

EPOXY RESINS

The most common epoxy resins are formed by the reaction of bisphenol A with epichlorohydrin.

Epoxy resins are intermediates for the production of other materials and, as such, must be cured, or cross-linked, to yield a useful resin. Cross-linking occurs by the opening of the epoxide ring by addition of a curing agent that must have active hydrogen atoms. Amines, acid anhydrides, and mercaptans are the most usual compounds used as curing agents.

Depending upon molecular weight, epoxy resins have a great many uses, ranging from adhesives to can and drum coatings. They have excellent chemical resistance, particularly to alkalis, very low shrinkage on cure, excellent adhesion and electrical insulating properties, and ability to cure over a wide range of temperatures.

See Bisphenol A.

ERYTHROMYCIN

Erythromycin is, like penicillin, isolated by solvent-extraction methods. It is an organic base, and extractable with amyl acetate or other organic solvents under basic conditions rather than the acidic ones that favor penicillin extraction.

ETHANE

Ethane (C_2H_6 , melting point: -172°C , boiling point: -88.6°C) is a colorless, odorless gas that has a very slight solubility in water but is moderately soluble in alcohol.

Ethane occurs in natural gas, from which it is isolated. Ethane is among the chemically less reactive organic substances. However, ethane reacts with chlorine and bromine to form substitution compounds. Ethyl iodide, bromide, or chlorides are preferably made by reaction with ethyl alcohol and the appropriate phosphorus halide. Important ethane derivatives, by successive oxidation, are ethyl alcohol, acetaldehyde, and acetic acid. Ethane can also be used for the production of aromatics by pyrolysis (Fig. 1).

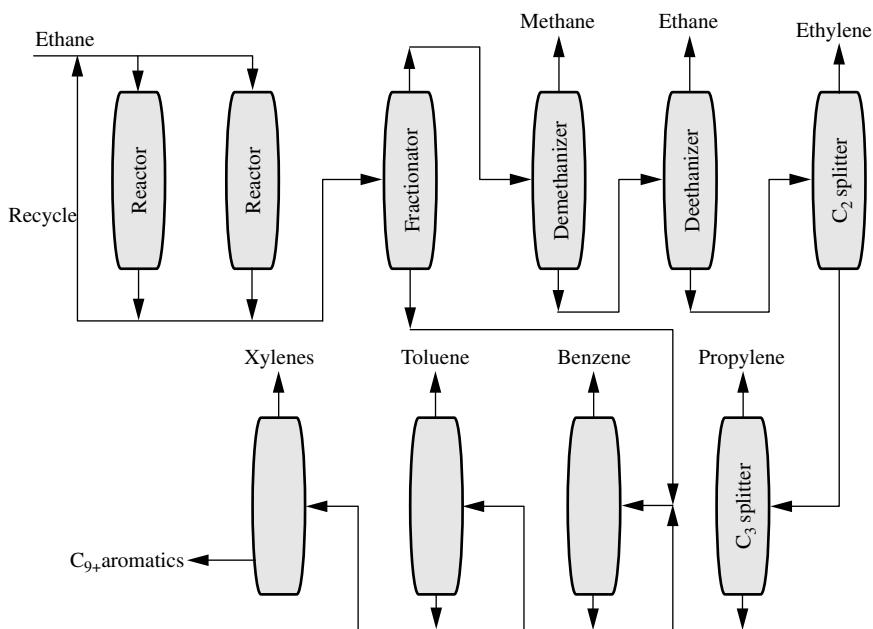


FIGURE 1 Manufacture of aromatics from ethane.

ETHANOLAMINES

The ethanolamines monoethanolamine (MEA, $\text{HOCH}_2\text{CH}_2\text{NH}_2$, melting point: 10.5°C , boiling point: 171°C , density: 1.018), diethanolamine [DEA, $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$, melting point: 28.0°C , boiling point: 270°C , density: 1.019], and triethanolamine [TEA, $(\text{HOCH}_2\text{CH}_2)_3\text{N}$, melting point: 21.2°C , boiling point: 360°C , density: 1.126] are manufactured by reacting ethylene oxide and excess ammonia, followed by separation of unreacted ammonia and the three ethanolamines. The proportion of the three products depends on reaction conditions.

Mono- and triethanolamine are miscible with water or alcohol in all proportions and is only slightly soluble in ether. Diethanolamine will dissolve in water, is very soluble in alcohol, and is only slightly soluble in ether. All of the compounds are clear, viscous liquids at standard conditions and white crystalline solids when frozen. They have a relatively low toxicity.

In early processes, the ethanolamines were manufactured by reacting ethylene chlorohydrin ($\text{ClCH}_2\text{CH}_2\text{OH}$) with ammonia (NH_3). Current processes react ethylene oxide ($\text{CH}_2\text{CH}_2\text{O}$) with ammonia usually in aqueous solution. The ratio of mono-, di-, and triethanolamines varies in accordance with the amount of ammonia present. This is controlled by the quantities of monoethanolamine and diethanolamine recycled.

Higher ammonia-ethylene oxide ratios favor high yields of diethanolamine and triethanolamine, whereas lower ratios are used where maximum production of monoethanolamine is desired. The reaction is noncatalytic. The pressure is moderate, just sufficient to prevent vaporization of components in the reactor. The bulk of the water produced in the reaction is removed by subsequent evaporation. The dehydrated ethanolamines then proceed to a further drying column, after which they are separated in a series of fractionating columns, not difficult because of the comparatively wide separation of their boiling points.

Industrially, the ethanolamines are important because they form numerous derivatives, notably with fatty acids, soaps, esters, amides, and

esteramides, and they have an exceptional ability for scrubbing acidic compounds out of gases. Monoethanolamine, for example, will effectively remove hydrogen sulfide (H_2S) from hydrocarbon gases, and carbon dioxide can also be removed from process streams and, where desired, heating the absorptive solutions can regenerate the carbon dioxide.

The soaps of the ethanolamines are extensively used in textile treating agents, in shampoos, and emulsifiers. The fatty acid amides of diethanolamine are applied as builders in heavy-duty detergents, particularly those in which alkylaryl sulfonates are the surfactant ingredients. The use of triethanolamine in photographic developing baths promotes fine grain structure in the film when developed.

Ethanolamine also is used as a humectant and plasticizing agent for textiles, glues, and leather coatings and as a softening agent for numerous materials. Morpholine is an important derivative.

See Amination.

ETHER

Diethyl ether (ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, melting point: -116.3°C , boiling point: 34.6°C , density: 0.708) is slightly soluble in water (1 volume in 10 volumes of water) and is miscible with alcohol in all proportions.

The long-used manufacturing procedure for ether has been the dehydration of alcohol (denatured with ether) by sulfuric acid. The anesthetic ether is especially purified and packaged. Ether is also supplied as a by-product from the manufacture of alcohol from ethylene.

Ether is a valuable solvent for organic chemicals. At one time ether was the major anesthetic, for which it must be scrupulously pure. In addition to various side effects that may result from the use of ether as an anesthetic, it is a definite hazard in the operating room because of its explosive properties, particularly in enriched oxygen atmospheres.

ETHYL ACETATE

Ethyl acetate (boiling point: 77.1, density: 0.9005, flash point: -4°C) is manufactured from ethyl alcohol and acetic acid.



A more recent process allows the manufacture of ethyl acetate from ethyl alcohol without the use of acetic acid or any other cofeedstocks. In the process (Fig. 1), ethyl alcohol is heated and passed through a catalytic dehydrogenation reactor where part of the ethyl alcohol is dehydrogenated to form ethyl acetate and hydrogen.

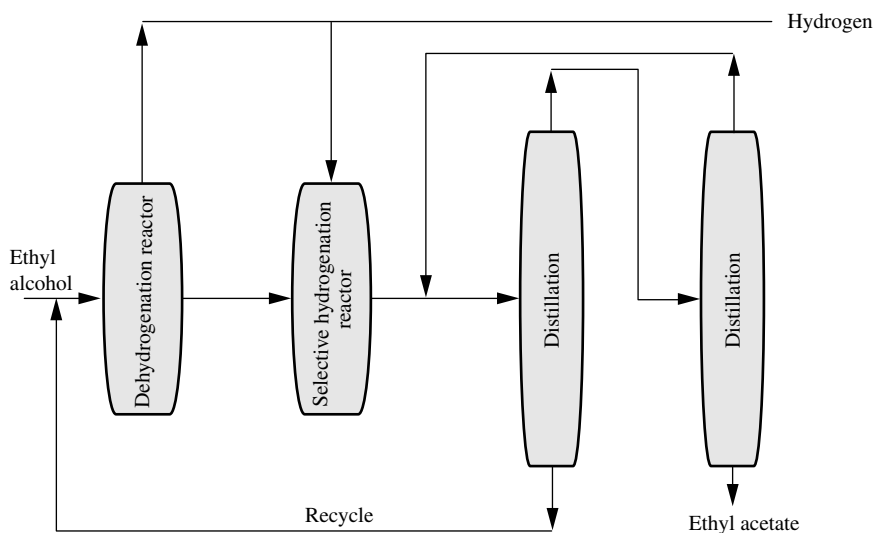
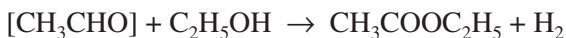
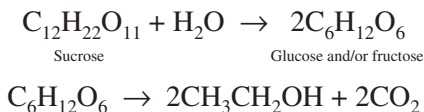


FIGURE 1 Manufacture of ethyl acetate.

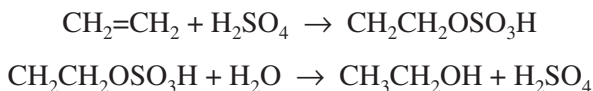
ETHYL ALCOHOL

Ethyl alcohol (ethanol, freezing point: -114.1°C , boiling point: 78.3°C , density: 0.7893, flash point: 14°C) is also named, industrial alcohol, grain alcohol, and alcohol. Ethyl alcohol is miscible in all proportions with water or with ether. When ignited, ethyl alcohol burns in air with a pale blue, transparent flame, producing water and carbon dioxide. The vapor forms an explosive mixture with air and is used in some internal combustion engines under compression as a fuel; such mixtures are frequently referred to as gasohol.

Much of the ethanol produced in the past has been manufactured by routes such as by the fermentation of sugars. Waste syrup (molasses) after crystallization of sugar from sugar cane processing, containing mostly sucrose, can be treated with enzymes from yeast to give ethyl alcohol and carbon dioxide. The enzymes require 28 to 72 hours at 20 to 38°C and give a 90 percent yield. This process is not used to any great extent for the current production of industrial alcohol.



The next method of manufacture, the esterification/hydrolysis of ethylene, was another method of choice, and an important side product in this electrophilic addition to ethylene was diethyl ether.



The current process of choice involves the direct hydration of ethylene with a catalytic amount of phosphoric acid (Fig. 1). Temperatures average 300 to 400°C with 1000 psi.

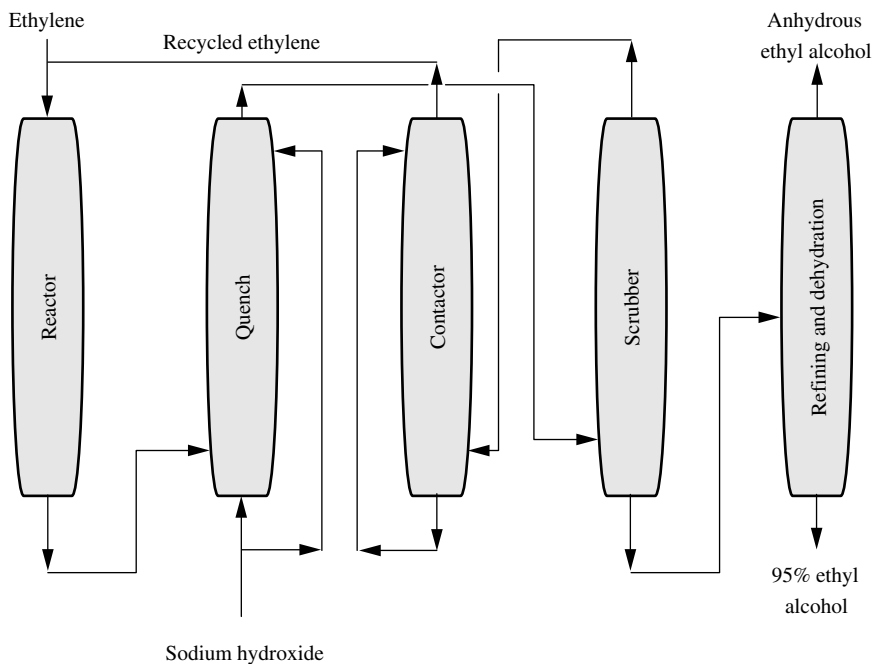


FIGURE 1 Manufacture of ethyl alcohol.



Only 4 percent of the ethylene is converted to alcohol per pass, but this cyclic process eventually gives a net yield of 97 percent.

In this direct hydration process, a supported acid catalyst usually is used. Important factors affecting the conversion include temperature, pressure, the water/ethylene ratio, and the purity of the ethylene. Further, some by-products are formed by other reactions taking place, a primary side reaction being the dehydration of ethyl alcohol into diethyl ether:



To overcome these problems, a large recycle volume of unconverted ethylene usually is required. The process usually consists of a reaction section in which crude ethyl alcohol is formed, a purification section with a product of 95% (volume) ethyl alcohol, and a dehydration section, which produces high-purity ethyl alcohol free of water. For many industrial uses, the 95%-purity product from the purification section suffices.

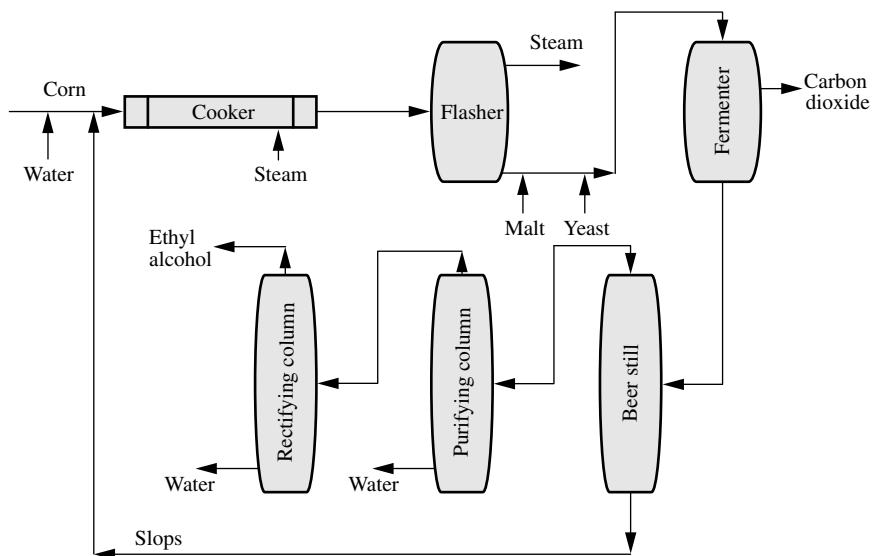
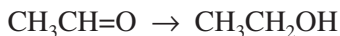


FIGURE 2 Production of ethyl alcohol by fermentation.

The fermentation process (Fig. 2) is in use again to produce ethyl alcohol for use in gasohol, an automobile fuel that is a simple mixture of 90% gasoline and 10% alcohol claimed to increase mileage.

Ethyl alcohol is also manufactured from a cellulose source (such as wood) (Fig. 3) but no matter what the process, it is often necessary to dehydrate the product for the production of pure alcohol (Fig. 4).

Ethyl alcohol is also produced by the vapor phase reduction of acetaldehyde in the presence of metal catalysts.



Suitable catalysts for the process are supported nickel and copper oxide.

Anhydrous ethyl alcohol is made from the constant boiling mixture with water (95.6% ethyl alcohol by weight) by heating with a substance such as calcium oxide, which reacts with water and not with alcohol, and then distilling, or by distilling with a volatile liquid, such as benzene (boiling point: 79.6°C) which forms a constant low-boiling mixture with water and alcohol (boiling point: 64.9°C), so that water is removed from the main portion of the alcohol; after which alcohol plus benzene distills over (boiling point: 78.5°C).

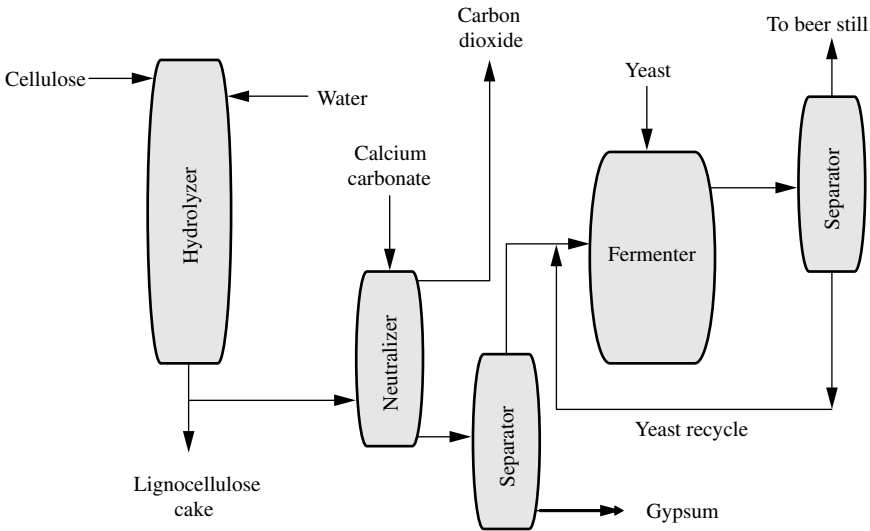


FIGURE 3 Production of ethyl alcohol from cellulose (wood)

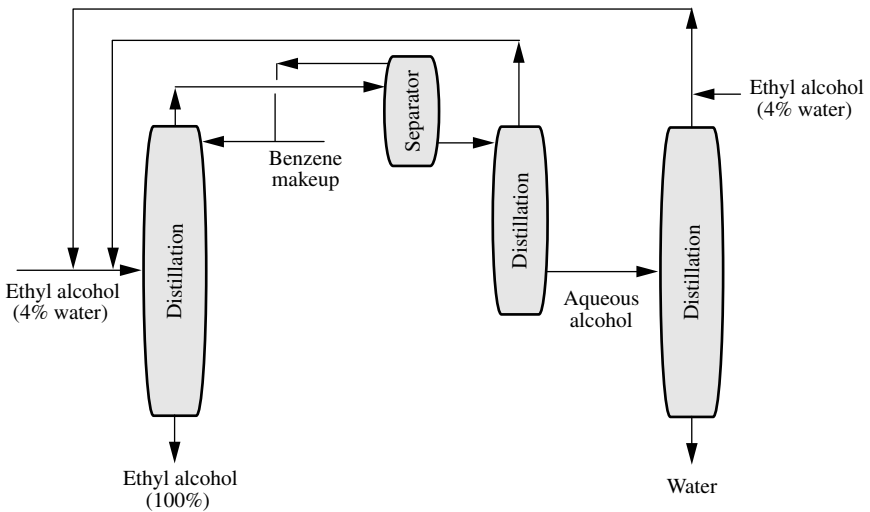


FIGURE 4 Dehydration of crude ethyl alcohol.

Most alcohol is sold as 95% ethanol–5% water since it forms an azeotrope at that temperature. To obtain absolute alcohol, a third component, such as benzene, must be added during the distillation. This tertiary azeotrope carries over the water and leaves the pure alcohol behind. Common industrial alcohol is *denatured*, and additives are purposely included to make it nondrinkable and therefore not subject to the high taxes of the alcoholic beverage industry.

The use and production values for ethanol do not include that amount produced for most alcoholic beverages.

U.S. proof was the term originally applied to a test of strong alcoholic beverages done by pouring the sample onto gunpowder and lighting it. Ignition of the gunpowder was considered proof that the beverage was not diluted. A value of 100 proof now refers to 50% alcohol by volume (42.5% by weight). Thus 190 proof is 95% alcohol by volume (92.4% by weight).

Industrial uses of ethanol include solvents (especially for toiletries and cosmetics, coatings and inks, and detergents and household cleaners), and chemical intermediates (especially ethyl acrylate, vinegar, ethylamines, and glycol ethers). Most corn fermentation alcohol is used in fuel, industrial solvents and chemicals, and beverages.

ETHYLBENZENE

Ethylbenzene (boiling point: 136°C, density: 0.8672, flash point: 21°C) is a colorless liquid that is manufactured from benzene and ethylene by several modifications of the older mixed liquid-gas reaction system using aluminum chloride as a catalyst (Friedel-Crafts reaction). The reaction takes place in the gas phase over a fixed-bed unit at 370°C under a pressure of 1450 to 2850 kPa. Unchanged and polyethylated materials are recirculated, making a yield of 98 percent possible. The catalyst operates several days before requiring regeneration.



Excess benzene is used if the formation of di- and trimethylbenzenes is to be avoided or minimized. The benzene is recycled.

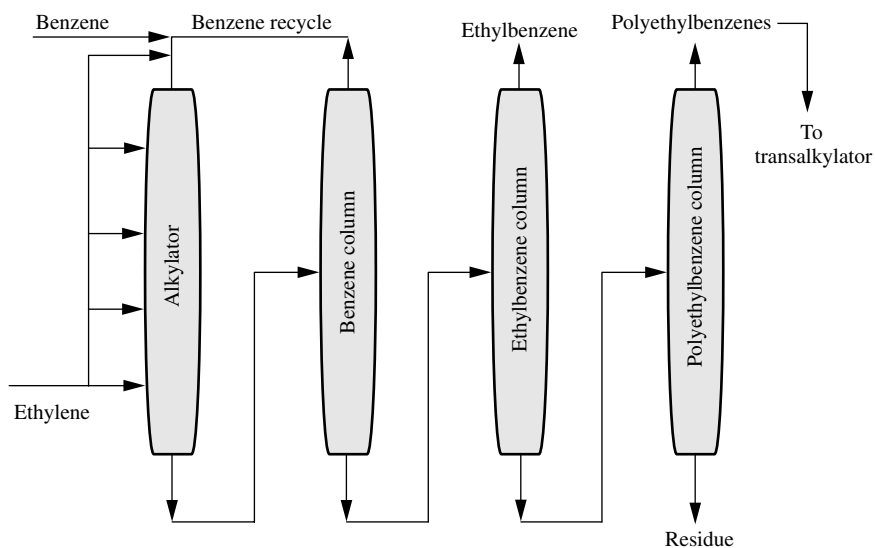


FIGURE 1 Manufacture of ethylbenzene.

In the more modern process (Fig. 1) the reaction takes place in the liquid phase, using a zeolite catalyst and cycle lengths in excess of 3 years are expected for the catalyst.

A vapor-phase method with boron trifluoride, phosphoric acid, or alumina-silica as catalyst has given away to a liquid-phase reaction with aluminum chloride at 90°C and atmospheric pressure. A zeolite catalyst at 420°C and 175 to 300 psi in the gas phase is also available.

Despite the elaborate separations required, including washing with caustic and water and three distillation columns, the overall yield of ethylbenzene is 98 percent. Ethylbenzene is used predominantly ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$) manufacture; a minor amount is used as a solvent.

*See **Benzene** and **Xylenes**.*

ETHYLENE

Ethylene (boiling point: -103.7°C , flash point: -136.1°C , ignition temperature: 450°C) is a colorless, flammable gas with a faint, pleasant odor that can be isolated from refinery gas (Fig. 1), but the majority of the ethylene (ethene) is produced by the thermal cracking of petroleum feedstocks (hydrocarbons) at high temperatures with no catalyst. In contrast to the catalytic cracking used by the petroleum industry to obtain high yields of gasoline, thermal cracking is used since it yields larger percentages of ethylene, propylene, and butylenes. Naphtha and gas oil fractions from petroleum can also be used as feedstock for ethylene manufacture.

Steam cracking (Fig. 2), consists of a furnace in which the cracking takes place is at 815 to 870°C (1500 to 1600°F). As many as 6 to 20 furnaces are in parallel to increase ethylene production. Steam is used as a diluent to inhibit coking in the tubes and to increase the percentage of ethylene formed. The amount of steam changes with the molecular weight of the hydrocarbon feedstock and varies from 0.3 kg steam/kg ethane to 0.9

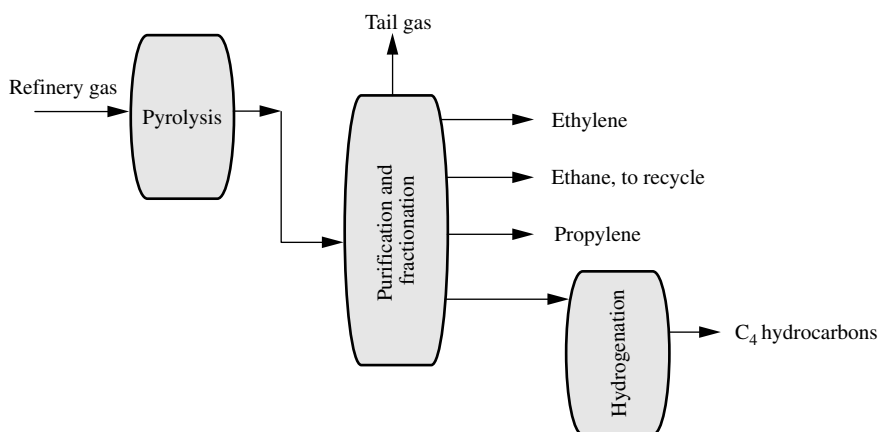


FIGURE 1 Production of ethylene from refinery gas.

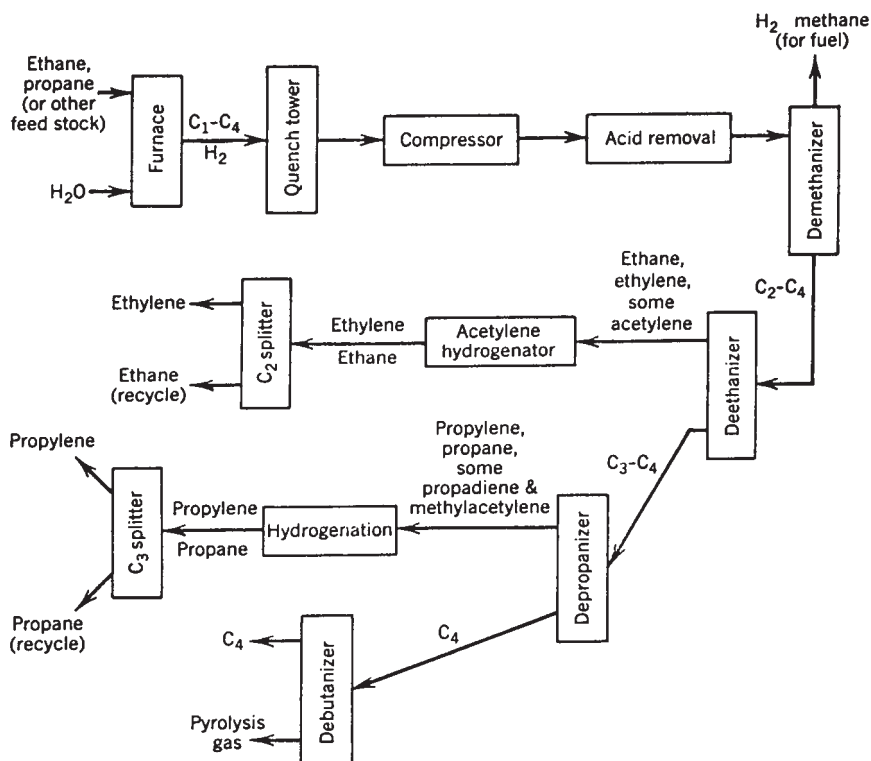


FIGURE 2 Olefin manufacture by thermal cracking.

kg steam/kg gas oil. Contact time is 1 second or less in the furnace. The exit gases are immediately cooled in the quench tower then placed under 500 psi pressure by a compressor. Monoethanolamine or caustic soda solution is used to remove hydrogen sulfide and carbon dioxide. The demethanizer, deethanizer, and debutanizer are fractionating columns that separate the lighter and heavier compounds from each other.

Traces of other unsaturated triple bonds are removed by catalytic hydrogenation with a palladium catalyst in both the C_2 and C_3 stream. Cumulated double bonds are also hydrogenated in the C_3 fraction. These are more reactive in hydrogenation than ethylene or propylene. The C_2 and C_3 fractionators are distillation columns that can be as high as 200 ft.

Lower-molecular-weight feedstocks, such as ethane and propane, give a high percentage of ethylene; higher-molecular-weight feedstocks, such as naphtha and gas oil, are used if propylene is required in significant quantities.

Ethylene is sold from 95% purity (technical) to 99.9% purity. It can be transported by pipeline or by tank car. Smaller amounts come in 100-lb cylinders.

Ethylene is used in the manufacture of a wide range of chemicals (Fig. 3) including polyethylene (Figs. 4 and 5), styrene, alcohols, ethylene oxide, and vinyl chloride.

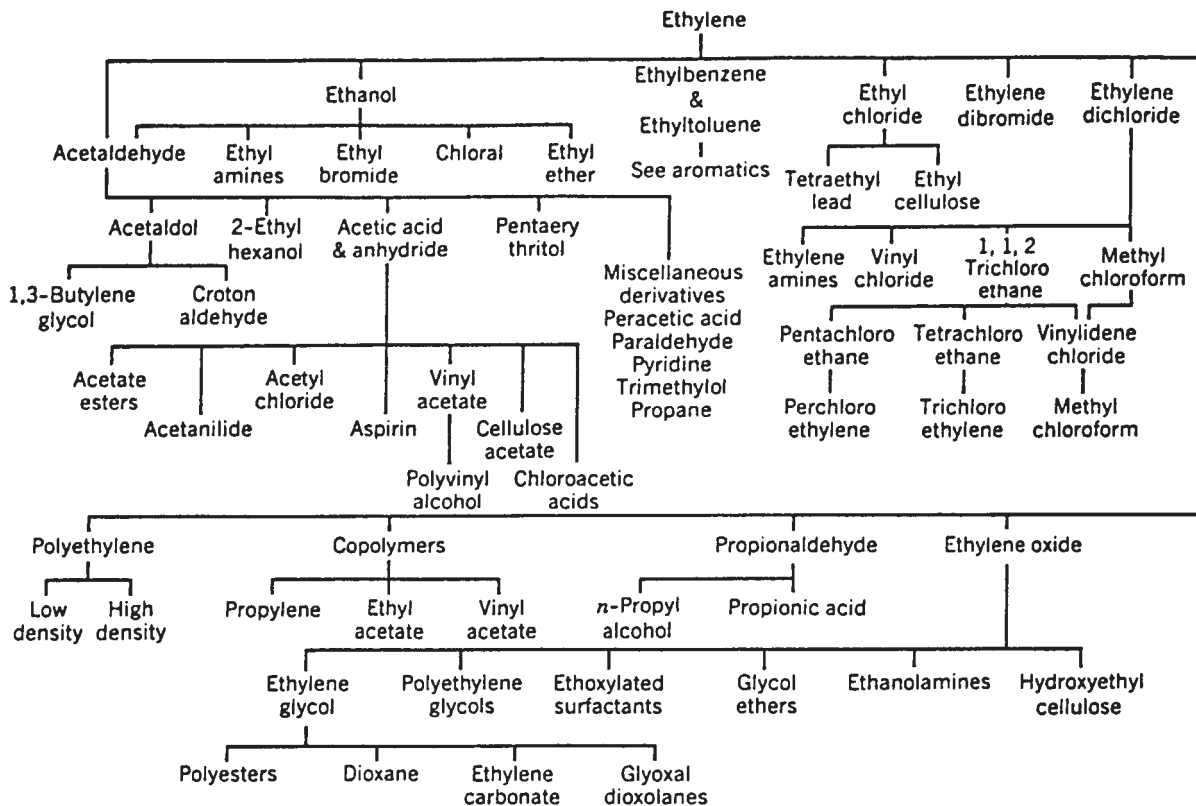


FIGURE 3 Chemicals produced from ethylene.

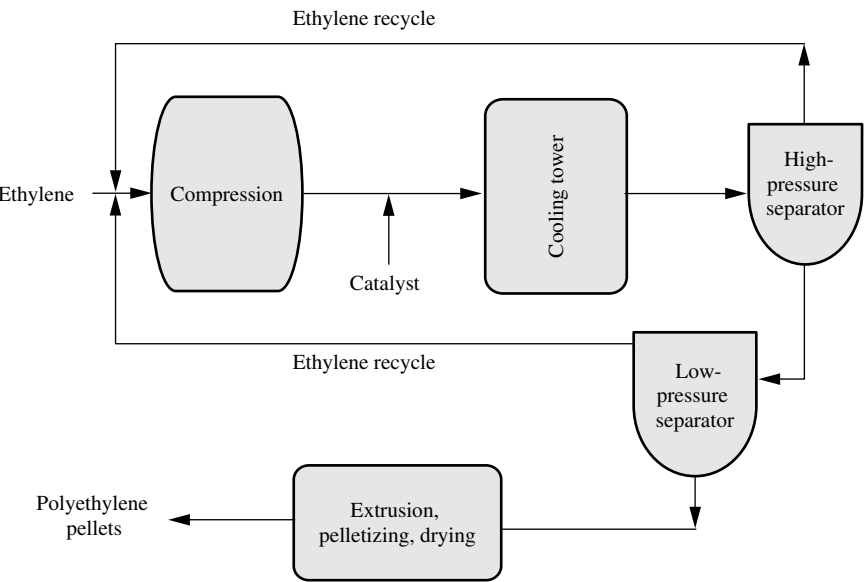


FIGURE 4 Manufacture of low-density polyethylene

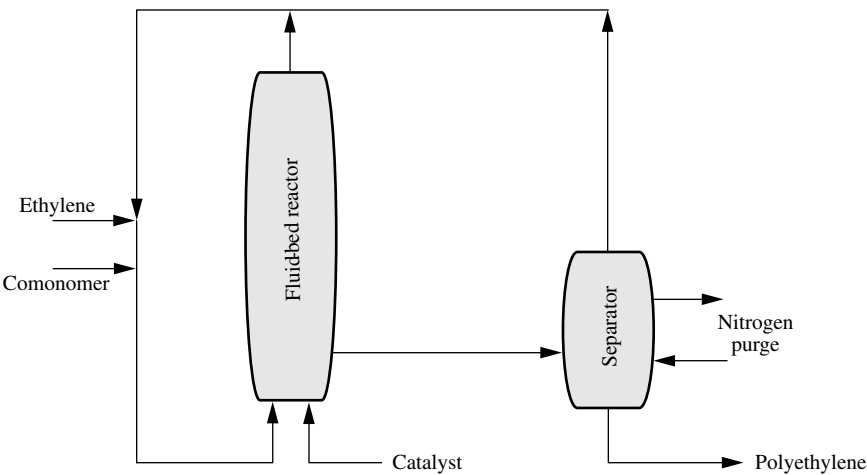
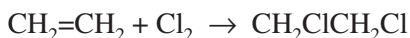


FIGURE 5 Manufacture of high-density polyethylene.

ETHYLENE DICHLORIDE

Ethylene dichloride (1,2-dichloroethane, $\text{CH}_2\text{ClCH}_2\text{Cl}$), a colorless toxic liquid (boiling point 84°C , density: 1.2560, flash point: 13°C) is manufactured by two methods.

The classical method for the manufacture of ethylene dichloride is the addition of chlorine to the double bond of ethylene (Fig. 1).



Ferric chloride is often used as the catalyst. The yield is high (96 to 98%, based on ethylene) and the reaction can be carried out in the vapor phase or in the liquid phase at varying temperatures and the product is easily purified by fractional distillation.

However, when chlorine is added to olefins such as ethylene, many and mixed derivatives are formed. In addition to ethylene dichloride, dichloroethylene, trichloroethylene, tetrachloroethane, and chloromethanes form. Other halogens produce similar mixtures. With good reaction control, high yields of the desired product are possible.

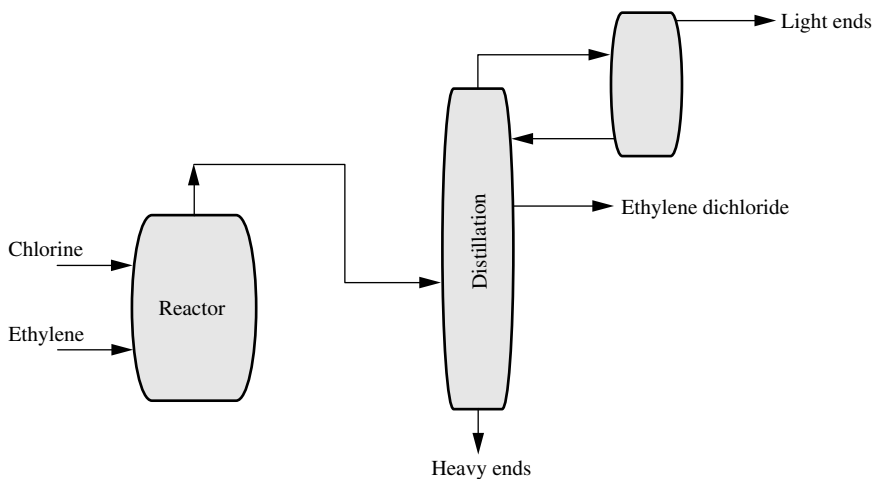


FIGURE 1 Manufacture of ethylene dichloride by direct chlorination.

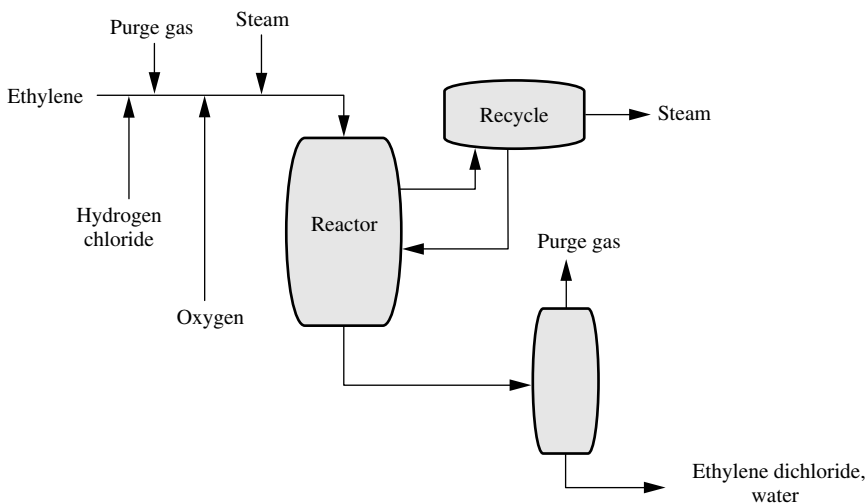
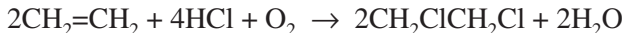


FIGURE 2 Manufacture of ethylene dichloride by oxychlorination.

In contrast to this direct chlorination there is the oxychlorination of ethylene using hydrogen chloride and oxygen (Fig. 2).



The catalysts for this reaction are cupric chloride (CuCl_2), potassium chloride (KCl), and alumina (Al_2O_3) or silica (SiO_2).

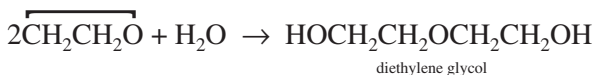
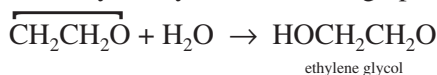
Most of the ethylene dichloride manufactured is converted into vinyl chloride by eliminating a mole of hydrogen chloride (HCl) that can then be recycled and used to make more ethylene dichloride by oxychlorination.



Ethylene is also used to manufacture perchloroethylene ($\text{CCl}_2=\text{CCl}_2$), methyl chloroform (CH_3CCl_3), vinylidene chloride ($\text{CH}_2=\text{CCl}_2$), and ethylamines (e.g., $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$).

ETHYLENE GLYCOL

The primary manufacturing method of making ethylene glycol (ethane-1,2-diol, boiling point: 197.6°C, density: 1.1155, flash point: 127°C) is from acid or thermal-catalyzed hydration and ring opening of the oxide.



In the process (Fig. 1), either a 0.5 to 1.0% sulfuric acid (H_2SO_4) catalyst is used at 50 to 70°C for 30 minutes or, in the absence of the acid, a temperature of 195°C and 185 psi for 1 hour will form the diol. A 90 percent yield is realized when the ethylene oxide/water molar ratio is 1:5-8. The advantage of the acid-catalyzed reaction is no high pressure; the thermal reaction however needs no corrosion resistance and no acid separation step.

The crude glycols are dehydrated and then recovered individually as highly pure overhead streams from a series of vacuum-operated purification columns. Ethylene glycol (boiling point: 197.6°C) is readily vacuum distilled and separated from the diethylene glycol (boiling point: 246°C, density: 1.118, flash point: 124°C) and triethylene glycol (boiling point: 288°C, density: 1.1274, flash point: 177°C).

Ethylene glycol is traditionally associated with use as permanent-type antifreeze for internal-combustion engine cooling systems. Other uses include the production of polyesters for fibers, films, and coatings, in hydraulic fluids, in the manufacture of low freezing-point explosives, glycol ethers, and deicing solutions.

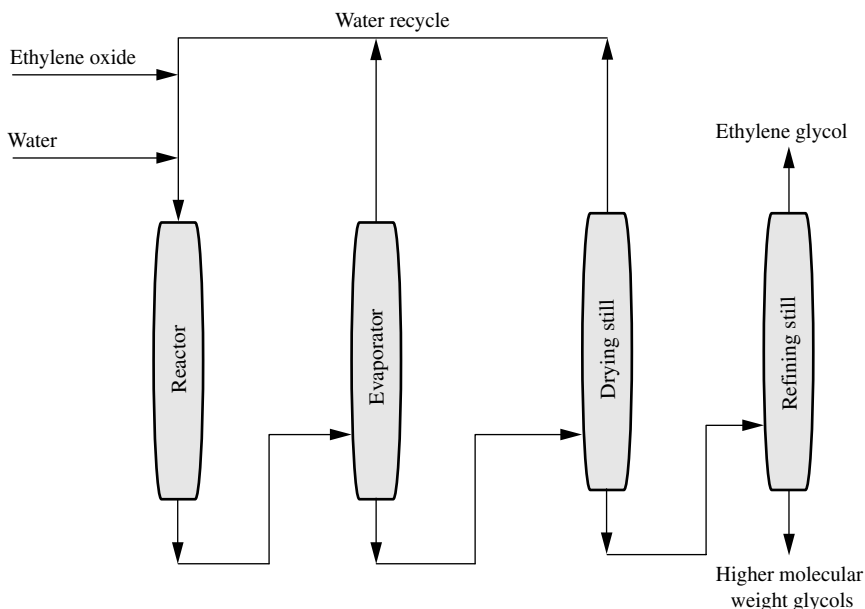


FIGURE 1 Manufacture of ethylene glycol.

Di and triethylene glycols are important co-products usually produced in the manufacture of ethylene glycol.

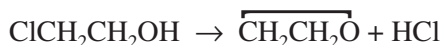
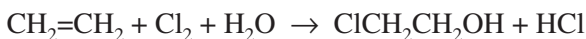
Diethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$), is used in the production of unsaturated polyester resins and polyester polyols for polyurethane-resin manufacture, as well as in the textile industry as a conditioning agent and lubricant for numerous synthetic and natural fibers. It is also used as an extraction solvent in petroleum processing, as a desiccant in natural gas processing, and in the manufacture of some plasticizers and surfactants.

Triethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$) finds principal use in the dehydration of natural gas and as a humectant.

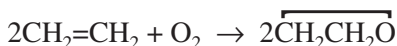
ETHYLENE OXIDE

Ethylene oxide (freezing point: -111.7°C , boiling point: 10.4°C , flash point: $<18^{\circ}\text{C}$) is a colorless gas that condenses at low temperature into a mobile liquid. Ethylene oxide is miscible in all proportions with water or alcohol and is very soluble in ether. Ethylene oxide is slowly decomposed by water at standard conditions, converting into ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$).

For many years the manufacture of ethylene oxide was carried out by chlorohydrin formation followed by dehydrochlorination to the epoxide.



Although the chlorohydrin route is still used to convert propylene to propylene oxide, a more efficient air epoxidation of ethylene in the presence of a silver catalyst is used and involves a direct oxidation method (Fig. 1).



The yield is approximately 70 percent of the theoretical. For maximum yield, very careful temperature control is required, the yield dropping as the temperature climbs. Excessive oxidation to carbon dioxide and water can occur, so precise temperature control at 270 to 290°C and pressures of 120 to 300 psi with a 1-second contact time on the catalyst are necessary. Tubular reactors containing several thousand tubes (20 to 50 mm diameter) are used. Even though metallic silver is placed in the reactor, the actual catalyst is silver oxide under the conditions of the reaction.

Ethylene oxide is used for manufacture of ethylene glycol, the latter being an antifreeze compound as well as a raw material for production of polyethylene terephthalate used in the manufacture of polyester fibers; for preparation of surfactants; for the manufacture of ethanolamines; for production of ethylene glycols used in plasticizers, solvents, and lubricants; and for making glycol ethers used as jet-fuel additives and solvents.

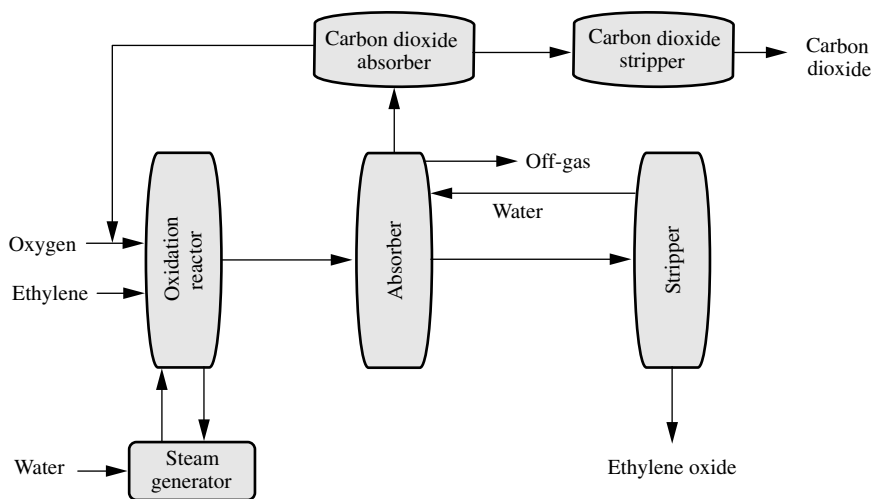


FIGURE 1 Manufacture of ethylene oxide.

Diethylene glycol and triethylene glycol (DEG and TEG) are produced as by-products of ethylene glycol and are used in polyurethane and unsaturated polyester resins and in the drying of natural gas. Diethylene glycol also used in antifreeze and in the synthesis of morpholine, a solvent, corrosion inhibitor, antioxidant, and pharmaceutical intermediate.

See Ethylene Glycol, Diethylene Glycol, Triethylene Glycol.

ETHYLHEXANOL

2-ethylhexanol is produced by aldol condensation of butylaldehyde followed by reduction.



2-ethylhexanol is used for the production of plasticizers, especially dioctyl phthalate, dioctyl adipate, and trioctyl trimellitate, as well as in the production of 2-ethylhexyl acrylate for adhesives and coatings, and for the production of 2-ethylhexylnitrate.

ETHYL VINYL ETHER

See Vinyl Ethers.

EXPLOSIVE D

See Ammonium Picrate.

EXPLOSIVES

An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of a great deal of heat and gas. The hot gases cause extremely high pressure if the explosive is set off in a confined space.

Initiating explosives (primary explosives) are materials that are quite shock and heat sensitive and that can be made to explode by the application of a spark, flame, friction, or heat source of appropriate magnitude.

Primary explosives include mercury fulminate [$\text{Hg}(\text{ONC})_2$, melting point: 160°C with explosion, density: 4.2], lead azide [$\text{Pb}(\text{N}_3)_2$, density: 4.0], basic lead styphnate (lead trinitroresorcinate), diazodinitrophenol, and tetrazine (a complex conjugated nitrogen compound, melting point: 140 to 160°C with explosion). Most priming compositions consist of mixtures of primary explosives, fuels, and oxidants.

Booster high explosives (energy amplifiers) are materials that are insensitive to both mechanical shock and flame but that explode with great violence when set off by an explosive shock, such as that obtained by detonating a small amount of a primary explosive in contact with the high explosive.

Boosters such as RDX (cyclotrimethylenetrinitramine, melting point: 204°C , density: 1.80), PETN (pentaerythritoltetranitrate, melting point: 143°C , density: 1.78), and TETRYL (2,4,6-trinitrophenyl methyl nitramine, melting point: 129.5°C , density: 1.73) are extremely important chemicals.

Blasting agents are powerful explosive agents that cannot be detonated by means of a blasting cap when unconfined and are, therefore, very safe to handle. A powerful booster is needed to start detonation. Blasting agents are usually ammonium nitrate (melting point: 169.6°C , density: 1.725) mixtures sensitized with nonexplosive fuels such as oil or wax.

Slurry explosives are ammonium nitrate mixtures that frequently contain another oxidizer as well as a fuel dispersed in a fluid medium that, among other functions, controls the rheology of the gel-slurry. Like blasting agents, slurry explosives are usually ammonium nitrate mixtures sensitized with nonexplosive fuels such as oil or wax.