*Kirk-Othmer Encyclopedia of Chemical Technology.*

# ETHANOL

## 1. Introduction

Ethanol [64-17-5] or ethyl alcohol, $CH_3CH_2OH$, is one of the most versatile oxygen-containing organic chemicals because of its unique combination of properties as a solvent, a germicide, a beverage, an antifreeze, a fuel, a depressant, and especially as a chemical intermediate for other organic chemicals. The use of fermentation-derived ethanol as an automotive fuel additive to enhance octane and reduce emissions has seen explosive growth. Ethanol is a replacement for methyl *tert*-butyl ether (MTBE) as an oxygenate for fuels. MTBE has been deemed an environmental risk because of its seepage into groundwater. The high cost of gasoline containing ethanol, however, is an issue.

The name alcohol is a generic name derived from two Arabic words, *al* and *kohl*, that described a finely ground antimony powder used by Oriental women to darken their eyebrows. The name evolved to indicate a great degree of fineness or purity and gradually became specific for ethyl alcohol, “spirits of wine rectified to the highest degree” (1). Ethyl alcohol is, of course, well known as a constituent of alcoholic beverages (see Beverage spirits, distilled).

As a beverage ethanol had been prepared and used long ago by the Egyptian pharaohs (2, 3). Some indication of the antiquity of the knowledge of ethyl alcohol is the fact that Noah is believed to have built a vineyard in which he grew grapes that he fermented into a type of alcoholic beverage (4).

## 2. Physical Properties

Ethyl alcohol under ordinary conditions is a volatile, flammable, clear, colorless liquid. Its odor is pleasant, familiar, and characteristic, as is its taste when suitably diluted with water. The most amazing property of ethanol is the volume shrinkage that occurs when it is mixed with water, or the volume expansion that occurs when it is mixed with gasoline. One volume of ethanol plus one volume of water results in only 1.92 volumes of mixture.

The physical and chemical properties of ethyl alcohol are primarily dependent upon the hydroxyl group. This group imparts polarity to the molecule and gives rise to intermolecular hydrogen bonding. These two properties account for the differences between the physical behavior of lower molecular weight alcohols and that of hydrocarbons of equivalent weight. Infrared spectrographic studies (5) have shown that, in the liquid state, hydrogen bonds are formed by the attraction of the hydroxyl hydrogen of one molecule and the hydroxyl oxygen of a second molecule. This bonding makes liquid alcohol behave as though it were largely dimerized. This behavior is analogous to that of water, which, however, is more strongly bonded and appears to exist in liquid clusters of more than two molecules. The association of ethyl alcohol is confined to the liquid state; in the vapor state it is monomeric.

**Table 1. Physical Properties of Ethanol**[a]

| Property | Value |
|---|---|
| freezing point, °C | −114.1 |
| normal boiling point, °C | 78.32 |
| critical temperature, °C | 243.1 |
| critical pressure, kPa[b] | 6383.48 |
| critical volume, L/mol | 0.167 |
| critical compressibility factor, $z$, in $PV = znRT$ | 0.248 |
| density, $d_4^{20}$, g/mL | 0.7893 |
| refractive index, $n_D^{20}$ | 1.36143 |
| $\Delta n_D/\Delta t$, 20–30°C, per °C | 0.000404 |
| surface tension, at 25°C, mN/m (=dyn/cm) | 23.1 |
| viscosity, at 20°C, mPa·s( =cP) | 1.17 |
| solubility in water, at 20°C | miscible |
| heat of vaporization, at normal boiling point, J/g[c] | 839.31 |
| heat of combustion, at 25°C, J/g[c] | 29676.69 |
| heat of fusion, J/g[c] | 104.6 |
| flammable limits in air, vol % | |
| lower | 4.3 |
| upper | 19.0 |
| autoignition temperature, °C | 423.0 |
| flash point, closed-cup, °C | 14 |
| specific heat, at 20°C, J/(g·°C)[c] | 2.42 |
| thermal conductivity, at 20°C, W/(m·K) | 0.170 |
| dipole moment, liq at 25°C, C·m[d] | $5.67 \times 10^{-30}$ |
| magnetic susceptibility at 20°C | $0.734 \times 10^{-6}$ |
| dielectric constant at 20°C | 25.7 |

[a] Refs. 6–14.

[b] To convert kPa to atm, divide by 101.3.

[c] To convert J to cal, divide by 4.184.

[d] To convert C·m to debye, divide by $3.336 \times 10^{-30}$ (esu = D $\times 10^{-18}$).

A summary of physical properties of ethyl alcohol is presented in Table 1. Detailed information on the vapor pressure, density, and viscosity of ethanol can be obtained from References 6–14. A listing of selected binary and ternary azeotropes of ethanol is compiled in Reference 15.

## 3. Chemical Properties

The chemistry of ethyl alcohol is largely that of the hydroxyl group, namely, reactions of dehydration, dehydrogenation, oxidation, and esterification. The hydrogen atom of the hydroxyl group can be replaced by an active metal, such as sodium, potassium, and calcium, to form a metal ethoxide (ethylate) with the evolution of hydrogen gas (see Alkoxides, metal).

$$2\ C_2H_5OH + 2\ M \longrightarrow 2\ C_2H_5OM + H_2$$

Sodium ethoxide [141-52-6] can be prepared by the reaction of absolute ethyl alcohol and sodium, or by refluxing absolute ethyl alcohol with anhydrous sodium hydroxide (16):

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CH_2ONa + H_2O$$

Commercially, water is removed by azeotropic distillation with benzene (17). Sodium ethoxide precipitates upon addition of anhydrous acetone (18). This strong base hydrolyzes readily to give ethyl alcohol and sodium and hydroxyl ions.

$$CH_3CH_2O^-Na^+ + H_2O \rightleftharpoons CH_3CH_2OH + Na^+ + OH^-$$

Sodium ethoxide can also be prepared by the reaction of sodium amalgam with ethyl alcohol.

Sodium ethoxide is used in organic synthesis as a condensing and reducing agent. The reaction between sodium ethoxide and sulfur monochloride yields diethyl thiosulfite (19).

$$2\ CH_3CH_2ONa + S_2Cl_2 \longrightarrow (CH_3CH_2O)_2\,S_2 + 2\ NaCl$$

Barbiturates (Veronal, Barbital, Luminal, Amytal), ethyl orthoformate, and other chemicals are produced commercially from sodium ethoxide.

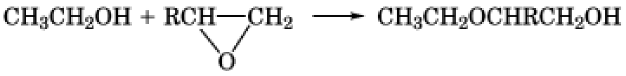
Aluminum and magnesium also react to form ethoxides, but the reaction must be catalyzed by amalgamating the metal (adding a small amount of mercury).

$$6\ CH_3CH_2OH + 2\ Al \longrightarrow 2\ (CH_3CH_2O)_3\,Al + 3\ H_2$$

$$2\ CH_3CH_2OH + Mg \longrightarrow (CH_3CH_2O)_2\,Mg + H_2$$

Well-cleaned aluminum filings react at room temperature in the presence of mercuric chloride (20, 21). In an autoclave, metallic aluminum and ethyl alcohol react without a catalyst at 120°C (22). The reaction can also be promoted by the addition of sodium ethoxide (23). Aluminum should be avoided as a material of construction for ethanol service.

Other reactions involving the hydrogen atom of the hydroxyl group in ethyl alcohol include the opening of epoxide rings to form hydroxy ethers,



and the addition to acetylene [74-86-2] to form ethyl vinyl ether [104-92-2].

$$CH_3CH_2OH + HC{\equiv}CH \longrightarrow CH_3CH_2OCH{=}CH_2$$

These reactions are carried out in the presence of acidic and basic catalysts. The acid-catalyzed addition of ethyl alcohol to acetylene or to a vinyl ether produces acetals (diethers of 1,1-dihydroxyethane). The acid-catalyzed reaction of ethyl alcohol with an aldehyde or ketone also gives acetals.

$$2\ CH_3CH_2OH + RCHO \rightleftharpoons RCH\,(OCH_2CH_3)_2 + H_2O$$

The hydroxyl group can be replaced by halogens from inorganic acid halides or phosphorus halides to give two different products, ethyl esters of the acid and ethyl halide (1). Phosphorus trihalides and thionyl chloride, $SOCl_2$, are used to make triethyl phosphite, diethyl sulfite, or ethyl chloride. The ethyl chloride yield is reduced by formation of mixed alkyl esters of phosphites, such as ethyl or diethyl phosphite, $CH_3CH_2OP(OH)_2$ and $(CH_3CH_2O)_2POH$, respectively.

*Triethyl phosphite or diethyl sulfite reaction*

$$3\ CH_3CH_2OH + PCl_3 \xrightarrow[\text{low temp}]{\textit{tert}\text{–amine}} (CH_3CH_2O)_3P + 3\ HCl$$

$$2\ CH_3CH_2OH + SOCl_2 \longrightarrow (CH_3CH_2O)_2\ SO + 2\ HCl$$

*Ethyl chloride reaction*

$$3\ CH_3CH_2OH + PCl_3 \longrightarrow 3\ CH_3CH_2Cl + H_3PO_3$$

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

Reaction of ethanol with phosphorus trichloride produces mainly triethyl phosphite; ethyl bromide is the principal product of reaction with phosphorus tribromide. However, reaction conditions strongly affect the composition of reaction products.

The halogen acids also produce alkyl halides.

$$CH_3CH_2OH + HX \longrightarrow CH_3CH_2X + H_2O$$

The halogen influences the rate of reaction, and, in general, the order of reactivity is $HI > HBr > HCl$. An important use of ethyl chloride is in the manufacture of ethylcellulose. Ethyl bromide can be used to produce ethyl Grignard reagent and various ethyl amines.

### 3.1. Esterification

Esters are formed by the reaction of ethanol with inorganic and organic acids, acid anhydrides, and acid halides. If the inorganic acid is oxygenated, eg, sulfuric acid, nitric acid, the ester has a carbon–oxygen linkage that is easily hydrolyzed (24–26).

$$CH_3CH_2OH + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H + H_2O$$

$$2\ CH_3CH_2OH + H_2SO_4 \longrightarrow (CH_3CH_2O)_2\ SO_2 + 2\ H_2O$$

$$CH_3CH_2OH + HONO_2 \longrightarrow CH_3CH_2ONO_2 + H_2O$$

Organic esters are formed by the elimination of water between an alcohol and an organic acid (see Esterification).

$$CH_3CH_2OH + RCOOH \rightleftharpoons RCOOCH_2CH_3 + H_2O$$

The reaction is reversible and reaches equilibrium slowly. Generally, acidic catalysts are used, such as strong sulfuric acid, hydrochloric acid, boron trifluoride, and *p*-toluenesulfonic acid (27). Batchwise and continuous processes are used for the esterification reaction.

Ethyl alcohol also reacts with acid anhydrides or acid halides to give the corresponding esters.

$$CH_3CH_2OH + (RCO)_2\,O \longrightarrow RCOOCH_2CH_3 + RCOOH$$

$$CH_3CH_2OH + RCOCl \longrightarrow RCOOCH_2CH_3 + HCl$$

The direct conversion of ethyl alcohol to ethyl acetate is believed to take place via acetaldehyde and its condensation to ethyl acetate (Tishchenko reaction) (28–34).

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2$$

$$2\ CH_3CHO \longrightarrow CH_3COOCH_2CH_3$$

An ethyl acetate yield of∼24% is obtained using a copper oxide catalyst with 0.1–0.2% thoria at 350°C.

### 3.2. Dehydration

Ethyl alcohol can be dehydrated to form ethylene or ethyl ether.

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$$

$$2\ CH_3CH_2OH \longrightarrow CH_3CH_2OCH_2CH_3 + H_2O$$

Generally, both ethylene and ethyl ether are formed to some extent, but the conditions can be altered to favor one reaction or the other.

### 3.3. Dehydrogenation

The dehydrogenation of ethyl alcohol to acetaldehyde can be effected by a vapor-phase reaction over various catalysts.

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2$$

### 3.4. Haloform Reaction

Ethyl alcohol reacts with sodium hypochlorite to give chloroform [67-66-3] (haloform reaction).

$$CH_3CH_2OH + NaCl \longrightarrow CH_3CHO + NaCl + H_2O$$

$$CH_3CHO + 3\ NaOCl \longrightarrow CCl_3CHO + 3\ NaOH$$

$$CCl_3CHO + NaOH \longrightarrow CHCl_3 + HCOONa$$

Similarly, bromoform [75-25-2], $CHBr_3$, and iodoform [75-47-8], $CHI_3$, are obtained from sodium hypobromite and hypoiodite, respectively. Ethyl alcohol is the only primary alcohol that undergoes this reaction.

### 3.5. Concentration Effects

The reactivity of ethyl alcohol–water mixtures has been correlated with three distinct alcohol concentration ranges (35, 36). For example, the chromium trioxide oxidation of ethyl alcohol (37), the catalytic decomposition of hydrogen peroxide (38), and the sensitivities of colloidal particles to coagulation (39) are characteristic for ethyl alcohol concentrations of 25–30%, 40–60%, and above 60% alcohol, respectively. The effect of various catalysts also differs for different alcohol concentrations (35).

## 4. Manufacture

Industrial ethyl alcohol can be produced synthetically from ethylene [74-85-1], as a by-product of certain industrial operations, or by the fermentation of sugar, starch, or cellulose. Fermentation processes accounted for 83% of total production in the U.S., Western Europe and Japan in 1997. By 2001 fermentation increased to 90% (40). The first synthesis of ethanol from ethylene occurred in 1828 in Michael Faraday's laboratory in Cambridge (41).

There are two main processes for the synthesis of ethyl alcohol from ethylene. The earliest to be developed (in 1930 by Union Carbide Corp.) was the indirect hydration process, variously called the strong sulfuric acid–ethylene process, the ethyl sulfate process, the esterification–hydrolysis process, or the sulfation–hydrolysis process. This process is still in use in Russia. The other synthesis process, designed to eliminate the use of sulfuric acid and which, since the early 1970s, has completely supplanted the old sulfuric acid process in the United States, is the direct hydration process. This process, the catalytic vapor-phase hydration of ethylene, is now practiced in the U.S. only by Dow Chemical, Texas City, Texas, Dow imports crude industrial ethanol, CIE, from Saudi Arabia in a tolling arrangement with shell chemicals, and refines it to industrial grade.

Other synthetic methods have been investigated but have not become commercial. These include, for example, the hydration of ethylene in the presence of dilute acids (weak sulfuric acid process); the conversion of acetylene to acetaldehyde, followed by hydrogenation of the aldehyde to ethyl alcohol; and the Fischer-Tropsch hydrocarbon synthesis. Synthetic fuels research has resulted in a whole new look at processes to make lower molecular weight alcohols from synthesis gas.

### 4.1. Fermentation Ethanol

Fermentation (qv), one of the oldest chemical processes known, it is used to make a variety of products, including fuel, foods, flavorings, beverages, pharmaceuticals, and chemicals.

Most of the fermentation ethanol is made from corn even though before World War II molasses was the chief feedstock. Ethanol can be made from a variety of agricultural products such as other grains, sugar cane and beets, fruit, whey, and sulfite waste liquor. Studies are underway to ferment garbage to ethanol. Generally, most of the agricultural products mentioned command higher prices as foods, and others, eg, potatoes, are uneconomical because of their low ethanol yield and high transportation cost. The use of fermentation ethanol in the industrial market depends on the availability and cost of the carbohydrate relative to the availability and cost of ethylene, and the economics and government policies relating to the fuel ethanol market.

Ethanol can be derived by fermentation processes from any material that contains sugar or compounds that can be converted to sugar. The many and varied raw materials used in the manufacture of ethanol via fermentation are conveniently classified under three types of agricultural raw materials: sugar, starches, and cellulose materials. Sugars (from sugar cane, sugar beets, molasses, or fruit) can be converted to ethanol directly. Starches (from grains, potatoes, or root crops) must first be hydrolyzed to fermentable sugars by the action of enzymes from malt or molds. Cellulose (from wood, agricultural residues, or waste sulfite liquor from pulp and paper mills) must likewise be converted to sugars, generally by the action of mineral acids. Once simple sugars are formed, enzymes from yeast can readily ferment them to ethanol (42). Because fermentation ethanol has been thoroughly and repeatedly discussed in the literature, the coverage here is illustrative rather than comprehensive, with special emphasis on the potential raw materials for ethanol production of the future (see also Beverage spirits, distilled).

#### *4.1.1. Sugars*

Prior to the late 1970s, the most widely used sugar for ethanol fermentation was blackstrap molasses (42–53) which contains about 35–40 wt % sucrose, 15–20 wt % invert sugars such as glucose and fructose, and 28–35 wt % of nonsugar solids. Blackstrap (derived from Java and the Dutch word *stroop*, meaning syrup) is collected as a by-product of cane sugar manufacture. The molasses is diluted to a mash containing $\sim 10-20$ wt % sugar. After the pH of the mash is adjusted to about 4–5 with mineral acid, it is inoculated with the yeast, and the fermentation is carried out nonaseptically at 20–32°C for about 1–3 d. The fermented beer, which typically contains $\sim 6-10$ wt % ethanol, is then sent to the product recovery and purification section of the plant.

The direct fermentation of sugar cane juice, sugar beet juice, beet molasses (a by-product in the production of beet sugar), fresh and dried fruits, cane sorghum, whey, and skim milk had been considered as a means of obtaining ethanol, but none of these raw materials could compete economically with molasses. Although the manufacture of ethanol from the sugar-containing waste products of the fruit industry appears to be a highly desirable operation, particularly as a means of reducing stream pollution in the vicinity of canning plants, such production is costly because of the need to remove most of the water (as much as 97%) contained in the waste product.

The results of the sugar-crop research on agronomics and fuels conversion undertaken by Batelle's Columbus Laboratories (44) lists several merits of sugar cane as a candidate energy resource. Sugar cane, a renewable raw material, is renowned for its agricultural productivity, and its juice is directly fermentable to ethanol. On the other hand, sugar cane products are valuable in food and feed applications and their conversion to chemicals and energy can be considered an underutilization of their potential value.

In 1975, Brazil embarked upon the ambitious ProAlcohol program for fermentation ethanol manufacture (48,49) from sugar cane to reduce the country's dependence on foreign oil, and to modernize and make more competitive Brazil's sugar mills in a lagging international sugar market. Gasohols have been used in Brazil since the early 1930s. The number of alcohol distilleries grew to over 500 while the number of big sugar plantations grew to over 1000 (54). Brazil is currently the world's largest producer of fermentation alcohol (40).

The subject of fermentation alcohol has always been of considerable interest to several tropical countries, but until the oil crisis of 1973, other than Brazil (47), only India appeared to appreciate the importance of fermentation alcohol as a strategic material in its economy. Ethanol prices in India have been maintained at an extremely low level by processing cane molasses, which has been a waste product of negligible value (47).

### 4.1.2. Starches

In the United States, all potable alcohol, most fermentation industrial alcohol, and most fuel alcohol is currently made principally from grains; corn is the principal feedstock for fuel alcohol. Fermentation of starch from grain is somewhat more complex than fermentation of sugars because starch must first be converted to sugar and then to ethanol. This process was known to the ancient Egyptians and Mesopotamians who brewed beer almost 5000 years ago (52). The simplified equations for the conversion of starch to ethanol are

$$C_6H_{10}O_5 + H_2O \xrightarrow{\text{enzyme}} C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\ C_2H_5OH + 2\ CO_2$$

Starch is converted enzymatically to glucose either by diastase present in sprouting grain or by fungal amylase. The resulting dextrose is fermented to ethanol with the aid of yeast, producing $CO_2$ as a coproduct. Other by-products depend on the type of process.

The basic process steps for converting corn into ethanol are degermination, milling, separation of starch-bearing endosperm from hulls, slurrying–liquefaction, hydrolysis of starch to sugar, fermentation, distillation, and dehydration (55). The hydrolysis or saccharification is usually carried out with an amylase enzyme and the fermentation is usually by the yeast *Saccharomyces cerevisiae*. Corn can be prepared for fermentation by three different processes: whole-grain grinding, dry milling, and wet milling. The fermentation process has been considerably refined and has led to an efficient process. The two main processes are dry milling and wet milling. The main difference is in the treatment of the grain (56).

For dry milling, the entire corn or starchy grain is ground into flour (meal), and processed without separating out the components. The meal is slurried to form mush. Enzymes are added to convert starch to dextrose. Ammonia is added for pH control and as a nutrient for yeast. The mash is processed in a high temperature cooker to reduce bacteria levels ahead of fermentation. The mash is cooled and then transferred to the fermenters where yeast is added and conversion of sugar to ethanol and carbon dioxide begins. The process takes about 40–50 hours. The mash is agitated and kept cool to facilitate yeast activity. The fermentation product is agitated and is kept cool. The ethanol is separated out. Ethanol is concentrated to 190 proof by distillation and then dehydrated to 200 proof by a molecular sieve system. Ethanol is treated with a denaturant to render it undrinkable, and thus, is not subject to beverage tax.

A by-product produced by centrifugation of coarse grain and soluble material is Condensed Distiller's Syrup. This is used for livestock feed.

In wet milling, the grain is soaked or steeped in water and sulfurous acid for 24–48 hours to separate it into components. After steeping, the corn slurry goes through grinders to separate corn germ and fiber components. Corn oil is extracted. The steepage liquor is concentrated by evaporation. Gluten is separated out and used in livestock feed. The remaining liquid is fermented to ethanol or dried to corn starch or corn syrup. The fermentation is the same as for the dry milling process.

The fuel alcohol program has spawned a tremendous amount of research aimed at improving the cost and efficiency of the corn process. Three promising technologies for lowering operating costs are (*1*) substituting yeast with a high temperature bacteria such as *Zymomonous mobilis*; (*2*) using a permeable membrane to separate dissolved solids and some of the water before distillation; and (*3*) immobilizing the yeasts and enzymes in the wet-mill process to provide continuous processes with higher productivities (57).

### 4.1.3. Cellulosic Materials

Over 900 × $10^6$ metric tons of carbohydrate-containing cellulosic wastes are generated annually. The technology for converting this material into ethanol is available, but the stoichiometry of the process is disadvantageous. Even if each step in the process of the conversion of cellulose to ethanol proceeded with 100% yields, almost two-thirds of the mass would disappear during the sequence, most of it as carbon dioxide in the fermentation of glucose to ethanol. This amount of carbon dioxide leads to a disposal problem rather than to a raw material credit (58).

Starch (qv) and cellulose (qv) are both polymers of glucose, but cellulose is much more difficult to hydrolyze to the sugar. Its structure is more crystalline which protects the internal bonds from hydrolysis, and cellulose in plants is protected by lignin (qv), a polyphenolic material that forms a seal around the cellulose for further protection against hydrolysis (59). Cellulosic wastes also contain substantial amounts of hemicellulose (qv), which is a polymer of pentoses. The aqueous mineral acids used to hydrolyze the cellulose to glucose destroy much of the sugars, particularly the pentoses, in the process. Nevertheless, a 1978 study claimed that forests could theoretically provide 50% of the oil and gas used by U.S. utilities, replacing 20% of annual fossil fuel consumption (60). None of this has taken place, but research has continued. A process utilizing low temperature hydrolysis to separate cellulose from paper have been licensed, with plans to construct a plant in Germany (61). The process uses electrodialysis rather than diffusion dialysis to recover hydrochloric acid for reuse. Other new ways of reducing the cost of converting cellulosic wastes from wood, newspapers, and municipal garbage into glucose include the use of less corrosive acids and reduced hydrolysis time. One way of making cellulose wastes more susceptible to hydrolysis is by subjecting them to a short burst of high energy electron beam radiation (62). Hydropulping of cellulose feedstocks followed by a 10 $\mu$s burst from a $3 \times 10^6-$eV electron-beam accelerator is claimed to reduce the time of hydrolysis by dilute acid from hours to seconds.

An alternative to acid hydrolysis is the use of enzymes. Although they avoid the corrosion problems and loss of fuel product associated with acid hydrolysis, enzymes have their own drawbacks (see enzyme applications, industrial). Enzymatic hydrolysis slows as the glucose product accumulates in a reaction vessel. This end-product inhibition eventually halts the hydrolysis unless some way is found to draw off the glucose as it is formed. In mid-1978, Gulf Oil researchers described the simultaneous enzymatic hydrolysis of cellulose and fermentation of the resulting glucose to ethanol, removing glucose as it is formed and overcoming the problem of product inhibition of hydrolysis (60). Mutated strains of the common soil mold *Trichoderma viride* can process 15 times as much cellulose as natural strains. The results have been encouraging; in some cases, cellulose from sawdust, bark, and effluent streams from the pulp and paper industries have produced ethanol in yields approaching 100% of the theoretical value. A sequential hydrolysis process has been proposed (59), in which the hemicellulose is hydrolyzed to pentose by aqueous sulfuric acid and then separated for fermentation. The remaining ligno-cellulose is then pretreated with the solvent cadoxen (5–7% cadmium oxide in 28% aqueous ethylenediamine) which breaks the lignin seal to allow enzyme-catalyzed hydrolysis to glucose. Pentose fermentation to ethanol is more difficult and this process allows the two sugars to be fermented separately. Research is underway on genetically engineered bacteria for cellulose conversion (63). A novel pretreatment for municipal solid waste consists of soaking the waste in high pressure liquid ammonia (64). An instant pressure release opens up the fiber structure so that enzymes can more easily penetrate and digest the cellulose. A 25% increase in the amount of waste digested to sugar is claimed. Steam explosion has been reported as an effective pretreatment for the enzymatic hydrolysis of wood (qv) and agricultural residues (65).

### 4.2. Indirect Hydration (Esterification–Hydrolysis) Process

The preparation of ethanol from ethylene by the use of sulfuric acid is a three-step process (Fig. 1):

(1) Absorption of ethylene in concentrated sulfuric acid to form monoethyl sulfate (ethyl hydrogen sulfate) and diethyl sulfate:

$$CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H$$

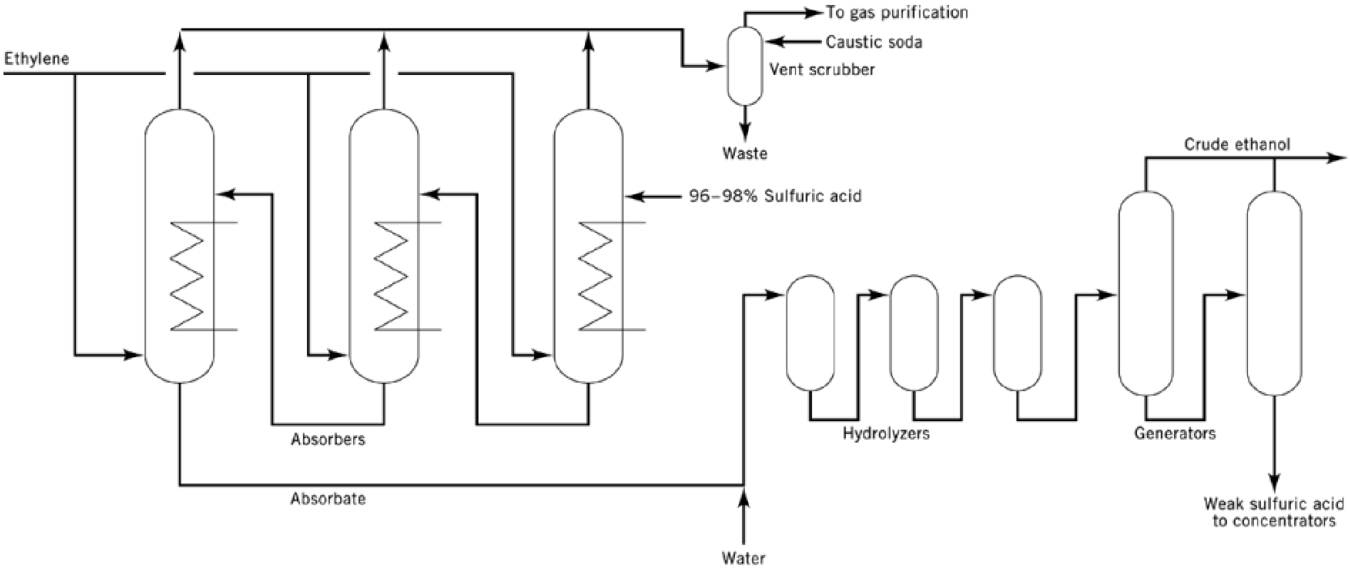


**Fig. 1.** Indirect hydration process for ethanol manufacture.

$$2\ CH_2{=}CH_2 + H_2SO_4 \longrightarrow (CH_3CH_2O)_2\,SO_2$$

(2) Hydrolysis of ethyl sulfates to ethanol:

$$CH_3CH_2OSO_3H + H_2O \longrightarrow CH_3CH_2OH + H_2SO_4$$

$$(CH_3CH_2O)_2\,SO_2 + 2\ H_2O \longrightarrow 2\ CH_3CH_2OH + H_2SO_4$$

$$(CH_3CH_2O)_2\,SO_2 + CH_3CH_2OH \longrightarrow CH_3CH_2OSO_3H + (CH_3CH_2)_2\,O$$

(3) Reconcentration of the dilute sulfuric acid.

The hydrocarbon feedstock contains 35–95% ethylene; the remaining gases are methane and ethane. Certain unsaturated hydrocarbons are undesirable as their presence leads to the formation of secondary alcohols.

The absorption is carried out by countercurrent passage of ethylene through 95–98% sulfuric acid in a column reactor at 80°C and 1.3–1.5 MPa (180–200 psig) (66). The absorption is exothermic, and cooling is required (67) to keep the temperatures down and thereby limit corrosion problems. The absorption rate increases when ethyl hydrogen sulfate is present in the acid (68–71). This increase is attributed to the greater solubility of ethylene in ethyl hydrogen sulfate than in sulfuric acid.

The effects of various catalysts (72,73), contaminants (74,75), acid concentration (76), temperature (77), and pressure (78–82) on the rate of absorption have been studied. The patent literature indicates that absorption can be improved by making the contact between the gaseous ethylene and liquid sulfuric acid more efficient (83–86), by suitable design of the absorption tower (87), and by various combinations of absorption and hydrolysis (88–93).

The absorbate containing the mixed ethyl sulfates is hydrolyzed with enough water to give an approximately 50–60% aqueous sulfuric acid solution. The hydrolysis mixture is separated in a stripping column to give dilute sulfuric acid bottoms and a gaseous alcohol–ether–water mixture overhead. The overhead mixture is washed with water or dilute sodium hydroxide and then purified by distillation (88,90,91,93,94).

Diethyl ether is the principal by-product of the reaction of ethyl alcohol with diethyl sulfate. Various methods have been proposed to diminish its formation (95–97), including separation of diethyl sulfate from the reaction product. Diethyl sulfate not only causes an increase in ether formation but is also more difficult to hydrolyze to alcohol than is ethyl hydrogen sulfate. The equilibrium constant for the hydrolysis of ethyl hydrogen sulfate is independent of temperature, and the reaction rate is proportional to the hydrogen ion concentration (98–100).

The reconcentration of dilute (50–60%) sulfuric acid is one of the more costly operations in the manufacture of ethanol by this process. An acid reboiler, followed by a two-stage vacuum evaporation system, raises acid concentration to about 90%. The 90% acid is then brought to 96–98% strength by fortification with 103% oleum (fuming sulfuric acid).

The buildup of carbonaceous materials in the sulfuric acid presents one of the most serious problems of acid concentration (101–105). Acid concentration also presents a corrosion problem. The vessels are mild steel lined with lead or brick; the steam heating elements are composed of silicon, iron, or tantalum, and pipelines are generally constructed of lead (106).

### 4.3. Direct Hydration of Ethylene

Hydration of ethylene to ethanol via a liquid-phase process catalyzed by dilute sulfuric acid was first demonstrated more than a hundred years ago (107). In 1923, the passage of an ethylene-steam mixture over alumina at 300°C was found to give a small yield of acetaldehyde, and it was inferred that this was produced via ethanol (108). Since the late 1920s, several industrial concerns have expressed interest in producing ethanol synthetically from ethylene over solid catalysts. However, not until 1947 was the first commercial plant for the manufacture of ethanol by catalytic hydration started in the United States by Shell; the same process was commercialized in the United Kingdom in 1951.

There are two main process categories for the direct hydration of ethylene to ethanol. Vapor-phase processes contact a solid or liquid catalyst with gaseous reactants. Mixed-phase processes contact a solid or liquid catalyst with liquid and gaseous reactants. Generally, ethanol is produced by a vapor-phase process; mixed-phase processes are used for the analogous hydration of propylene to 2-propanol. Important exceptions to these two generalizations exist, but the discussion that follows emphasizes technology associated with the commercially important vapor-phase direct hydration of ethylene.

#### *4.3.1. Chemistry*

The stoichiometric equations pertinent to the vapor-phase hydration of ethylene over a catalyst support impregnated with phosphoric acid have been summarized (109).

$$C_2H_4 + H_2O \rightleftarrows CH_3CH_2OH$$

Diethyl ether can be formed from the alcohol, or conversely, ether can be hydrated to ethanol.

$$2\ CH_3CH_2OH \rightleftharpoons (CH_3CH_2)_2O + H_2O$$

Acetaldehyde, a deleterious by-product, is most likely formed from trace amounts of acetylene in the feed (110,111).

$$C_2H_2 \xrightarrow{H_2O} CH_3CHO$$

The acetaldehyde is particularly undesirable as it leads to the formation of crotonaldehyde (112), an impurity that adversely affects ethanol quality even at parts per million levels.

$$2\ CH_2CHO \longrightarrow CH_3CH(OH)CH_2CHO \longrightarrow CH_3CH{=}CHCHO + H_2O$$

Both aldehydes can be hydrogenated to their saturated normal alcohols.

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

$$CH_3CH{=}CHCHO + 2\ H_2 \longrightarrow C_4H_9OH$$

Higher hydrocarbons are formed by the polymerization of ethylene. Any higher unsaturated hydrocarbons present are converted to the corresponding alcohols by hydration.

#### *4.3.2. Catalysts*

At ambient temperatures, only a relatively small amount of ethanol is present in the vapor-phase equilibrium mixture, and an increase in temperature serves only to decrease the alcohol concentration. An increase in pressure helps to shift the equilibrium toward the production of ethanol because of a decrease in the number of molecules (Le Chatelier's principle). On the other hand, reaction velocity is low at low temperatures. Hence it is necessary to use catalysts and relatively high temperatures (250–300°C) to approach equilibrium within a reasonably short time.

Many catalysts for the hydration of olefins in general, and of ethylene in particular, are described in the patent literature. Practically all of them are acidic. There has been a patent literature review through 1937 of the types of catalysts used (72,73) and a general review of olefin hydration (113).

The use of phosphoric acid on a charcoal support was claimed in one of the earliest patents (114) on olefin hydration. Since then many claims have appeared for the use of phosphoric acid on supports and for the use of metal and boron phosphates (115). Phosphoric acid on a porous inert support such as Celite diatomite (calcined diatomaceous earth) has been commercially used by Shell as a catalyst (116). The support is impregnated with aqueous phosphoric acid concentration of less than 70% and then dried to give an acid concentration of 75–85%. A catalyst prepared this way appears dry and there is no "drooling" (weeping) of acid from the support. The main factor determining the catalytic activity is the concentration of phosphoric acid (a function of reaction temperature and steam pressure) in the pores of the support. If the concentration falls, the reaction rate declines; if the concentration becomes too high, there is an increasing tendency to polymerize ethylene. It has been pointed out (110) that iron and aluminum oxides in the Celite carrier react with the phosphoric acid. This promotes cracking of the ethylene, loss of physical strength of the support, and an entrainment of fines with resultant plugging of the reactor equipment. Leaching with a mineral acid to reduce iron and aluminum content prior to impregnation with phosphoric acid yields a catalyst that operates at lower temperatures, gives higher conversions of ethylene, and has a longer life (110). Treatment of the calcined support with superheated steam at 200–260°C, prior to leaching with acid, improves the mechanical strength of the catalyst (117,118).

For commercial application, catalyst activity is only one of the factors to be considered. Equally important is catalyst life, but little has been published on this aspect. Partly because of entrainment losses and partly through loss of acid as volatile triethyl phosphate, the catalyst loses activity unless compensating steps are taken. This decline in activity can be counteracted by the periodic or continuous addition of phosphoric acid to the catalyst during use, a fact that seems to have been disclosed as early as 1940 (119). A catalyst subjected periodically to acid addition could remain in service indefinitely, according to a report by Shell (116). A later Shell patent (110) states that complete reimpregnation with acid is required every 200 run-days.

Catalyst longevity also requires a support material that does not crumble or disintegrate during preparation and use. Bentonites and montmorillonite (see Clays), extracted with HCl to reduce the alumina content to below 10%, are claimed by Hibernia-Chemie (120) to be better than Celite since they have superior mechanical strength and greater acid absorptivity. Hibernia also claims (121) porous carbon to be a robust and long-lasting support for phosphoric acid. Regular density silica gel as a support is reported to have low mechanical strength (110) and suffers fairly rapid disintegration (122), but a U.S.I. (National Distillers) patent (111) extolled the stability and high activity of their granular silica gel support of low density and high pore volume. Water-vapor treatment of a preformed silica xerogel prior to phosphoric acid impregnation gives a catalyst with superior crush strength and microporosity (98). Other later patents claim improved performance for silica gel supports containing 0.3–10 wt % of an alkali hydroxide and carbonate that are subjected to thermal treatment before impregnation.

Many other acids and acidic oxides have been mentioned as catalysts for ethylene hydration (124–128) as have ion-exchange resins (129,130).

Blue tungsten oxide and combinations thereof (131–138) have been the subject of a number of patents, as have copper(II) fluoborate (139) and alkali metal or ammonium sulfate-hydrogen sulfate catalysts (140,141).

### *4.3.3. Reaction Mechanism and Kinetics*

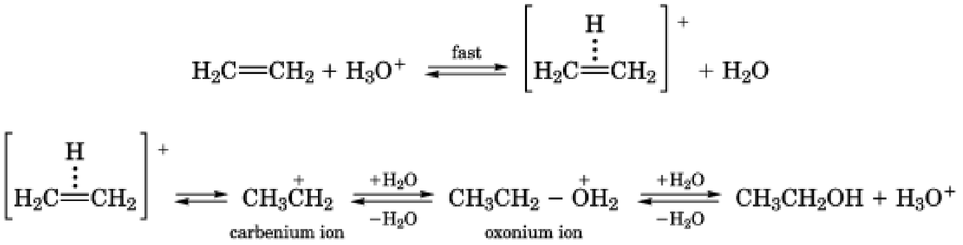
The equilibria involved in the hydration–dehydration of ethylene first proposed (142) can be expressed as follows:

$$C_2H_4 \xrightleftharpoons[-H^+]{+H^+} C_2H_5^+ \xrightleftharpoons[-OH^-]{+OH^-} CH_3CH_2OH$$

$$C_2H_5^+ + C_2H_5OH \xrightleftharpoons[+H^+]{-H^+} (C_2H_5)_2O$$

The rate-determining step involves addition or subtraction of the proton (143) which is donated by the catalyst.

With phosphoric acid-based catalysts, in which the active component is liquid acid absorbed in the pores of the support, the reaction probably follows the path (144) for the hydration of olefins in aqueous solution:



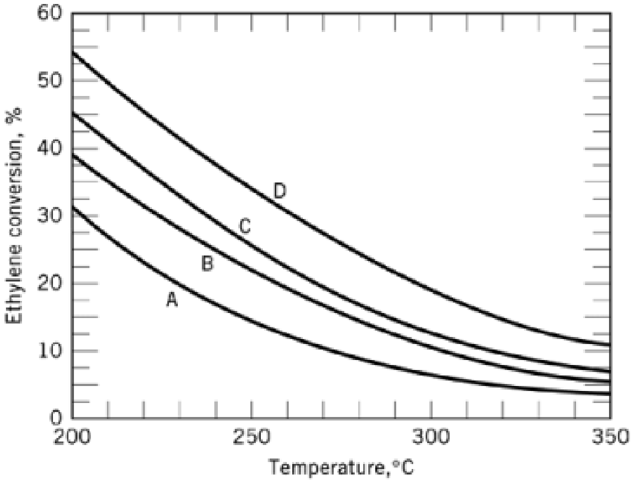


**Fig. 2.** Calculated conversions at equilibrium in vapor-phase hydration with equimolar ethylene and water at A, 5.1 MPa; B, 8.1 MPa; C, 10.1 MPa; and D, 15.2 MPa (150). To convert MPa to atm, divide by 0.101.

Formation of the carbenium ion is the rate-limiting step.

The kinetics of the ethylene hydration reaction have been investigated for a tungstic oxide–silica gel catalyst, and the energy of activation for the reaction determined to be ~125 kJ/mol (~30 kcal/mol) (131,145). The kinetics over a phosphoric acid-silica gel catalyst have been examined (146). By making some simplifying assumptions to Taft's mechanism, a rate equation was derived:

$$rate = k_1 \left(P_e - P_a/P_w K_f\right)$$

where $k_1$ = rate constant for the forward reaction, $P_e$ = partial pressure of ethylene, $P_a$ = partial pressure of ethanol, $P_w$ = partial pressure of water vapor, and $K_f$ is the equilibrium constant.

#### 4.3.4. Equilibrium Constant

At the pressures used in commercial production of ethanol (6.1–7.1 MPa or 60–70 atm), alcohol yield per pass is significantly limited by equilibrium considerations. This fact has focused attention on determination of equilibrium constants and equilibrium yields (147–149). The results of these determinations are as follows:

$$\log K_f = 2132/T - 6.241$$

$$\Delta F_f = 28.6/T - 9.740$$

where $f$ = fugacity, $K_f$ = equilibrium constant based on fugacity of components, and $F_f$ = free energy based on fugacity.

On the basis of a calculated equilibrium constant (150), the equilibrium conversions have been calculated at various temperatures (Fig. 2), pressures, and water–ethylene ratios (150).

#### 4.3.5. Effect of Process Variables

Several investigators (128,131) have studied the effects of the following reaction parameters:

**Table 2. Vapor-Phase Process Conditions**

| Condition | value |
|---|---|
| temperature, °C | 265 |
| pressure, MPa (atm) | 7.115 (70.23) |
| space velocity, $h^{-1}$ | 1727 |
| mole ratio, ethylene–water at inlet | 1.2 |
| conversion per pass, % | 6.18 |
| yield per pass, % | 5.98 |
| selectivity, % | 96.8 |

(1) An increase in pressure causes a corresponding increase in ethanol production rate. Higher pressures also increase polymer formation; hence, there is little practical advantage to be gained above a certain limit.

(2) An optimum temperature exists at which the ethanol production rate is maximal. Ethylene conversion is limited by catalyst activity at lower temperatures and by equilibrium considerations at higher temperatures.

(3) An optimum ethylene-to-water ratio exists that gives a maximum ethanol production rate. However, as expected, the highest ethylene conversion is obtained at the lowest ethylene-to-water mole ratio.

(4) An increases in space velocity increases the ethanol production rate, but at the expense of incurring higher recycling costs.

Hibernia-Chemie described a vapor-phase process that passes fresh and recycled 85 wt % phosphoric acid over a catalyst of hydrochloric acid-leached bentonite impregnated with phosphoric acid. Catalyst activity was claimed to remain constant over a period of one year at the conditions listed in Table 2 (151):

#### *4.3.6. Process*

Figure 3 shows a simplified flow diagram for the process previously employed by Union Carbide to produce ethanol by the direct hydration of ethylene (152). An ethylene-rich gas is combined with process water, heated to the desired reaction temperature, and passed through a fixed-bed catalytic reactor to form ethanol. The vapor leaving the reactor is slightly hotter than the feed because the reaction is exothermic. The reactor product is cooled by heat exchange with the reactor feed stream and is separated into liquid and vapor streams. The liquid stream goes to the ethanol refining system, and the vapor stream is scrubbed with water to remove ethanol. The washed gas, mostly unreacted ethylene, is enriched with fresh ethylene feed and recycled to the reactor. A small vent or purge stream is removed from the recycled ethylene to prevent buildup of unwanted impurities in the gas cycle.

The liquid product streams are fed to a distillation system to remove the light impurities and to recover the ethanol as a 95% volume ethanol–water azeotrope. To produce anhydrous ethanol, the ethanol–water azeotrope is fed to a dehydration system.

An advantage provided by this process is the recycling of process water recovered in the refining stills to the reaction system. This reduces the amount of boiler feed water to less than one-fifth of the total amount of water fed to the reactor. The investment and operating cost required for supporting boiler-feed water facilities are correspondingly reduced. Recycling process water also reduces the amount of water discharged to the sewer, thus decreasing the ethanol losses and the load on pollution-abatement facilities.

Several patents (153–155) deal with methods for preventing the formation of deposits in heat exchangers, reducing corrosion and avoiding the need for corrosion–resistant materials. Copper is widely used for lining the reactors and for piping, and some heat exchangers are made of phosphor bronze. Eastman Kodak Co. (156) advocates the use of a stainless-steel-clad reactor lined with overlapping copper curtains or shingles for

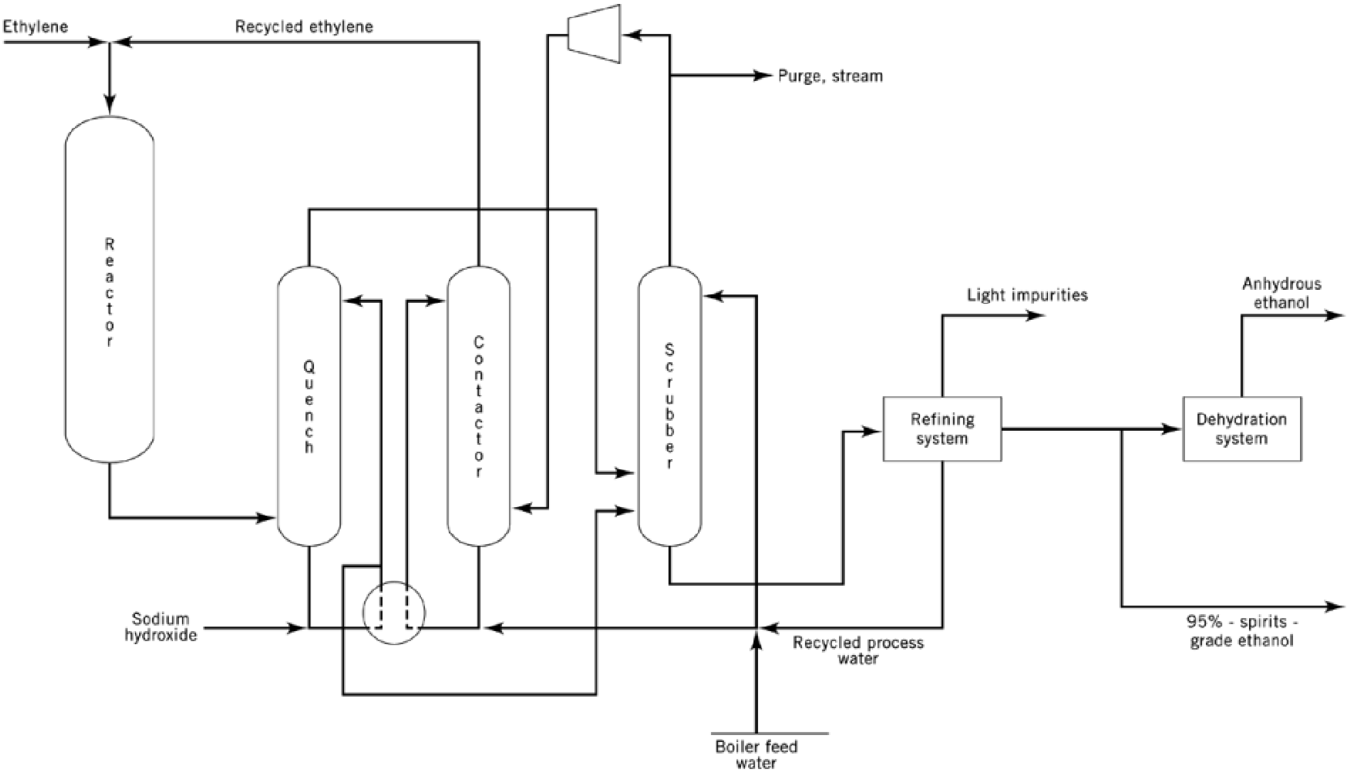


**Fig. 3.** Direct hydration process for ethanol manufacture.

corrosion resistance. A Hibernia-Chemie patent (121) claims that a copper lining in the reactor has a limited life and can promote the formation of cuprene. A porous carbon brick lining with a Cu–Ag alloy between the brick and the reactor wall is described (151).

## 5. Recovery and Purification

Various distillation and equipment modifications are used to ensure a pure water azeotrope of ethanol (95% by weight ethanol). A review of the patent literature concerning the many methods used for the purification of ethanol obtained from various synthetic processes is given in Reference 157. Some phosphoric acid is vaporized, or entrained as liquid, from the reactor. During recovery the reactor effluent is cooled, causing the condensation of acid on exchanger and piping walls, creating a potential corrosion problem. Corrosion can be prevented by spraying the effluent with caustic solutions so that the resultant condensate has a pH in the range 6.5–7.5. A second benefit is that this treatment aids in achieving an acceptable odor in the purified product (158). Eastman (159) and Hibernia (158) describe the use of a spray directly into the reactor effluent; Shell (158) partially cools the effluent in a heat exchanger before contacting with a spray.

The specifications for an industrial alcohol depend on the intended use. Probably for this reason noncomparable purification schemes are frequently found in the patent literature (160–164). Premium-grade ethanol has low water content, low odor ratings, and high permanganate-time-test values. Odor is improved by the partial hydrogenation of ethanol using Raney nickel catalyst (165) or by contact with unglazed porcelain and iron (166). The permanganate test is extremely sensitive to the presence of aldehydes. One ppm of crotonaldehyde or 2 ppm of sorbaldehyde is reported to decrease the test time from 60 to 30 min (158). This sensitivity suggests that purification by distillation alone is inadequate for achieving high permanganate test times (158). Carbonyl-containing and unsaturated materials are removed by treatment with sodium borohydride (167,168) and boric acid (169). Other methods used to remove carbonyl impurities include treatment with hydroxyl amine hydrochloride, potassium permanganate, or *N*-hydroxybenzenesulfonamide (169).

Purification schemes have generally emphasized the following techniques: (*1*) extractive distillation using water reflux to distill a large share of the impurities and concentrate the crude alcohol–water mixture; (*2*) efficient fractionation to produce approximately 190 proof alcohol; (*3*) hydrogenation to convert aldehyde impurities to alcohols, together with the use of chemicals such as inorganic bases and sodium sulfite (162); and (*4*) ion-exchange resins or azeotropic distillation to dehydrate 190-proof to 200-proof or absolute alcohol.

Fuel-grade ethanol does not meet the high purity requirements of the industrial market and requires further purification for crossover to industrial markets. Much research has been carried out to lower the costs of separating ethanol from fermentation processes. Fuel use requires anhydrous ethanol, less than 0.5 wt % water, so the ethanol–water azeotrope must be overcome. Conventional distillation schemes consume 50–80% of the energy used in a typical fermentation plant (170). Techniques involving extraction (171,172), critical fluid extraction (173), extractive distillation (170,174), membrane separation (175), and water adsorption by molecular sieves (176) or cellulose, carboxymethylcellulose, cornmeal, cracked corn, corn cobs, wheat straw, bagasse, starch, hemicellulose, wood chips, other grains, and other agricultural residues (177) have been reported.

## 6. Shipment

Commercial ethyl alcohol is shipped in railroad tank cars, tank trucks, 208-L (55-gal) and 19-L (5-gal) drums, and in smaller glass or metal containers having capacities of 0.473 L (one pint), 0.946 L (one quart), 3.785 L (one U.S. gal), or 4.545 L (one Imperial gal). The 208-L drums may be of the unlined iron type. If a guarantee of more meticulous quality is desired, the drums may be lined with phenolic resin. All containers, of course, must comply with the specifications of the U.S. Department of Transportation. Both 190 proof and 200 proof ethyl alcohol are considered red label (flammable) materials by the DOT, as both have flash points below 37.8°C by the Tag closed-cup method.

## 7. Economic Aspects

Brazil is the world's largest producer of fermentation alcohol, which has over $15 \times 10^9$ liters of capacity. Fermentation processes accounted for over 83% of the total production in the United States, Western Europe, and Japan in 1997. In 2001 that capacity increased to 90%. Fermentation accounts for 95% of total ethanol capacity (40).

Table 3 gives United States producers of ethanol and their capacities (both synthetic and fermentation). Synthetic alcohol is made by ethylene hydration at high temperature and high pressure over phosphoric acid catalyst. Dow Chemical uses its Texas facility to refine crude ethanol imported from Saudi Arabia (179).

In Brazil and the U.S., fermentation ethanol is used primarily in motor fuels. Small amounts of ethanol are used in motor fuels in Western Europe, however, more than two-thirds of the industrial market is supplied by fermentation alcohol. In Japan, both synthetic and fermentation sources are supplied. Ethanol is not used in motor fuels in Japan.

In 2000, the United States, Western Europe, and Japan consumed $9.0 \times 10^6$ kiloliters of ethanol.

Table 3. U.S. Producers of Ethanol and Their Capacities, $10^6$ L[a]

| Producer | Capacity[b] |
|---|---|
| **Synthetic** | |
| Dow Chemical, Texas City, Tex. | 454 |
| Equistar Chemical, Tuscola, III. | 189 |
| *Total synthetic* | *643* |
| **Fermentation** | |
| Ace Ethanol, Stanley, Wis. | 57 |
| Adkins Energy, Lena, III. | 151 |
| AE Staley Manufacturing, Loudon, Tenn. | 246 |
| Ag Processing, Hastings, Neb. | 197 |
| Agn-Energy, Luveme, Minn. | 79 |
| Alchem, Grafton, N.D. | 42 |
| Al-Corn Clean Fuel, Claremont, Minn. | 114 |
| American Agri-Technology, Great Falls, Mont. | 114 |
| Archer Daniels Midland, Ceder Rapids, lowa; Clinton, lowa; Columbus, Neb.; Decatur, III.; Marshall, Minn., Peoria, III.; Walhalla, N.D. | 3,796 |
| Badger State Ethanol, Monroe, Wis. | 151 |
| BCI Louisiana Jennings, La. | 76 |
| Cargill, Blair, Neb.; Eddyville, lowa | 447 |
| Central Minnesota Ethanol Co-op, Little Falls, Minn. | 76 |
| Chief Ethanol Fuels, Hastings, Neb. | 235 |
| Chippewa Valley Ethanol, Benson, Minn. | 76 |
| Corn Plus, Winnebago, Minn. | 166 |
| Dakota Ethanol, Wentworth, S.D. | 178 |
| Denco, Morris, Minn. | 151 |
| Ethanol 2000, Bingham Lake, Minn. | 114 |
| Exol, Albert Lea, Minn. | 140 |
| Glacial Lakes Energy, Watertown, S.D. | 170 |
| Golden Triangle Energy, Craig, Mo. | 76 |
| Gopher State Ethanol, St. Paul, Minn. | 57 |
| Grain Processing, Muscatine, lowa | 38 |
| Heartland Corn Products, Winthrop, Minn. | 132 |
| Heartland Grain Fuels, Aberdeen, S.D.; Huron, S.D. | 83 |
| High Plains, Colwich; Kan.; Portales, N.M.; York, Neb. | 321 |
| Michigan Ethanol, Caro, Mich. | 170 |
| MGP Ingredients, Atchison, Kan.; Pekin, III. | 326 |
| Midwest Grain Processors, Lakota, lowa | 170 |
| Minnesota Energy, Buffalo Lake, Minn. | 68 |
| New Energy, South Bend, lnd. | 360 |
| Northeast Missouri Grain, Macon, Mo. | 83 |
| Northern Lights Ethanol, Big Stone City, S.D. | 170 |
| Pro-Corn, Preston, Minn. | 151 |
| Quad County Corn Processors, Galva, lowa | 68 |
| Reeve Agri-Energy, Garden City, Kan. | 45 |
| Siouxland Energy and Livestock Co-op, Sioux Center, lowa | 53 |
| Sutherland Associates, Sutherland, Neb. | 57 |
| Tall Corn Ethanol, Coon Rapids, lowa | 170 |
| Tri-State Ethanol, Rosholt, S.D. | 68 |
| US Energy Partners, Russell, Kan. | 151 |
| US Liquids Loulsville, Ky.; Bartow, Fa.; Cucamonga, Callf. | 45 |
| Williams Bio-Energy, Pekin, III.; Aurora, Neb. | 511 |
| others 15 plants under 38 million liters capacity each | 238 |
| *Total fermentation* | *10,781* |
| *Grand total* | *11,424* |

[a] Ref. 179.

[b] Numbers were converted from gallons to liters. These numbers have been rounded to avaid decimals.

Industrial demand in the United States in 2001 was $1018 \times 10^6$ L. Projected demand for 2005 is $1086 \times 10^6$ L. Demand for fuel, food, and beverage alcohol made by fermentation was $6794 \times 10^6$ L. Projected demand for 2005 is $10{,}560 \times 10^6$ L. Demand equals production plus imports minus exports. In 2001 exports were $144 \times 10^6$ L for industrial ethanol and $151 \times 10^6$ L for fuel, food, and beverage ethanol.

Prices for the period 1996–2002 (industrial) for 190 proof ethanol were in the range of $0.48-0.74/L ($1.80-2.80/gal). The 2003 price was $0.70/L ($2.65/gal). Fuel grade prices for 1996–2002 were $0.26-0.48/L ($0.99-1.81/gal), tanks fob. The 2003 price was $0.41/L ($1.55/gal) (179).

The United States industrial market is mature. Use as a solvent is regulated as a volatile organic solvent. It is still used as a chemical intermediate for a number of compounds, but is being displaced by other lower-cost alternatives. The industrial sector is expected to grow at the rate of 1.6%/yr.

Demand for ethanol for fuel consumption is expected to amount to $10 \times 10^6$ kiloliters in 2005. Much uncertainty exists in this market because it is highly sensitive to political influences. The Clean Air Act Amendments of 1990 mandated the use of oxygen-containing compounds in gasoline as an oxygenate in certain areas of the U.S. Methyl-*tert*-butyl ether (MTBE) has been the major additives, but is subject to growing environmental concerns. There has been an announced ban in California and several other states are reviewing oxygenate use. Some oil companies have already switched to ethanol in their California gasoline blends. Ethanol has already been used as and oxygenate in some areas. If MTBE is banned, ethanol can be used as a replacement. However, it is possible that oxygenates may not be required by 2005. However, projected growth is still expected at 10%/yr through 2005.

In Western Europe, ethanol is not used widely in fuels. France and Spain use ethyl-*tert*-butyl ether (made for ethanol) as an additive in gasoline. In Japan, fermentation ethanol is used in the food industry; synthetic ethanol is used in solvents and other chemical applications. Consumption is expected to grow at the rate of 2%/yr in Japan (40).

## 8. Units and Specifications

### 8.1. Units

The alcohol content of spirits is usually given in terms of proof, an archaic term inherited from early distillers of fermentation alcohol. In England, the proof was to pour some of the spirit over gunpowder, and ignite the spirit; at or above a limiting concentration (11 parts of alcohol by volume to 10 parts of water), the gunpowder would explode. Because volumes were at the time much easier to measure accurately than weights, this measurement of alcohol persisted, even though there is a considerable volume change on mixing ethyl alcohol with water.

In the United States the proof is twice the alcohol content by volume, thus 190-proof alcohol contains 95% ethyl alcohol by volume (Table 4). According to Federal statute, "... proof spirits shall be held to be that alcoholic liquor which contains one-half of its volume of alcohol of a specific gravity of 0.7939 at 15.5°C." A gallon (3.785 L) of proof spirits can be made by mixing 0.5000 gal (1.8925 L) of absolute alcohol with 0.5373 gal (2.0337 L) water; it contains 42.49% alcohol by weight. A wine gallon is a measure of quantity, 231 in.$^3$ (3.785 L), of any proof. A proof gallon (tax gallon) is a wine gallon of 100-proof spirits, or its equivalent.

The determination of the proof (the alcohol content) is usually made by measuring specific gravity with hydrometers at the standard temperature of 15.5°C, since only very small amounts of impurities other than water are usually present.

### 8.2. Specifications

The specifications for ethyl alcohol are designed with sufficient latitude to allow for the two principal means of production, synthesis from ethylene and fermentation. The requirements given by the *U.S. Pharmacopeia*

**Table 4. Conversion of U.S. Proof to Alcohol by Volume, Alcohol by Weight, and British Proof[a]**

| U.S. proof[b] | Alcohol, vol %[b] | Alcohol wt % | British proof |
|---|---|---|---|
| 0 | 0.0 | 0.00 | 100.0 |
| 2 | 1.0 | 0.80 | 98.4 |
| 4 | 2.0 | 1.59 | 96.8 |
| 6 | 3.0 | 2.39 | 95.2 |
| 8 | 4.0 | 3.19 | 93.6 |
| 10 | 5.0 | 4.00 | 91.9 |
| 20 | 10.0 | 8.05 | 83.5 |
| 30 | 15.0 | 12.14 | 75.0 |
| 40 | 20.0 | 16.27 | 66.1 |
| 50 | 25.0 | 20.44 | 57.0 |
| 60 | 30.0 | 24.67 | 48.0 |
| 70 | 35.0 | 28.97 | 39.3 |
| 80 | 40.0 | 33.36 | 30.6 |
| 90 | 45.0 | 37.86 | 21.7 |
| 100 | 50.0 | 42.49 | 12.9 |
| 110 | 55.0 | 47.24 | 4.0 |
| 120 | 60.0 | 52.15 | 4.8[c] |
| 130 | 65.0 | 57.21 | 13.5[c] |
| 140 | 70.0 | 62.44 | 22.3[c] |
| 150 | 75.0 | 67.87 | 31.3[c] |
| 160 | 80.0 | 73.53 | 39.9[c] |
| 170 | 85.0 | 79.44 | 48.6[c] |
| 180 | 90.0 | 85.69 | 57.3[c] |
| 190 | 95.0 | 92.42 | 66.0[c] |
| 200 | 100.0 | 100.0 | 76.0[c] |

[a] Underproof, unless otherwise indicated (proof is given a value of zero).
[b] At 15.5°C.
[c] Overproof.

**Table 5. Typical Ethanol Specifications**

| Requirement | 190-Proof | 200-Proof |
|---|---|---|
| specific gravity, 20/20°C, max | 0.8126 | 0.7912 |
| purity, vol %, min | 95 | 99.9 |
| acidity, wt % as $CH_3COOH$, max | 0.002 | 0.002 |
| nonvolatile matter, g/100 mL, max | 0.0025 | 0.0025 |
| miscibility with water | complete | complete |
| permanganate time test, minutes, min | 40 | 25 |
| odor | no foreign or residual | no foreign or residual |
| color, APHA,[a] max | 10 | 10 |
| water, wt %, max |  | 0.1 |

[a] American Public Health Association.

(USP) and the American Chemical Society (ACS) generally form the foundation for the most widely used specifications (180,181). A tabulation of the specifications from the major alcohol producers, with consideration for the USP and ACS requirements, is shown in Table 5.

The primary producers of ethyl alcohol also market the specially denatured and completely denatured alcohols, as well as various proprietary solvents in which ethyl alcohol is the basic ingredient. These various products can also be described by rigid and descriptive specifications, but the requirements must make allowance for the chemical and physical character of the denaturants.

**Table 6. Respective Volumes of Alcohol and Water and Specific Gravity**[a]

| U.S. proof | Alcohol, vol | Water, vol | Apparent sp gr[b] |
|---|---|---|---|
| 101 | 50.60 | 53.24 | 0.93320 |
| 110 | 55.00 | 48.76 | 0.92409 |
| 120 | 60.00 | 43.71 | 0.91333 |
| 130 | 65.00 | 38.60 | 0.90190 |
| 140 | 70.00 | 33.43 | 0.88986 |
| 150 | 75.00 | 28.19 | 0.87714 |
| 160 | 80.00 | 22.87 | 0.86364 |
| 170 | 85.00 | 17.46 | 0.84927 |
| 180 | 90.00 | 11.93 | 0.83362 |
| 190 | 95.00 | 6.18 | 0.81582 |
| 198 | 99.00 | 1.29 | 0.79866 |
| 200 | 100.00 | 0.00 | 0.79365 |

[a] Table 6 may also be used to determine the quantity of water needed to reduce the strength of ethanol by a definite amount. Divide the alcohol in the given strength by the alcohol in the required strength, multiply the quotient by the water in the required strength, and subtract the water in the given strength from the product. The remainder is the number of liters (gallons) of water to be added to 378.5 L (100 gal) of spirits of the given strength to produce a spirit of a required strength.

[b] 15.6/15.6°C.

The use of ethyl alcohol in some medicinal and cosmetic products requires a very meticulous grade, particularly with reference to odor. In some instances, the odor can be correlated with the concentration of certain minor impurities; in most instances it cannot be directly associated with any measurable contaminant, and the quality can be ascertained only by odor comparison with previously accepted material.

## 9. Analytical Methods

The most generally used means of ascertaining the purity of commercial ethyl alcohol is by specific gravity determination, sometimes referred to as alcoholometry. For this reason, the specific gravity should be determined very accurately to the fourth decimal place by means of a calibrated pycnometer or hydrometer (182). The value obtained is referred to standard U.S. Dept. of the Treasury tables relating specific gravity to alcohol content. Table 6 is extracted from more detailed government tables. Of course, this procedure is valid only for undenatured alcohol, since the purity nomograph is based on the two-component alcohol-water mixture.

The other analytical methods necessary to control the typical specification given in Table 5 are, for the most part, common quality-control procedures. When a chemical analysis for purity is desired, acetylation or phthalation procedures are commonly employed. In these cases, the alcohol reacts with a measured volume of either acetic or phthalic anhydride in pyridine solution. The loss in titratable acidity in the anhydride solution is a direct measure of the hydroxyl groups reacting in the sample. These procedures are generally free from interference by other functional groups, but both are affected adversely by the presence of excessive water, as this depletes the anhydride reagent strength to a level below that necessary to ensure complete reaction with the alcohol. Both procedures can be adapted to a semimicro- or even microscale determination.

Of course, acetylation and phthalation are not selective for ethyl alcohol, but determine any reactive OH group present. A survey of methods applicable to the determination of ethyl alcohol has been published (183). A method using a solution of acetyl chloride in toluene has been described (184). Owing to both the reactivity and volatility of the reagent, special techniques and careful handling are required for accurate

**Table 7. Ethanol Vapor Concentration and Its Effects in Humans**[a]

| Concentration | | |
|---|---|---|
| mg/L of air | ppm/vol of air | Effects in humans |
| 10–20 | 5,300–10,640 | some transient coughing and smarting of the eyes and nose which disappear after 5–10 min; not comfortable but tolerable |
| 30 | 15,960 | continuous lacrimation and marked coughing; could be tolerated but with discomfort |
| 40 | 21,280 | just tolerable for short periods |
| >40 | >21, 280 | intolerable and suffocating for even short periods |

[a] Ref. 201.

analyses, and in general the method is less satisfactory than that using acetic anhydride. To overcome the difficulties of using acetyl chloride solutions, 3,5-dinitrobenzoyl chloride can be used, and after hydrolysis, titration with tetrabutylammonium hydroxide (185) is carried out. Pyromellitic dianhydride has also been used as an acylating agent (186) in the presence of aldehydes.

Colorimetric methods have been successfully used for determining trace amounts of ethanol. Ammonium hexanitratocerate(IV) has been used as a reagent (187) and for continuous automatic analysis. Alcohols form colored complexes with 8-hydroxyquinoline and vanadic compounds. The absorbance of these complexes, measured at 390 $\mu$m has been used to provide an analytical procedure (188).

Acetone (189) and ethyl acetate (190) have been used as internal standards for the gas chromatographic determination of ethanol. This technique and enzymatic methods (191) have become widely used for estimation of ethanol in blood samples. Capillary gas chromatographs are replacing packed column chromatographs because of their higher sensitivity and better reproducibility. Automatic versions of the alcohol dehydrogenase method have been devised (192) and evaluated (193). The content of alcohol in wines has been measured using a differential refractometer (194). An automatic online head-space gas chromatographic method has been developed for quantitative determination of fermentation ethanol (195). The determination of ethanol in exhaled air by such equipment as the Breathalyzer (196) and Alcotest (197) depends on color changes in a solid adsorbent.

## 10. Health and Safety Factors

Ethyl alcohol is a flammable liquid requiring a red label by the DOT and Coast Guard shipping classifications; its flash point is 14°C (Tag, closed cup). Vapor concentrations between 3.3 and 19.0% by volume in air are explosive. Liquid ethyl alcohol can react vigorously with oxidizing materials. Ethyl alcohol has found wide application in industry, and experience shows that it is not a serious industrial poison (198–200). If proper ventilation of the work environment is maintained, there is little likelihood that inhalation of the vapor will be hazardous.

The threshold limit value for ethyl alcohol vapor in air has been set at 1000 ppm for an 8-h time-weighted exposure by the ACGIH; OSHA PEL is TWA 1000 ppm (200). The minimum identifiable odor of ethyl alcohol has been reported as 350 ppm. Exposure to concentrations of 5,000–10,000 ppm result in irritation of the eyes and mucous membranes of the upper respiratory tract and, if continued for an hour or more, may result in stupor or drowsiness. Concentrations of this latter order of magnitude have an intense odor and are almost intolerable to begin with, but most people can become acclimated to the exposure after a short time. Table 7 gives the effects of exposure to even heavier concentrations.

Ethyl alcohol is oxidized completely to carbon dioxide and water in the body, thus it is not a cumulative poison. An average adult is able to oxidize each hour the equivalent of 19 g of 100 proof whiskey (202). Less than 10% of the absorbed alcohol is excreted, chiefly in urine, measurably in expired air, and detectably in sweat (203). Alcohol poisoning and alcohol intoxication are almost invariably the result of using alcohol as a beverage, rather than inhalation as a vapor. About 75–80 g of ingested alcohol will produce symptoms of intoxication in an average (70-kg) person. About 150–200 g will cause stupor, and 250–500 g may be a fatal dose. Severe hypoglycemia in certain individuals following a heavy drinking bout is now well established (204).

Because alcohol intoxication may be simulated by many pathologic conditions, including diabetic acidosis, the postconvulsive depression of epilepsy, uremia, head injuries, and poisonings by any other central nervous depressant and some stimulants (205), a diagnosis of acute alcoholism should not be made casually; chemical testing of blood, urine, or expired air is always desirable.

Some authorities question whether drunkenness can result from the inhalation of ethyl alcohol vapors. Experience has demonstrated that in any event such intoxication is indeed rare (206). There is no concrete evidence that the inhalation of ethyl alcohol vapor will cause cirrhosis. Liver function is definitely impaired during alcohol intoxication (207), making the subject more susceptible to the toxic effects of chlorinated hydrocarbons.

Repeated exposure to ethyl alcohol results in the development of a tolerance as evidenced by decreasing symptomatic reactions. It has been demonstrated that the symptoms of exposure are less clear and the time required to produce them is greater in subjects accustomed to alcohol. There is no proof, however, of physiological adaptation in humans in terms of metabolic changes or resistance to cellular injuries. The subject of the interaction of alcohol with other drugs has received much attention (202).

## 11. Uses

The uses for ethanol in the United States for 2003 break down as following.

Uses for industrial ethanol were: solvents, 60% (toiletries and cosmetics, 33%; coatings and inks, 30% detergents and household cleaners, 15%; processing solvents, 10%; external pharmaceuticals, 7%, miscellaneous, 5%) and chemical intermediates, 40% (ethyl acrylate, 27%; distilled vinegar, 25%; ethylamines, 13%; ethyl acetate, 10%; glycol ethers, 8%; miscellaneous 17%). Uses for fermentation ethanol were: fuels, 92%; industrial solvents and chemicals, 4%; beverages, 4% (179).

As an intermediate for other chemical derivatives, ethanol has been displaced by lower cost alternatives.

### 11.1. Denatured Ethanol

For hundreds of years alcoholic beverages have been taxed all over the world to generate government revenue. When ethanol emerged as a key industrial raw material, the alcohol tax was recognized as a burden to many essential manufacturing industries. To lift this burden, the Tax-Free Industrial and Denatured Alcohol Act of 1906 was passed in the United States. The U.S. Treasury, Bureau of Alcohol, Tobacco, and Firearms (BATF), now oversees the production, procurement, and use of ethanol in the United States.

The concern of the government is to prevent tax-free industrial ethanol from finding its way into beverages. To achieve this end, the regulations call for a combination of financial and administrative controls (bonds, permits, and scrupulous record keeping) and chemical controls (denaturants that make the ethanol unpalatable). Regulations establish four distinct classifications of industrial ethanol. The classifications with the most stringent financial and administrative controls call for little or no chemical denaturants. The classifications that call for the most effective chemical denaturants require the least financial and administrative controls. For a list of denaturants currently authorized, see Reference 208.

#### *11.1.1. Completely Denatured Alcohol*

Completely denatured alcohol (CDA) escapes the involved financial and administrative controls required of the other classifications of industrial ethanol. No tax is applied, no bond is required, no permit is needed to enable a customer to purchase CDA. Requirements for records by both producer and user are minimal. These simplified regulations are possible because CDA is denatured with substances that render it totally unfit for beverage purposes. It is also unsuitable where odor is objectionable. CDA and products made from it are, however, governed by special labeling requirements of the BATF. Repackaging of completely denatured alcohol is permitted as long as labeling requirements are met.

#### *11.1.2. Proprietary Solvents and Special Industrial Solvents*

Proprietary solvents and special industrial solvents are made with specially denatured alcohols according to the formulas authorized by the BATF. They can be purchased by customers without payment of tax, without posting a bond for tax, and without securing a permit from the BATF. Suppliers are required, however, to notify the BATF of the name, address, type of business, and approximate annual requirements and intended end use for any user buying in bulk.

Proprietary solvents may be repackaged for retail, wholesale, and industrial sales. Retail sales of special industrial solvents are prohibited. Agents may repackage special industrial solvents for wholesale and industrial sales, but only in drum quantities and with the producer's label. Special labeling requirements of the BATF apply to both proprietary and special industrial solvents.

#### *11.1.3. Specially Denatured Alcohol*

Specially denatured alcohols (SDA) are formulations of ethanol containing denaturant substances that generally render them unfit for beverage use but do not limit their use in specified applications. To use a specially denatured alcohol, a manufacturer must apply to the BATF, giving quantitative formulas and processes. Specimen labels and a sample of the finished product are also required. Then, the prospective user must obtain a bond for the total amount of specially denatured alcohol on hand or in transit at any given time.

#### *11.1.4. Pure Ethanol*

Undenatured ethanol can be bought on either a tax-free or tax-paid basis. Approved educational, scientific or medical organizations and public agencies can buy tax-free alcohol. Use and withdrawal permits are required, as are a bond and detailed records. Resale of tax-free ethanol is prohibited. Approved industrial uses for pure tax-paid ethanol include pharmaceuticals, cosmetics, flavoring extracts, and foods.

### 11.2. Chemicals Derived From Ethanol

#### *11.2.1. Acetaldehyde*

Until the early 1970s, the main use of industrial ethanol was for the production of acetaldehyde [75-07-0]. By 1977, the ethanol route to acetaldehyde had largely been phased out in the United States as ethylene and ethane became the preferred feedstocks for acetaldehyde production (209–227). Acetaldehyde usage itself has also changed; two primary derivatives of acetaldehyde, acetic acid, and butanol, are now produced from feedstocks other than acetaldehyde. Acetaldehyde is still produced from ethanol in India.

There are two ways to produce acetaldehyde from ethanol: oxidation and dehydrogenation. Oxidation of ethanol to acetaldehyde is carried out in the vapor phase over a silver or copper catalyst (228). Conversion is slightly over 80% per pass at reaction temperatures of 450–500°C with air as an oxidant. Chloroplatinic acid selectively catalyzes the liquid-phase oxidation of ethanol to acetaldehyde giving yields exceeding 95%. The reaction takes place in the absence of free oxygen at 80°C and at atmospheric pressure (229). The kinetics of the vapor and liquid-phase oxidation of ethanol have been described in the literature (230,231).

The reaction kinetics for the dehydrogenation of ethanol are also well documented (232–235). The vapor-phase dehydrogenation of ethanol in the presence of a chromium-activated copper catalyst at 280–340°C produces acetaldehyde in a yield of 89% and a conversion of 75% per pass (236). Other catalysts used include neodymium oxide and samarium hydroxide (237).

### 11.2.2. Ethylene

Where ethylene is in short supply and fermentation ethanol is made economically feasible, such as in India and Brazil, ethylene is manufactured by the vapor-phase dehydration of ethanol. The production of ethylene [74-85-1] from ethanol using naturally renewable resources is an active and useful alternative to the pyrolysis process based on nonrenewable petroleum. This route may make ethanol a significant raw material source for producing other chemicals.

Dehydration of ethanol has been effected over a variety of catalysts, among them synthetic and naturally occurring aluminas, silica-aluminas, and activated alumina (238–245), hafnium and zirconium oxides (244), and phosphoric acid on coke (246). Operating space velocity is chosen to ensure that the two consecutive reactions,

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2\,O + H_2O$$

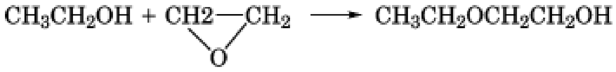
$$(C_2H_5)_2\,O \longrightarrow 2\,C_2H_4 + H_2O$$

go to completion, avoiding the need to recover and recycle unreacted ethanol. The dehydration is endothermic, and temperature is a critical operating parameter; high temperatures produce aldehydes and low temperatures, ethers. The catalyst is usually regenerated with steam and air every few weeks to remove carbon deposits.

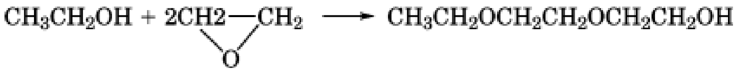
A fluidized-bed catalytic reactor system developed by C. E. Lummus (246) offers several advantages over fixed-bed systems in temperature control, heat and mass transfer, and continuity of operation. Higher catalyst activity levels and higher ethylene yields (99% compared to 94–96% with fixed-bed systems) are accomplished by continuous circulation of catalyst between reactor and regenerator for carbon burn-off and continuous replacement of catalyst through attrition.

### 11.2.3. Glycol Ethers

The addition of one mole of ethylene oxide [75-21-8] to ethanol gives ethylene glycol monoethyl ether [109-86-4].



Addition of two moles of oxide gives the monoethyl ether of diethylene glycol.



The oxide–alcohol route is the only commercially important route to glycol ethers now in use. Anhydrous alcohols must be used; otherwise the water present forms contaminating glycols.

The reactions are highly exothermic. Under liquid-phase conditions at about 200°C, the overall heat of reaction is $-83.7$ to $-104.6$ kJ/mol ($-20$ to $-25$ kcal/mol) ethylene oxide reacting (247). The opening of the oxide ring is considered to occur by an ionic mechanism with a nucleophilic attack on one of the epoxide carbon atoms (248). Both acidic and basic catalysts accelerate the reactions, as does elevated temperature. The reaction kinetics and product distribution have been studied by a number of workers (249,250).

Ethylene oxide (qv), propylene oxide (qv), butylene oxide, and other epoxides react with ethanol to give a variety of liquid, viscous, semiwax, and solid products. These products are used in the coatings industry as solvents, and as paints, antioxidants, corrosion inhibitors, and special-purpose polymers. Recent concerns about the health effects of ethanol containing glycol ethers have led to the decline in the production of these compounds.

### 11.2.4. Vinegar

Dilute solutions of alcohol as fermented worts are oxidized by air at 30–40°C in the presence of various organisms such as (251) *Mycoderma aceti*, *B. aceti*, and *B. xylinus*, to produce dilute acetic acid as vinegar. Vinegar based on synthetic ethanol has a fully acceptable aroma and taste (252) and has gained a healthy share of the market for vinegar used in such products as pickles, ketchup, and mustard. However, vinegar based on fermentation ethanol is gaining back some of this market because of the "all natural ingredients" trend in advertising.

### 11.2.5. Ethylamines

Mono-, di-, and triethylamines, produced by catalytic reaction of ethanol with ammonia (253), are a significant outlet for ethanol. The vapor-phase continuous process takes place at 1.38 MPa (13.6 atm) and 150–220°C over a nickel catalyst supported on alumina, silica, or silica–alumina. In this reductive amination under a hydrogen atmosphere, the ratio of the mono-, di-, and triethylamine product can be controlled by recycling the unwanted products. Other catalysts used include phosphoric acid and derivatives, copper and iron chlorides, sulfates, and oxides in the presence of acids or alkaline salts (254). Piperidine can be ethylated with ethanol in the presence of Raney nickel catalyst at 200°C and 10.3 MPa (102 atm), to give *N*-ethylpiperidine [766-09-6] (255).

### 11.2.6. Ethyl Acrylate

The esterification of acrylic acid is a primary use for ethanol. Acrylic acid can also react with either ethylene or ethyl esters of sulfuric acid.

$$\mathrm{CH_2{=}CHCOOH + C_2H_5OH \longrightarrow CH_2{=}CHCOOC_2H_5 + H_2O}$$

These processes have supplanted the condensation reaction of ethanol, carbon monoxide, and acetylene as the principal method of generating ethyl acrylate [140-88-5] (256). Acidic catalysts, particularly sulfuric acid (257–261), are generally effective in increasing the rates of the esterification reactions. Care is taken to avoid excessive polymerization losses of both acrylic acid and the esters, which are accentuated by the presence of strong acid catalysts. A synthesis for acrylic esters from vinyl chloride (262) has also been examined.

$$\mathrm{CH_2{=}CHCl + C_2H_5OH + CO \longrightarrow CH_2{=}CHCOOC_2H_5 + HCl}$$

Vinyl chloride reacts at 270°C at >6.9 MPa (68 atm) with ethanol and carbon monoxide in the presence of a cobalt and palladium catalyst to give ethyl acrylate in 17% yield.

### 11.2.7. Ethyl Ether

Most ethyl ether is obtained as a by-product of ethanol synthesis via the direct hydration of ethylene. The procedure used for production of diethyl ether [60-29-7] from ethanol and sulfuric acid is essentially the same as that first described in 1809 (263). The chemical reactions involved in the production of ethyl ether by the indirect ethanol-from-ethylene process are like those for the production of ether from ethanol using sulfuric acid.

$$\mathrm{C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O}$$

$$C_2H_5HSO_4 + C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2SO_4$$

Another concept (264) is that ether is principally derived from the reaction between diethyl sulfate and ethanol.

$$(C_2H_5O)_2SO_2 + C_2H_5OH \rightleftharpoons (C_2H_5)_2O + C_2H_5HSO_4$$

An alternative route for the formation of diethyl ether from ethanol is by dehydration:

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

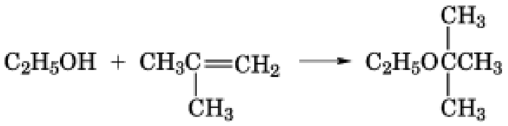
The reaction is catalyzed by all but the weakest acids. In the dehydration of ethanol over heterogeneous catalysts, such as alumina (265–268), ether is the main product below 260°C; at higher temperatures both ether and ethylene are produced. Other catalysts used include silica–alumina (269,270), copper sulfate, tin chloride, manganous chloride, aluminum chloride, chrome alum, and chromium sulfate (271,272).

### *11.2.8. Ethyl Vinyl Ether*

The addition of ethanol to acetylene gives ethyl vinyl ether [104-92-2] (273–277). The vapor-phase reaction is generally run at 1.38–2.07 MPa (13.6–20.4 atm) and temperatures of 160–180°C with alkaline catalysts such as potassium hydroxide and potassium ethoxide. High molecular weight polymers of ethyl vinyl ether are used for pressure-sensitive adhesives, viscosity-index improvers, coatings and films; lower molecular weight polymers are plasticizers and resin modifiers.

### *11.2.9. Ethyl tert-Butyl Ether*

Ethanol can react with isobutylene to form ETBE much the same way as methanol is now processed into MTBE, methyl *tert*-butyl ether (see ethers).



$$C_2H_5OH + CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2 \longrightarrow C_2H_5O\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$$

Ethyl *t*-butyl ether [637-92-3] (ETBE) is a viable octane enhancer and oxygenate for fuel and does not increase the vapor pressure of gasoline as ethanol does when blended. Although there is no current production of ETBE, this could change now that the government has extended the tax credit for ethanol in gasolines to ETBE (278). ETBE is more desirable than ethanol to gasoline refiners and blenders because it is easier to transport and is not ruined by water. Ethanol in gasoline absorbs water when transported through pipelines and tanks to local terminals. Too much water absorption causes phase separation.

### *11.2.10. Ethyl Acetate*

The esterification of ethanol by acetic acid was studied in detail over a century ago (274), and considerable literature exists on determinations of the equilibrium constant for the reaction. The usual catalyst for the production of ethyl acetate [141-78-6] is sulfuric acid, but other catalysts have been used, including cation-exchange resins (280), $\alpha$-fluoronitrites (281), titanium chelates (282), and quinones and their partly reduced products.

Ethyl acetate is made industrially by both batch and continuous processes (283,284). Glacial acetic acid is commonly the starting material, and any water formed during the esterification has to be removed. Sulfuric acid may be added periodically to the reactor to replace the acid lost in side reactions. The vapor-phase esterification of ethanol has also been studied extensively (285,286), but it is not used commercially. The reaction can be catalyzed by silica gel (287,288), thoria on silica or alumina (289), zirconium dioxide (290), and by xerogels and aerogels (291). Above 300°C the dehydration of ethanol becomes appreciable. Ethyl acetate can also be produced from acetaldehyde by the Tischenko reaction (292–294) using an aluminum alkoxide catalyst and, with some difficulty, by the boron trifluoride-catalyzed direct esterification of ethylene with organic acids (295).

### *11.2.11. Other Derivatives and Reactions*

The vapor-phase condensation of ethanol to give acetone has been well documented in the literature (296–305); however, acetone is usually obtained as a by-product from the cumene (qv) process, by the direct oxidation of propylene, or from 2-propanol.

The Guerbet reaction (306–309) involving condensation of ethanol in the presence of sodium ethoxide, catalyzed by potassium hydroxide and boric anhydride (310,311) or alkaline phosphates (312), gives *n*-butanol [71-36-3]:

$$2\ CH_3CH_2OH + CH_3CH_2ONa \longrightarrow CH_3CH_2CH_2CH_2OH + CH_3COONa + 2\ H_2$$

However, the oxo reaction starting frompropylene and proceeding via the hydrogenation of butyraldehyde, has become the more widely employed commercial route for preparing *n*-butanol (see Butyl alcohols; Oxo process).

During World War II, production of butadiene (qv) from ethanol was of great importance. About 60% of the butadiene produced in the United States during that time was obtained by a two-step process utilizing a 3:1 mixture of ethanol and acetaldehyde at atmospheric pressure and a catalyst of tantalum oxide and silica gel at 325–350°C (313–317). Extensive catalytic studies were reported (318–321) including a fluidized process (322). However, because of later developments in the manufacture of butadiene by the dehydrogenation of butane and butenes, and by naphtha cracking, the use of ethanol as a raw material for this purpose has all but disappeared.

An extensive listing of 35 other reactions including alkylation, etherification, alcoholysis, and halogenation has been compiled (1) to show the versatility of ethanol as a reactant.

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