Wine

Wine is the product made by the normal alcoholic fermentation of the juice of sound, ripe grapes and the usual cellar treatment. Beverages produced by the alcoholic fermentation of other fruits and certain vegetable products-are also called wines for example, peach wine, orange wine, cherry wine. Wine making is a much simpler process. It can be made by a direct fermentation of sugars, i.e. glucose and fructose, instead of starch which requires hydrolysis to yield sugars. Many fruits have the wine yeast *Saccharomyces cerevisiae* var. *ellipsoideus* on them. All that is necessary is to crush the fruits. An alcoholic fermentation starts spontaneously. The characteristic qualities of famous wines are attributed in part to strains of yeast found in certain localities. However, undesirable moulds, wild yeasts, and bacteria are also likely to be present and the fermentation may not give a predictably good product. Many wine makers now destroy natural yeasts by adding sulphur dioxide to the raw juice.

The grapes are crushed carefully and the juice is collected. To the raw juice or *must;* sulphur dioxide is added as sodium meta-bisulphite. The *must* is then inoculated with a starter culture-of a selected strain *of S. cerevisiae var. elliposideus.* At the start the *must* is aerated slightly to promote vigorous yeast growth. Once the fermentation sets in, the rapid production of carbon dioxide maintains anaerobic condition. The temperature of fermentation is usually 25 to 30°C and the process may extend from few days to 2 weeks. The yield of ethanol varies from 7 to 15 percent (by volume). The wine is placed in large casks to settle, clarify and age for two to five years to develop a good flavour and aroma.

Wines are endless in their varieties and differ in so many attributes that it is difficult to classify them. According to colour, the two most basic types are *red* and *white wine.* In making *red wines* the grapes are crushed and stemmed but the skins and seeds are left in the must. *White wines* are made from white grapes or from the juice of grapes from which the skins have been removed. *Dry wines* are those which contain too little sugar to be detected by taste. In *sweet wines* the sugar content is high enough to be detected by taste. *Sparkling wines* contain carbon dioxide. They are made effervescent by secondary fermentation in closed containers, generally in the bottle itself. *Still wines* are those which do not contain carbon dioxide. *Fortified wines* contain added alcohol in the form of *brandy.*

High quality, red wine grapes have colourless juice. The entire red colour is in the grape skins, and winemakers must leave the juice in contact with the skins for a considerable time to extract the colour. Red wine is made by crushing the grapes and then fermenting the juice, the pulp, the skins and the seeds together for several days. Near the end of sugar fermentation, a wine press is used to separate the liquid from the solid materials.

White wine is made by a different process. First the grapes are crushed and pressed immediately to separate the juice from the solids. After pressing, the skins, stems and seeds are discarded, and the juice is cooled to a low temperature. Then the cold juice is allowed to settle for several hours, and the clear juice is decanted off the residue before it is fermented. White wine is made by fermenting clarified juice. These are the fundamental differences between making quality, red wine and white wine. At first glance, the two winemaking processes may appear similar because several steps are identical. Nevertheless, the steps are done in a different sequence, and the sequence makes a large change in wine characteristics.

- **Ethyl alcohol production from carbohydrates by fermentation (yeast)**

Ethyl alcohol can be produced by fermentation of any carbohydrate containing a fermentable sugar, or a polysaccharide that can be hydrolysed to a fermentable sugar. The equation that describes the net result of alcoholic fermentation by yeast is:

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

It indicates that a sugar is the substrate and that the process is anaerobic. Selected strains of *Saccharomyces cerevisiae* are commonly employed for fermentation. It is imperative that the strain must have a high tolerance for alcohol, must grow vigorously and produce a large quantity of alcohol.

In recent years the production of industrial alcohol by the fermentation process has declined because of the-increased cost of raw materials and the rapid developments of synthetic ethanol production. Industrial alcohol will probably continue to be obtained on a diminished scale from certain processes. For example alcohol is obtained as the end product in the processes designed to reduce biological oxygen demand (BOD) of some industrial wastes, including whey and sulphite waste of paper mills. The large amount of carbon dioxide evolved from decarboxylation of pyruvate during the fermentation period is recovered and converted to solid carbon dioxide.

- **Ethyl alcohol (ethanol) production from Molasses by fermentation**

Sugar industries produce molasses from the sugar cane processing. Molasses have 50 -55% concentration of sugar in the form of sucrose, with chemical formula $C_{12}H_{22}O_{11}$. This source of compound is used for preparing ethyl alcohol. Ethanol in the form of absolute and rectified spirit can be made from molasses. Basis raw materials for an industry to produce 1 ton of ethyl alcohol requires, molasses up to 5.6 tons, sulfuric acid 27 kg and ammonium sulphate 2.5 kg.

The chemical reactions involved for ethanol production from molasses:

Main reaction:

$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$, with enzyme invertase.

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ -٣١٫٢ KCal, with enzyme zymase.

Side reaction:

$2C_6H_{12}O_6 + H_2O \rightarrow ROH + RCHO$ (high molecular weight alcohols C_2H_5OH)

Description of the ethanol production process:

Large volume storage tanks of molasses provide continuous supply of molasses and store the fresh molasses from sugar processing section during the fermentation process. The molasses from the tanks are diluted with water to obtain the sugar concentration around 10-15%. The acidic nature of molasses supports the growth of yeast during breaks up of sucrose, for that purpose acids are added to maintain the pH between 4 and 5. Continuous diluter equipment takes up this task. A yeast culture tank, which is provided with nutrition supply of ammonium and magnesium phosphate or sulphate, is used as nutrient to the yeast. The acidic condition favours the yeast to produce catalytic enzymes, invertase and zymase.

Diluted and treated molasses and the yeast from storage are fed to the fermentation chamber. Modern fermentation tanks are made with stainless steel material provided with heating coils or jacket provision. The temperature 20-30 ^{o}C is maintained in the tanks by the heating and cooling system. The process of fermentation takes place around 30-70 hours based on the temperature and sugar concentration to yeast count. Final temperature 35 °C is attained at the end of the process. During the fermentation process, microorganism yeast produces carbon dioxide as by-product.

After the process cycle, the product liquid mixture is fed to beer still to perform distillation. Solid and slurry mass is separated leaving the solution of alcohol and water. The concentration of alcohol in the liquid mixture would around 8-10%. A series of beer still work out to produce different quality of beer products. The slurry form of material obtained from bottom of beer still is called as slops. It is used for cattle feed and fertilizer after some waste treatment operations.

However, the aldehydes are not allowed in consumable beer so aldehydes present in the solution are removed by aldehyde column. The streams coming out at different section of the column are aldehydes from top, fusel oil and ethanol mixture from middle and bottom stream with water. The middle stream is fed to rectification column to produce a product called rectified spirit having 95% ethanol. Rectified spirit further made to absolute alcohol by anhydrous still using benzene as third component. Absolute alcohol with 100% ethanol concentration is a standard product used as intermediate for producing other chemical products and blending agent in power fuels. The end use of the ethanol would be largely in solvent, acetaldehyde, acetic acid, polyethylene and synthetic rubber production.

- **Ethanol production from starch and sugar based materials**

Current commercial production of ethanol is based almost exclusively on starch and sugar based feed stocks. In the United States, the ethanol industry is dominated by corn, with 91.5 percent of production capacity from facilities using corn alone and another 7.9 percent of capacity from facilities using a blend of corn and other grain (e.g., corn and milo), with corn as the primary feedstock (EPA, 2010). Facilities using other grains (e.g., wheat, milo) without corn make up an additional 0.4 percent of capacity.

There are two main processes for producing ethanol from corn: **dry-milling** and **wet-milling**. Both processes involve breaking down the starch in the corn kernel into simple sugars and then fermenting the sugars to create ethanol. The primary difference between the two methods is whether the entire kernel is processed, as in corn dry-milling; or if the corn kernel is first broken down into its individual components (i.e., germ, fiber, gluten, and starch) prior to processing, as in corn wet-milling. Dry mill ethanol plants generally produce only one primary co-product, distillers grain with solubles (DGS), which can be sold wet (WDGS) or dried (DDGS) for use as animal feed. In contrast, the corn wet-milling process of separating shelled corn into its components, prior to processing, increases the number of co-products realized, usually gluten feed, gluten meal, food-grade corn oil, and DGS.

Table 1. Production steps in Corn Dry-Milling

Production Steps	**Primary Inputs**	**Primary Outputs**	**Operations Performed**
Receipt, storage, and inspection	Shelled corn	Stored corn	- Receive shelled corn by truck or rail - Unload corn into receiving pits - Transfer corn to storage bins or silos - Inspect corn upon receipt
Cleaning	Shelled corn from storage	Cleaned whole corn kernels	- Pass corn through screeners or scalpers to remove oversized and smaller material - Pass corn through other steps (e.g., destoner, magnet) to remove other unwanted objects
Milling	Cleaned whole corn kernels	Fine corn flour	- Transfer whole kernels to a hammer mill, impact mill, or other milling operation - Crush and grind shelled corn into a fine flour
Liquefaction	Fine corn flour	"Mash" (liquid mixture of corn flour and other corn parts)	- Mix fine corn flour with water in large cook or slurry tanks - Add chemicals to adjust the slurry's pH - Add enzymes (alpha amylase) to solution to break down corn starch into dextrins
Saccharification	"Mash"	Mash with starch broken down into simple sugars	- Add enzymes (glucoamylase) to mash to breakdown dextrins into glucose
Fermentation	Mash with starch broken down into simple sugars	"Beer" mixture containing ethanol and solids from grain and yeast; and carbon dioxide	- Add yeast to convert glucose in mash into ethanol and carbon dioxide - Pump beer to separate storage vessel

Distillation and dehydration	"Beer" mixture (fermented mash)	Denatured ethanol	Pump beer mixture into a continuous distillation system, which may contain multiple columns - Collect purified ethanol from the vapor portion of columns and spent solids (stillage) from the bottom - Purify ethanol stream in rectifying column, molecular sieve, or other production equipment - Add denaturant to ethanol in cases where ethanol is not used for human consumption - Store denatured ethanol in tanks until distribution
Co-product processing	Stillage from distillation columns	Wet distillers' grain and/or dried distillers' grain with solubles (DDGS)	Reduce moisture content in stillage by using centrifuges, dryers, or other equipment - Make selected co-products by mixing varying quantities of dry products with other materials - Load dry products into trucks, railcars, or other means of transport for distribution

Methanol Production

Production methods

The by far dominating production method of methanol synthesis is through the synthesis gas process first developed during the 1920s. A gas mixture of hydrogen and carbon monoxide (usually also carbon dioxide), known as synthesis gas (syngas) is the basis for almost all methanol production today.

- **Methanol production from biomass**

In contrast to ethanol, methanol can rather easily be produced from virtually all biomass such as wood, algae, agricultural waste and municipal waste through gasification. Production from biomass does however offer challenges that need to be addressed especially regarding the cost of production. The conventional method to produce methanol from biomass is through gasification of the feedstock material.

The gasification process of biomass is similar to the synthesis gas process from coal. For gasification of biomass the feedstock is first dried and pulverized. The moist content should generally be no higher than 15-20 wt%. The first step in a two-step gasification process is called pyrolysis, or destructive distillation. The dried biomass is heated to 400-600 °C in an oxygen deficient environment to prevent complete combustion. Carbon monoxide, carbon dioxide, hydrogen, methane as well as water and volatile tars are released. The remaining biomass (≈10–25 wt%),called charcoal. is further reacted with oxygen at high temperature (1300-1500 °C) to produce mainly carbon monoxide.

The synthesis gas produced from the pyrolysis and charcoal conversion is purified before the methanol synthesis. Compared to coal biomass consists of much less sulphur but the tar content offers operational challenges as it condense easily in pipes, filters and boilers. This can to an extent be controlled by choosing the right operational pattern and technique according to the composition of the available biomass. A one step partial oxidation process is an attractive alternative but the technical challenges have so far prevented large scale operation.

An alternative that has been proposed to solve or ease the transportation demands is to first convert the biomass to bio-crude through fast pyrolysis. Dried and atomized biomass is quickly heated to about 400-600 °C in atmospheric pressure and then quenched to avoid cracking. The result is a black liquid called bio crude that can be transported more easily.

- **Methanol production in chemical industry**

Methanol is primarily used 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.

Condensation of methanol molecules to produce hydrocarbon chains and even aromatic systems has been demonstrated with loss of water, carbon monoxide, and/or carbon dioxide (loss of oxygen is prohibited on thermodynamic grounds). As early as 1880, an aromatisation reaction which generated hexamethylbenzene as a minor product with a mixture of mostly aliphatic hydrocarbons directly from methanol, using zinc chloride as catalyst, had been demonstrated. At 283 °C, the melting point of $ZnCl_2$, the idealised reaction for the production of hexamethylbenzene has a ΔG of -261 kcal mol^{-1}.

$$15CH_3OH \rightarrow C_6(CH_3)_6 + 3CH_4 + 15H_2O$$

In the early 1970s, a process was developed by Mobil for producing gasoline fuel for 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. Methanol (or less commonly, ethanol) is a component in the transesterification of triglycerides for production of biodiesel.

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

Of high interest to the petrochemical marketplace, methanol is an important ingredient in new and lower-cost methods for producing propylene, which is much in demand. Such methods include Methanol-to-Olefins (MTO), Methanol-to-Propylene (MTO/MTP), Metathesis, Propane Dehydrogenation (PDH), High Severity FCC, and Olefins Cracking.

The market for proponyl became tight when the ethane prices fell in the USA with the exploration of shale gas reserves. The low priced 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.

- **Methanol production as fuel for vehicles**

Methanol is occasionally used 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, mainly because, in the event of an accident, methanol does not produce an opaque cloud of smoke. Since the late 1940s, Methanol is also used as the primary fuel ingredient in the powerplants for radio control, control line, free flightairplanes, cars and trucks; such engines use a platinum filament glow plug that ignites the methanol vapor through a catalytic reaction. Drag racers, mud racers, and heavily modified tractor pullers also use methanol as the 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 on methanol. As a fuel for mud racers, methanol mixed with gasoline and nitrous oxide produces more power than gasoline and nitrous oxide alone.

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

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

One problem with high concentrations of methanol in fuel is that alcohols corrode some metals, particularly aluminium. An acid, albeit weak, methanol 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. Methanol's corrosivity has been addressed with methanol-compatible materials and fuel additives that serve as corrosion inhibitors.

Organic methanol, produced from wood or other organic materials (bioalcohol), has been suggested as a renewable alternative to petroleum-based hydrocarbons. Low levels of methanol can be used in existing vehicles with the addition of cosolvents and corrosion inhibitors.

Methanol fuel has been proposed for ground transportation. The chief advantage of a methanol economy is that it could be adapted to gasoline internal combustion engines with minimum modification to the engines and to the infrastructure that delivers and stores liquid fuel.

Isopropyl alcohol (propan-2-ol), also called **isopropanol** or **dimethyl carbinol**, is a compound with the chemical formula $\mathbf{C_3H_8O}$ or C_3H_7OH or $CH_3CHOHCH_3$. It is a colorless, flammable chemical compound with a strong odor. As a propyl group linked to a hydroxyl group, it is the simplest example of a secondary alcohol, where the alcohol carbon atom is attached to two other carbon atoms, sometimes shown as $(CH_3)_2CHOH$. It is a structural isomer of 1-propanol. It has a wide variety of industrial and household uses.

Production

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 using 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.

- **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. Di-isopropyl ether is a significant by-product of this process; it is recycled back to the process and hydrolyzed to give the desired product.

- **Direct hydration**

Direct hydration reacts propene and water, either in gas phase or in liquid phase, 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 that 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 cyclohexane as azeotroping agents.

- **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.

Isobutanol

Isobutanol (2-methylpropan-1-ol) 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, the other butanols, include *n*-butanol, 2-butanol, and *tert*-butanol, all of which are important industrially.

Biosynthesis of Isobutanol

Escherichia coli

Escherichia coli, is a Gram-negative, rod-shaped bacteria. *E. coli* is the microorganism most likely to move on to commercial production of isobutanol. In its engineered form *E. coli* produces the highest yields of isobutanol of any microorganism. Methods such as elementary mode analysis have been used to improve the metabolic efficiency of *E. coli* so that larger quantities of isobutanol may be produced.

Clostridium

Researchers have developed a strain of *Clostridium cellulolyticum*, a native cellulose-degrading microbe that could synthesize isobutanol directly from cellulose.

Cyanobacteria

Cyanobacteria, are a phylum of photosynthetic bacteria. Cyanobacteria are suited for isobutanol biosynthesis when genetically engineered to produce isobutanol and its corresponding aldehydes. Isobutanol producing species of cyanobacteria offer several advantages as biofuel synthesizers:

- Cyanobacteria grow faster than plants and also absorb sunlight more efficiently than plants. This means they can be replenished at a faster rate than the plant matter used for other biofuel biosynthesizers.
- Cyanobacteria can be grown on non-arable land (land not used for farming). This prevents competition between food sources and fuel sources.

Ethylene glycol

Ethylene glycol (ethane-1,2-diol) is an organic compound with the formula $(CH_2OH)_2$. It is mainly used for two purposes, as a raw material in the manufacture of polyester fibers and for antifreeze formulations. It is an odorless, colorless, sweet-tasting syrup. Ethylene glycol is moderately toxic.

Manufacturing processes

The different processes followed for the production of ethylene glycol are as follows:

- **Ethylene carbonate process:** In this method, ethylene oxide is converted to an intermediate, ethylene carbonate, by reaction with carbon dioxide, which is then hydrolyzed by water to give ethylene glycol. This process was in use in the 1970s, but this process was replaced later by combined ethylene oxide-glycol plants.

- **Halcon Acetoxylatin Process:** Two reaction steps were used in the Oxirane plant. In the first, ethylene glycol diacatate was obtained by the oxidation of ethylene in an acetic acid solution, catalyzed by tellurium and a bromine compound. The reaction complex, which is quite complicated, is believed to proceed via a tellurium-bromoethylene complex. The oxidation, which is carried out at 90-200 ° C and 20-30 atm pressure, results in a mixture of acetates due to partial hydrolysis of the diacetate. The reaction liquid effluent is withdrawn and processed to recover glycol acetates and glycol and provide the recycle streams back to oxidation. In the second step of the process, the glycol acetates are hydrolyzed to ethylene glycol and acetic acid. The process however is not popular due to operating difficulties. A plant started at Channelview to produce 800 million lb/yr of ethylene glycol was shut down after difficulties in startup.

- **Teijin Oxychlorination Process:** The Teijin process, which has not been commercialized yet, produces ethylene glycol by the reaction of ethylene with thallium salts in the presence of water and chloride or bromide ions. A redox metal compound (such as copper) oxidizable with molecular oxygen is added to the reaction medium to permit the regeneration of the thallium salt.

Union Carbide Syngas Process: The following process developed by Union Carbide, Inc. Uses synthesis gas for the production of ethylene glycol. Glycerol and propylene oxide are the major byproducts. Methanol, methyl formate and water are also produced. An expensive rhodium based catalyst catalyzes the reaction. The process is yet to be commercialized. Union Carbide has already started work on a modified process in association with Ube Industries. It plans to set up a commercial scale plant soon.

- **Hydrolysis of Ethylene Oxide:** This method is by far the most widely used method for the production of ethylene glycol. The simplicity and reliability of the process makes it popular. Furthermore, it can be used in plants that manufacture ethylene oxide and glycol together. *Chemistry of the Reaction:* The reaction chemistry is quite simple, and can be summarized as follows: ethylene oxide reacts with water to form ethylene glycol, and then further reacts with ethylene glycol and higher homologues in a series of consecutive reactions as shown in the following equations:

$$(CH_2)_2O + H_2O \rightarrow (CH_2OH)_2 \ \Delta H = -21.8 \text{ kcal}$$

Monoethylene Glycol

$$(CH_2)_2O + (CH_2OH)_2 \rightarrow HOCH_2CH_2OCH_2CH_2OH$$

Diethylene Glycol

$$(CH_2)_2O + HOCH_2CH_2OCH_2CH_2OH \rightarrow HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

Triethylene Glycol

Butanol

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 modifying their amino acid metabolism.

- **Biobutanol** (also called biogasoline) is often claimed to provide a direct replacement for gasoline, because it can be used directly in a gasoline engines. Biobutanol has slightly less energy than gasoline, but can run in any car that uses gasoline without the need for modification to engine components.