

# OCHER

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Ocher is a naturally occurring pigment consisting of clay colored with 10 to 30% ferric hydroxide  $[\text{Fe}(\text{OH})_3]$ . It must be ground and levigated.

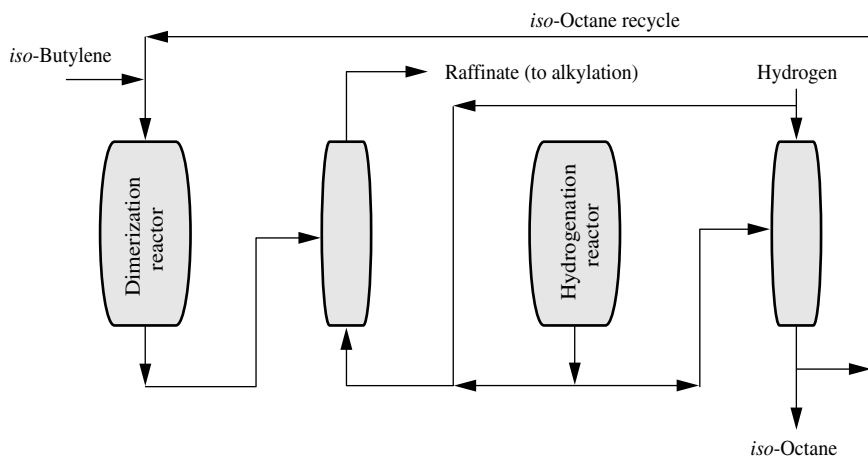
Ocher is a weak tinting agent and is often replaced by synthetic hydrated yellow iron oxides for brighter color and better uniformity.

# ISO-OCTANE

*Iso*-octane (2,2,4-trimethylpentane; boiling point: 99.2°C, density: 0.6918, flash point: -12°C) is produced from *iso*-butylene by catalytic dimerization followed by hydrogenation (Fig. 1).



Fractionation is required so that the product can to meet the desired specifications.



**FIGURE 1** Manufacture of *iso*-octane.

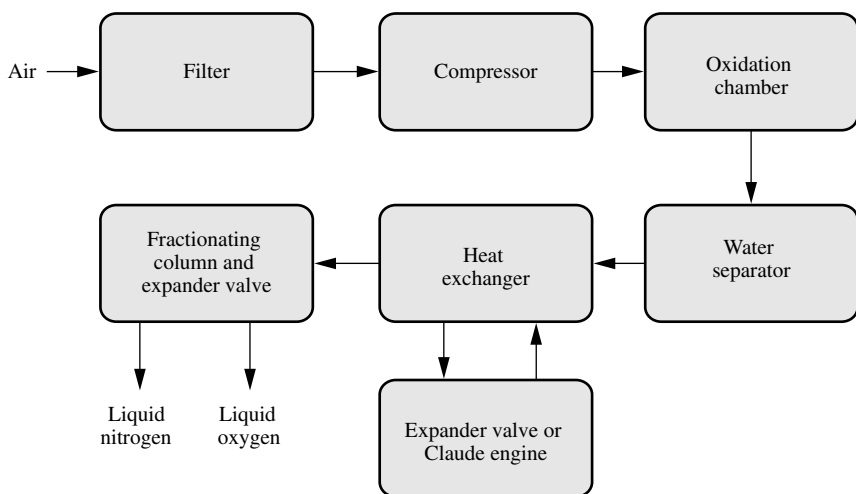
# OXYGEN

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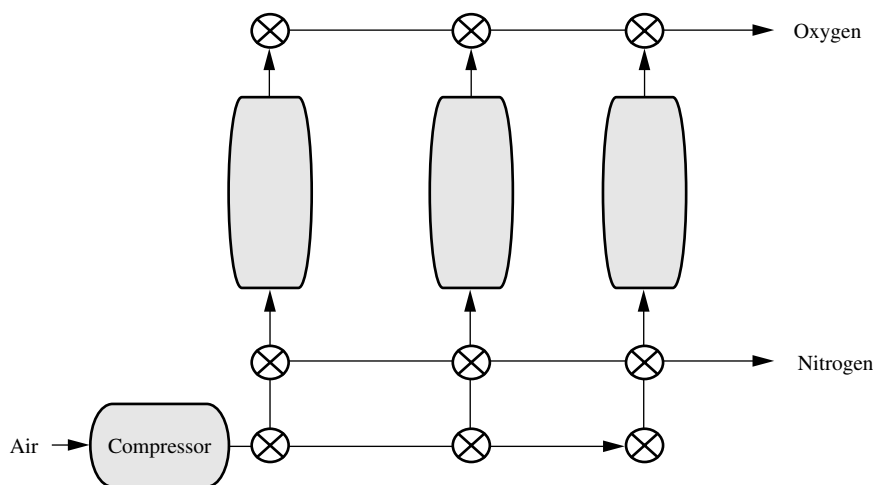
Oxygen is colorless, odorless, and tasteless as a gas, but it is slightly blue in the liquid state. Up to 99.995% purity is available commercially.

The manufacture of oxygen is described along with that of nitrogen (Fig. 1) during the liquefaction of air. Pressure swing adsorption (Fig. 2) is also used to generate pure oxygen.

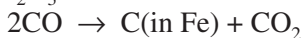
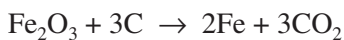
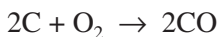
Oxygen is used for primary metals manufacturing, chemicals manufacturing, oxidation processes, and partial oxidation processes. The steel industry prefers to use pure oxygen rather than air in processing iron. The oxygen reacts with elemental carbon to form carbon monoxide, which is processed with iron oxide so that carbon is incorporated into the iron metal, making it much lower melting and more pliable (fusible pig iron). The following equations summarize some of this chemistry.



**FIGURE 1** Manufacture of oxygen by the liquefaction of air.



**FIGURE 1** Pressure swing adsorption for oxygen generation and purification.



Common pig iron contains 4.3% carbon and melts at 1130°C, whereas pure iron has a melting point of 1539°C.

In other oxygen applications, metal fabrication involves cutting and welding with an oxygen-acetylene torch. Chemical manufacture use includes the formation of ethylene oxide, acrylic acid, propylene oxide, and vinyl acetate. Miscellaneous uses include sewage treatment, aeration, pulp and paper bleaching, and missile fuel.

*See Nitrogen.*

# PAINTS

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Liquid paint is a dispersion of a finely divided pigment in a liquid (the vehicle) composed of a resin or binder and a volatile solvent (Fig. 1). The pigment, although usually an inorganic substance, may also be a pure, insoluble organic dye known as a *toner*, or an organic dye precipitated on an inorganic carrier such as aluminum hydroxide, barium sulfate, or clay, thus constituting a *lake*.

The solid particles in the paint reflect many of the destructive light rays, and thus help to prolong the life of the paint. In general, pigments should be opaque to ensure good covering power and chemically inert to secure stability, hence long life.

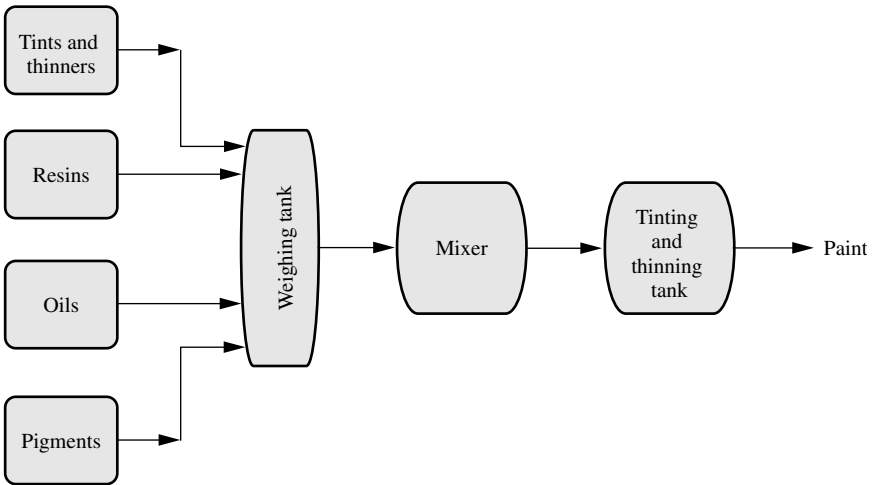


FIGURE 1 Manufacture of paint.

# N-PARAFFINS

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The production of *n*-paraffins, especially C<sub>10</sub>–C<sub>14</sub>, involves the use of zeolites to separate straight chain compounds from the kerosene fraction of petroleum.

The main use of *n*-paraffins is in the production of linear alkylbenzenes for the detergent industry and the production of linear alcohols, solvents, and chlorinated paraffins.

*See Synthesis Gas.*

# PARALDEHYDE

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Paraldehyde (2,4,6-trimethyl-1,3,5-trioxane, boiling point 125.4°C), a cyclic trimer of acetaldehyde, is formed when a mineral acid, such as sulfuric acid, phosphoric acid, or hydrochloric acid, is added to acetaldehyde. Paraldehyde can also be formed continuously by feeding liquid acetaldehyde at 15 to 20°C over an acid ion-exchange resin.

Depolymerization of paraldehyde occurs in the presence of acid catalysts, and, after neutralization with sodium acetate, acetaldehyde and paraldehyde are recovered by distillation.

*See Acetaldehyde.*



# PENICILLIN

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Penicillin is practically nontoxic (except to certain species of mold) and was the first antibiotic to be produced for widespread use.

The current viable process for the production of penicillin is large-scale fermentation. Large tanks of 5000 to 30,000-gal capacity are used. The penicillin is separated by solvent extraction. The mold grows best at 23 to 25°C, pH 4.5 to 5.0. The fermentation broth is made from corn steep liquor with lactose and inorganic materials added. Sterile air permits growth of the mold over a 50- to 90-hour period.

# PENTAERYTHRITOL

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Pentaerythritol (melting point: 261°C, density: 1.396, flash point: 260°C) belongs to the class of polyhydric alcohols, or polyols, that contain three or more methylene hydroxyl ( $\text{CH}_2\text{OH}$ ) functional groups and have the general formula  $\text{R}(\text{CH}_2\text{OH})_n$ , where  $n = 0.3$  and R is an alkyl group or  $\text{CCH}_2\text{OH}$  group.

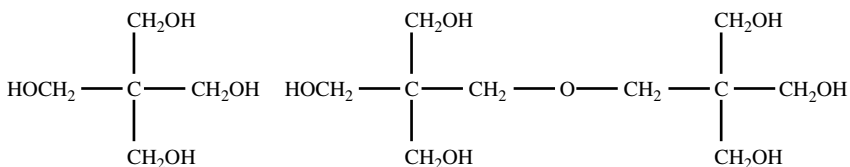
The most important polyhydric alcohols (Fig. 1) are white solids, ranging from crystalline pentaerythritol to the waxy trimethylol alkyls. The trihydric alcohols are very soluble in water, as is ditrimethylol propane. Pentaerythritol is moderately soluble and dipentaerythritol anti-tripentaerythritol are less soluble.

Pentaerythritol is manufactured by reaction of formaldehyde and acetaldehyde in the presence of a basic catalyst, generally an alkali or alkaline-earth hydroxide.

In the process (Fig. 2), the main concern in mixing is to avoid loss of temperature control in this exothermic reaction, which can lead to excessive by-product formation and/or reduced yields of pentaerythritol. The reaction time depends on the reaction temperature and may vary from about 0.5 to 4 hours at final temperatures of about 65 and 35°C, respectively. The reactor product, neutralized with acetic or formic acid, is then stripped of excess formaldehyde and water to produce a highly concentrated solution of pentaerythritol reaction products. This is then cooled under carefully controlled crystallization conditions so that the crystals can be readily separated from the liquors by subsequent filtration.

Staged reactions, where only part of the initial reactants is added, either to consecutive reactors or with a time lag to the same reactor, may be used to reduce dipentaerythritol content. This technique increases the effective formaldehyde-to-acetaldehyde mole ratio, maintaining the original stoichiometric one. It also permits easier thermal control of the reaction. Both batch and continuous reaction systems are used.

Dipentaerythritol and tripentaerythritol are obtained as by-products of the pentaerythritol process and may be further purified by fractional crystallization or extraction.

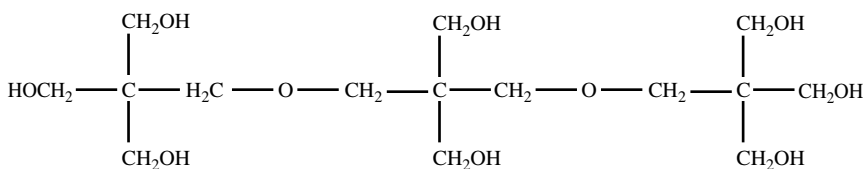


(1)

pentaerythritol,  
tetramethylolmethane

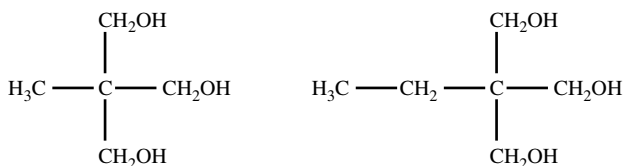
(2)

dipentaerythritol



(3)

tripentaerythritol

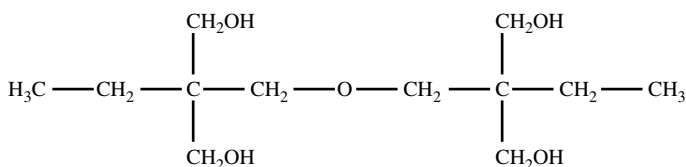


(4)

trimethylolpropane

(5)

trimethylolpropane



(6)

ditrimethylolpropane

Systematic names:

1. 2,2-bis(hydroxymethyl)1,3-propanediol
2. 2,2-oxybismethylene-bis(2-hydroxymethyl)-1,3-propanediol
3. 2,2-bis(3-hydroxy)-2,2-bis(hydroxymethyl)propoxy]methyl-1,3-propanediol
4. 2-hydroxymethyl-2-methyl-1,3-propanediol
5. 2-ethyl-2-hydroxymethyl-1,3-propanediol
6. 2,2-oxybismethylene-bis(2-ethyl)-1,3-propanediol

FIGURE 1 Formulae and names of the polyhydric alcohols.

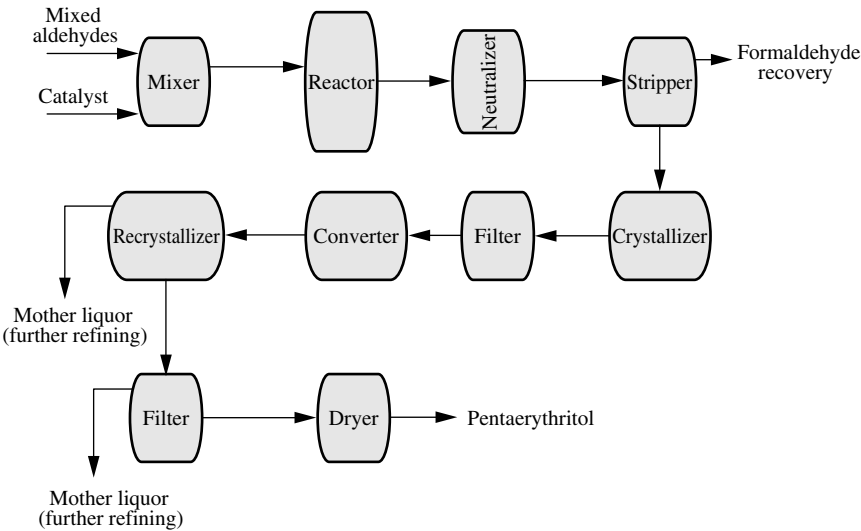


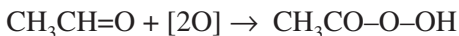
FIGURE 1 Manufacture of pentaerythritol.

# PERACETIC ACID

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There are two commercial processes for the production of peracetic acid:

(1) Low-temperature oxidation of acetaldehyde in the presence of metal salts, ultraviolet irradiation, or treatment with ozone yields acetaldehyde monoperoxacetate, which can be decomposed to peracetic acid and acetaldehyde.

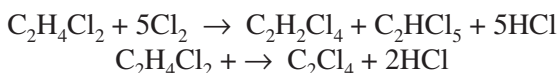


(2) Peracetic acid can also be formed directly by liquid-phase oxidation at 5 to 50°C with a cobalt salt catalyst. Nitric acid oxidation of acetaldehyde yields glyoxal and the oxidation of p-xylene to terephthalic acid and of ethanol to acetic acid is activated by acetaldehyde.

# PERCHLOROETHYLENE

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There are three processes used in the making of perchloroethylene (tetrachloroethylene; melting point:  $-19^{\circ}\text{C}$ , boiling point:  $121^{\circ}\text{C}$ , density: 1.6227), but the majority is made from ethylene dichloride.



Perchloroethylene and trichloroethylene are produced in a single-stage oxychlorination process from ethylene dichloride and chlorine.



Chlorination of hydrocarbons, such as propane, and acetylene with chlorine also produces perchloroethylene via trichloroethylene.

1,1,1-trichloroethylene is usually made in the same apparatus or as a co-product. Both chlorination and oxychlorination are used to supply the reagents needed. The reactions follow the same pattern as those for ethane and methane chlorination. Temperatures, pressures, and reagent ratios are somewhat different, however.

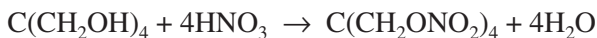
The main use of perchloroethylene is in dry cleaning and textile processing; other uses are as a chemical intermediate, in industrial metal cleaning (vapor and cold degreasing), in adhesives, in aerosols, and in electronics.

# PETN

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PETN [pentaerythritol tetranitrate,  $C(CH_2ONO_2)_4$ ] is an extremely sensitive high explosive. When used as a booster explosive, a bursting charge, or a plastic demolition charge, it is desensitized by mixture with trinitrotoluene or by the addition of wax.

PETN is made by the nitration of pentaerythritol with strong (96%) nitric acid at about  $50^{\circ}\text{C}$ .



PETN is used in making detonating fuses and commercial blasting caps, and also has a medicinal use.

# PETROCHEMICALS

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Petrochemicals are relatively pure, identifiable substances derived from petroleum or natural gas (Fig. 1). Thus, ammonia and synthetic rubber made from natural gas components can be classed as petrochemical compounds. Among the most important petrochemicals manufactured include:

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Acetic acid	Ethylene dichloride	Phenol
Acetone	Ethylene glycol	Polyethylene
Acrylonitrile	Ethylene oxide	Polypropylene
Benzene	Formaldehyde	Polyvinyl chloride
Cumene	Isopropyl alcohol	Styrene
Cyclohexane	Maleic anhydride	Toluene
Ethylbenzene	Methanol	Vinyl chloride
Ethylene	Phthalic anhydride	Xylenes

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Refinery operations such as distillation, extraction, and various separation operations, and the chemical unit processes, such as alkylation, dehydrogenation, hydrogenation, and isomerization, are essentially identical to those operations used in the manufacture of chemicals from other sources.

Most processes for separating individual species from petroleum involve use of refined engineering methods, with distillation and selective adsorption the most important. Once separated, however, most materials then undergo chemical conversion into more desirable products. Alkylation involving propene and butenes yields  $C_6$  to  $C_8$  hydrocarbons for high-octane gasoline. Propylene becomes polypropylene, propylamine, or propylene glycol and ethers.

The most basic raw petrochemical materials are liquefied petroleum gas, natural gas, gas from cracking operations, liquid distillate ( $C_4$  to  $C_6$ ), distillate from special cracking processes, and selected or isomerized cyclic fractions for aromatics. Mixtures are usually separated into their components at the petroleum refineries, then chemically converted into reactive precursors before being converted into salable chemicals within the plant.



The lower members of the paraffin and olefin series have been the preferred and most economical sources of organic raw material for conversion, so figures and tables are shown concerning the derivations from methane (Fig. 2), ethylene (Fig. 3), propylene and butylene (Fig. 4), and ring-containing (cyclic) chemicals (Fig. 5).

Starting material	Process	Product
Petroleum	Distillation	Light ends
		Methane
		Ethane
		Propane
		Butane
	Catalytic cracking	Ethylene
		Propylene
		Butylenes
		Higher olefins
	Coking	Ethylene
		Propylene
		Butylenes
Higher olefins		
Natural gas	Refining	Methane
		Ethane
		Propane
		Butane

**FIGURE 1** Production of starting materials for a petrochemical refinery.

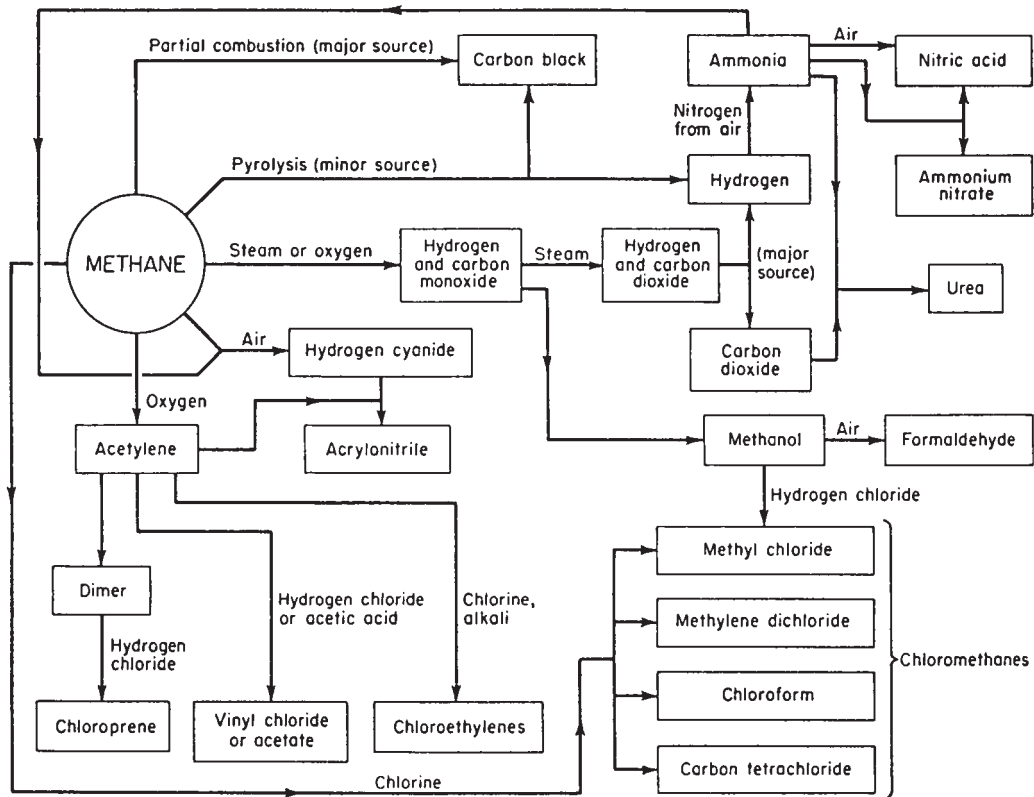


FIGURE 2 Chemicals from methane.

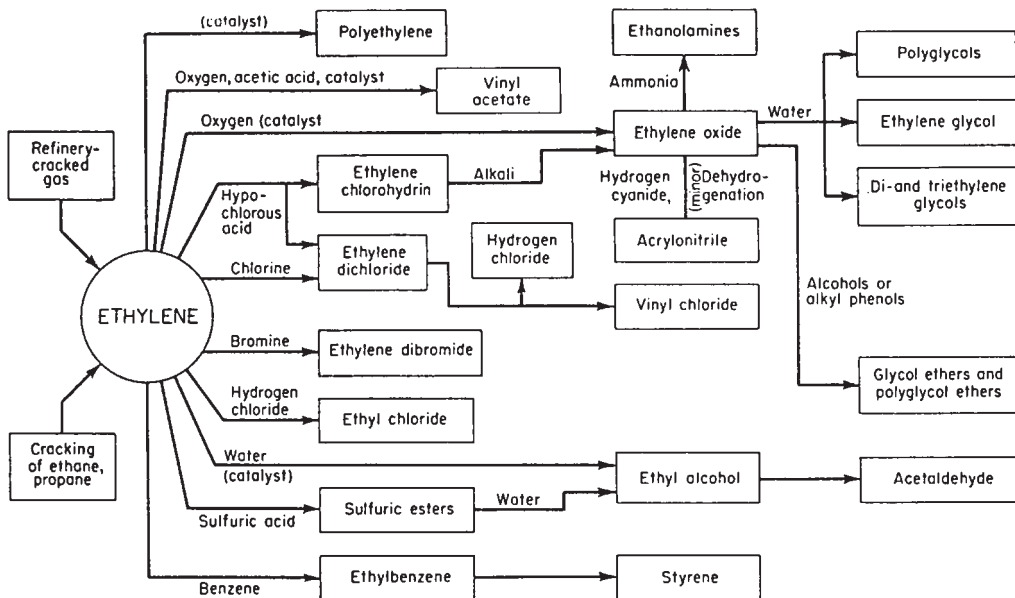


FIGURE 3 Chemicals from ethylene.

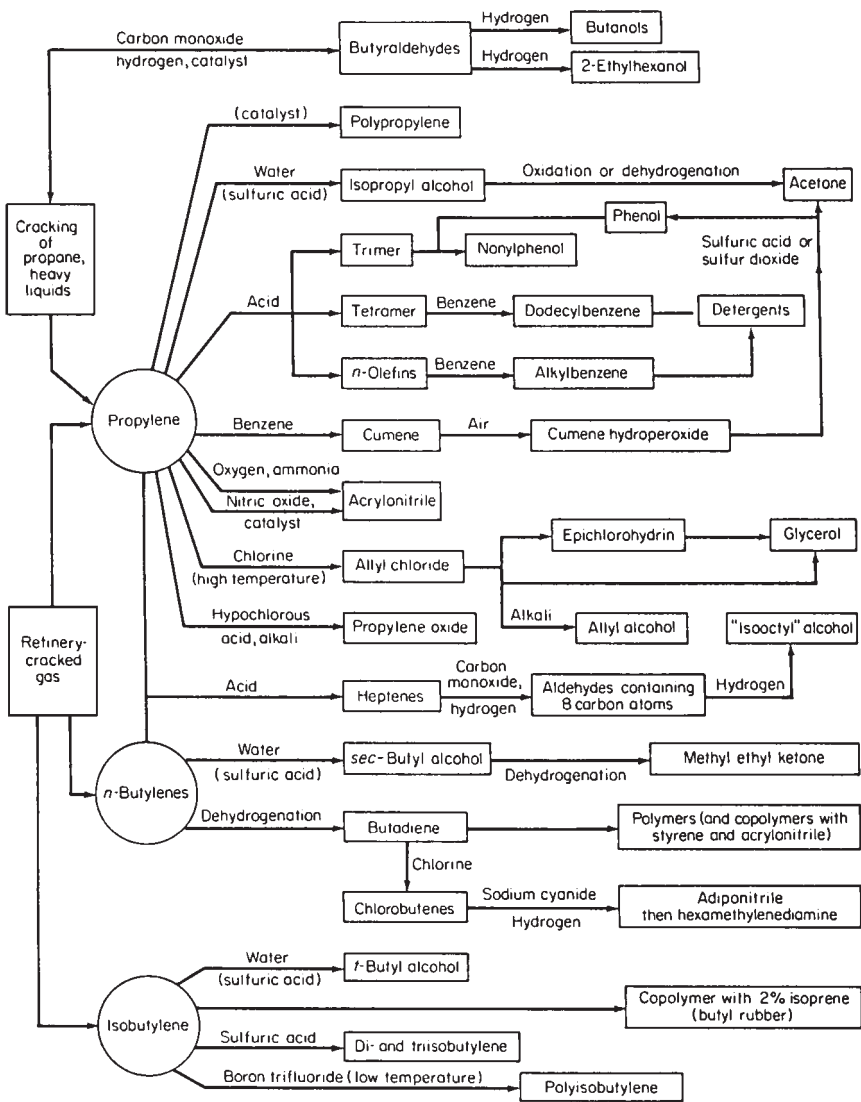


FIGURE 4 Chemicals from propene and butene(s).

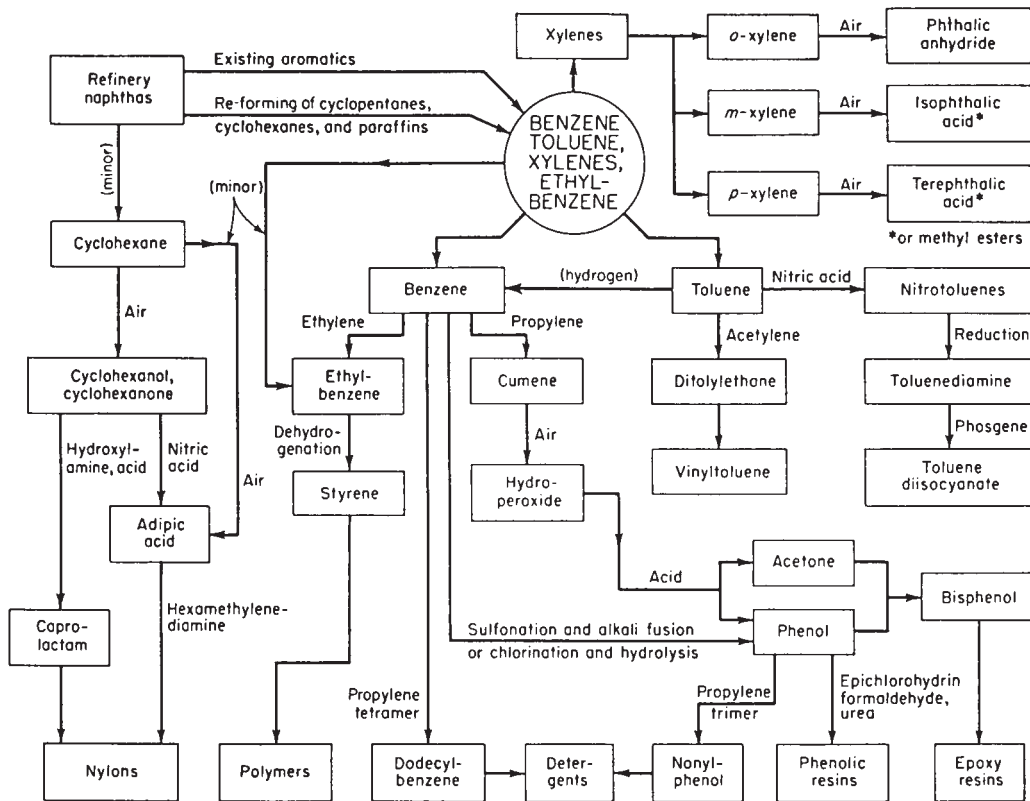


FIGURE 5 Cyclic chemicals.

# PHENOBARBITAL

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Phenobarbital (5-ethyl-5-phenylbarbituric acid) possesses specific usefulness in epilepsy.

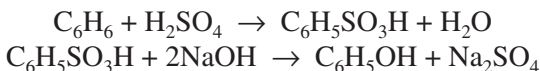
Phenobarbital, like other barbituric acid derivatives, is manufactured from phenylethylmalonic diethyl ester, which is condensed with urea to form the product.

# PHENOL

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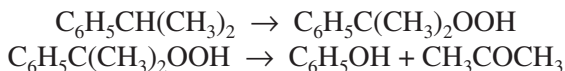
Phenol (hydroxybenzene; freezing point: 40.9°C, boiling point: 181.8°C, density: 1.0722; flash point: 79°C) at room temperature is a white, crystalline mass. Phenol gradually turns pink if it contains impurities or is exposed to heat or light. It has a distinctive sweet, tarry odor, and burning taste. Phenol has limited solubility in water between 0 and 65°C. Above 65.3°C, phenol and water are miscible in all proportions. Phenol is very soluble in alcohol, benzene, chloroform, ether, and partially disassociated organics in general, but it is less soluble in paraffinic hydrocarbons.

Phenol has been made, over the years, by a variety of processes. Historically, an important method was the sulfonation of benzene followed by desulfonation with caustic soda:



This route to phenol is no longer used.

The principal process in use is the peroxidation of cumene (*iso*-propyl benzene) at 130°C in the presence of air and a catalyst followed by decomposition of the peroxide at 55 to 65°C in the presence of sulfuric acid.



In the *cumene process* (Fig. 1), cumene is oxidized to form cumene hydroperoxide that is then concentrated and cleaved to produce phenol and acetone. By-products of the oxidation reaction are acetophenone and dimethyl benzyl alcohol, which is dehydrated in the cleavage reaction to produce alpha-methylstyrene.

The *toluene-benzoic acid process* involves three chemical reactions: (1) oxidation of toluene to form benzoic acid, (2) oxidation of benzoic acid to form phenyl benzoate, and (3) hydrolysis of phenyl benzoate to form phenol.

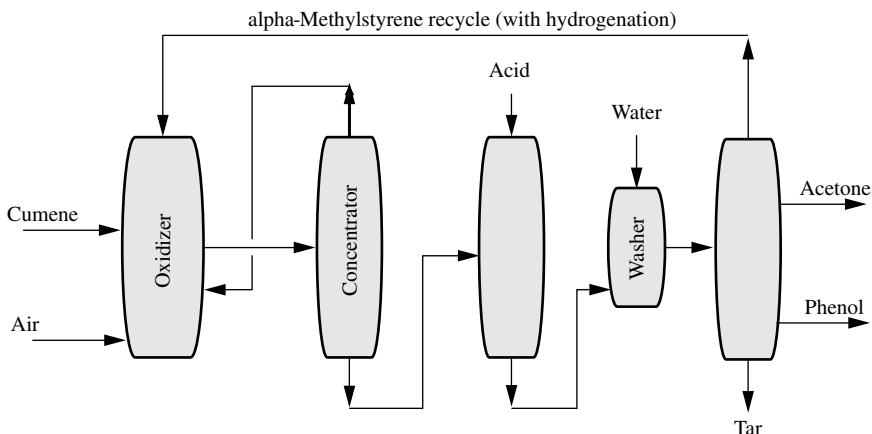
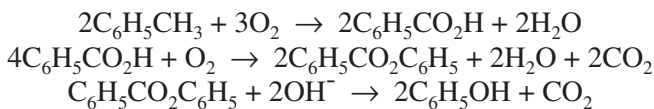


FIGURE 1 Manufacture of phenol from cumene.



A typical process (Fig. 2) consists of two continuous steps. In the first step the oxidation of toluene to benzoic acid is achieved with air and cobalt salt catalyst at a temperature between 121 and 177°C (206 kPa gauge), and the catalyst concentration is between 0.1 and 0.3%. The reactor effluent is distilled, and the purified benzoic acid is collected. In the second processing step, the benzoic acid is oxidized to phenyl benzoate in the presence of air and a catalyst mixture of copper and magnesium salts (234°C, 147 kPa gauge). The phenyl benzoate is then hydrolyzed with steam in the second reactor to yield phenol and carbon dioxide (200°C and atmospheric pressure).

Other processes include the production of *phenol from cyclohexene* in which phenol is produced from cyclohexene (benzene is partially hydrogenated to cyclohexene in the presence of water and a ruthenium-containing catalyst). The cyclohexene is then reacted with water to form cyclohexanol or oxygen to form cyclohexanone, and the cyclohexanol or cyclohexanone is dehydrogenated to phenol.

In the *benzene sulfonation process*, benzene reacts with concentrated sulfuric acid to form benzenesulfonic acid at about 150°C. The benzenesulfonic acid is neutralized with sodium sulfate to produce sodium benzenesulfonate, which is then fused with caustic soda to yield sodium phenate, which, after acidification with sulfur dioxide and a small amount of sulfuric acid, releases phenol from the sodium salt.



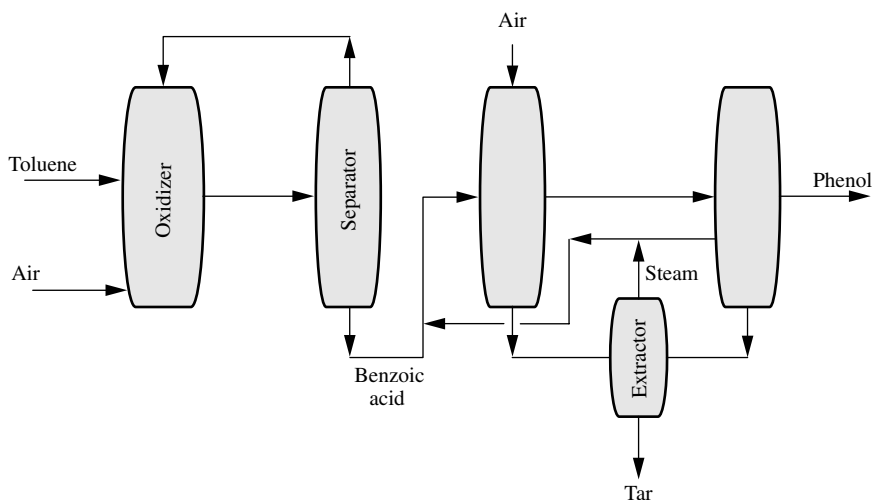


FIGURE 2 Manufacture of phenol from toluene.

In the *chlorobenzene* process, benzene is chlorinated at 38 to 60°C in the presence of ferric chloride ( $\text{FeCl}_3$ ) catalyst. The chlorobenzene is hydrolyzed with caustic soda at 400°C and 11,000 psi (2.56 kPa) to form sodium phenate. The impure sodium phenate reacts with hydrochloric acid to release the phenol from the sodium salt.

In the *benzene oxychlorination process*, also known as the Raschig process, benzene is oxychlorinated with hydrogen chloride and air in the presence of iron and copper chloride catalyst to form chlorobenzene. The reaction occurs at 200 to 260°C and atmospheric pressure. The chlorobenzene is hydrolyzed at 480°C in the presence of a suitable catalyst to produce phenol and chloride.

Phenol is used in the manufacture of formaldehyde resins, bisphenol A, caprolactam, aniline, xlenols, and alkylphenols. Phenol-formaldehyde polymers (phenolic resins) have a primary use as the adhesive in plywood formulations. The use of phenol in detergent synthesis to make alkylphenols is an important aspect of phenol utility.

*See Cumene, Cyclohexane, Toluene.*

# PHENOLIC RESINS

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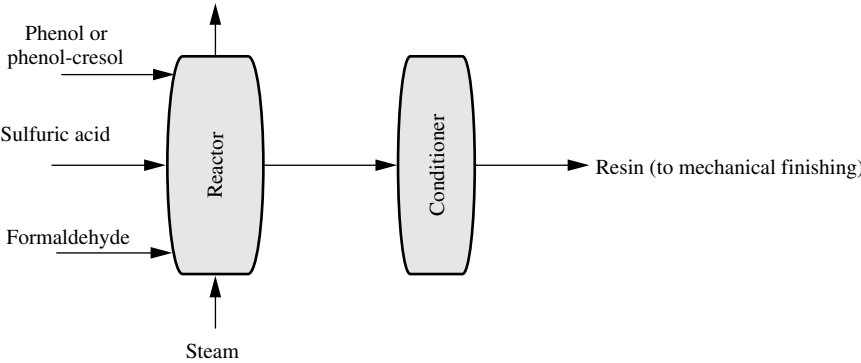
Phenolic resins (phenol-formaldehyde polymers), copolymers of phenol and formaldehyde, were the first fully synthetic polymers made. They were discovered in 1910 by Leo Baekeland and given the trade name Bakelite®.

Two processes, both involving step growth polymerization, are used for the manufacture of phenolic resins.

A *one-stage* resin may be obtained by using an alkaline catalyst and excess formaldehyde to form linear, low-molecular-weight resol resins. Acidification and further heating causes the curing process to give a highly cross-linked thermoset polymer. The *o*- and *p*-methylolphenols are more reactive toward formaldehyde than the original phenol and rapidly undergo further reaction to give di- and trimethylol derivatives. The methylolphenols will react to form di- and trinuclear phenols at still-free ortho and para positions. The final structure of the product involves a high degree of branching. Most linkages between aromatic rings are methylene ( $\text{CH}_2$ ) groups, though some ether ( $\text{CH}_2\cdot\text{OCH}_2$ ) linkages are present.

The second process (Fig. 1) uses an acid catalyst and excess phenol to give a linear polymer (*novolac*) that has no free methylol groups for cross-linking. In a separate second part of this two-stage process, a cross-linking agent is added and further reaction occurs. In many instances, hexamethylenetetramine is used, which decomposes to formaldehyde and ammonia.

Other modifications in making phenolic polymers are the incorporation of cresols or resorcinol as the phenol (Fig. 1) and acetaldehyde or furfural as the phenol.



**FIGURE 1** Manufacture of phenolic resins.

# PHENOLPHTHALEIN

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Phenolphthalein, in addition to its use as an indicator in analytical chemistry, is a widely used cathartic agent.

Phenolphthalein is manufactured by adding melted phenol (10 parts) to a cooled solution of phthalic anhydride (5 parts) in concentrated sulfuric acid (4 parts) and heating the mixture 10 to 12 hours at 120°C. The hot condensation product is poured into boiling water and boiled with successive changes of hot water. The condensate is then dissolved in warm, dilute caustic soda and precipitated with acetic acid. It may be purified by crystallization from absolute alcohol after treatment with, and being filtered through activated carbon.

# PHENOTHIAZINES

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Phenothiazines are tranquilizing drugs in which the basic structure consists of two benzene rings fused to a central six-membered ring containing a sulfur and a nitrogen. They are sometimes administered as the hydrochloride salt by quaternarization of the side chain nitrogen.

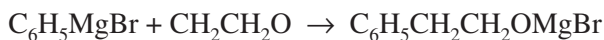
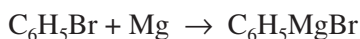
The production of phenothiazines involves heating the appropriate meta-substituted diphenylamine with sulfur and an iodine catalyst to close the ring. Treatment with the strong base sodium amide gives the anion on the ring nitrogen, which then displaces the chlorine of the appropriate second reactant.

There are three main therapeutic applications of the phenothiazine drugs: (1) they have an antiemetic effect (stop vomiting); (2) they are used with anesthetics, potent analgesics (pain relievers), and sedatives to permit their use in smaller doses; and (3) they are used most widely to relieve anxiety and tension in various severe mental and emotional disorders.

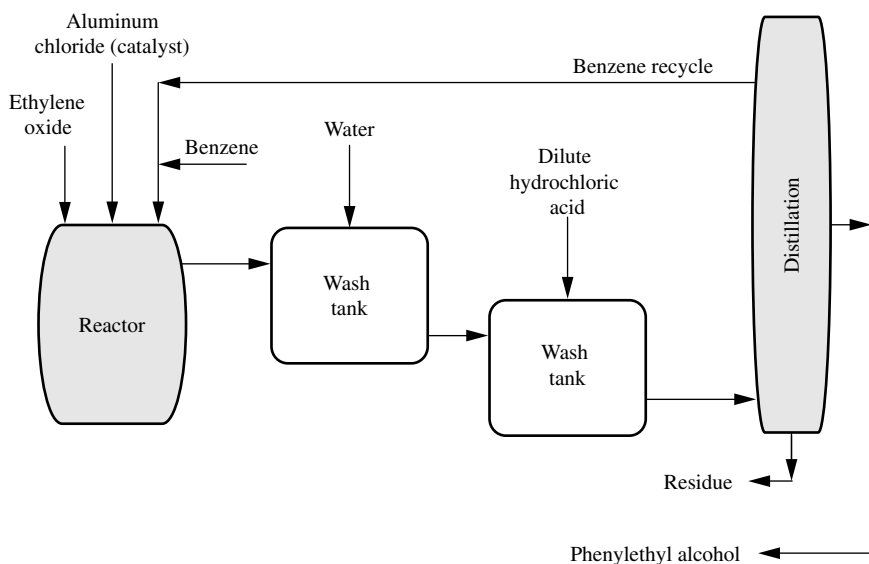
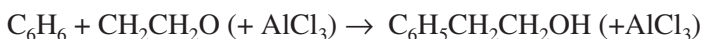
# PHENYLETHYL ALCOHOL

Phenylethyl alcohol has a roselike odor and occurs in the volatile oils of rose, orange flowers, and others. It is an oily liquid and is much used in perfume formulation.

Phenylethyl alcohol can be made by a number of procedures; the Grignard reaction is used generally:



However, the Friedel-Crafts reaction (Fig. 1) is also employed to manufacture this particular chemical.

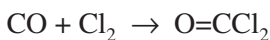


**FIGURE 1** Manufacture of phenylethyl alcohol.

# PHOSGENE

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Phosgene is manufactured by reacting chlorine gas and carbon monoxide in the presence of activated carbon.



Uses of phosgene include the manufacture of toluene diisocyanate, methylene diisocyanate, and polycarbonate resins.

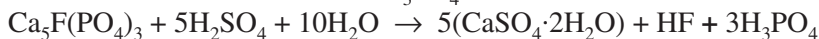
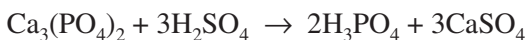
# PHOSPHORIC ACID

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Phosphoric acid ( $\text{H}_3\text{PO}_4$ , melting point:  $42^\circ\text{C}$ ), in the pure state, is a colorless solid. The usual laboratory concentration is 85% phosphoric acid, since a crystalline hydrate separates at 88% concentration.

Crude phosphoric acid is often black and contains dissolved metals and fluorine, and dissolved and colloidal organic compounds. Suspended solid impurities are usually removed by settling and solvent extraction (using a partially miscible solvent, such as *n*-butanol, *iso*-butanol, or *n*-heptanol), or solvent precipitation is used to remove the dissolved impurities. The phosphoric acid is extracted, and the impurities are left behind. Back-extraction with water recovers the purified phosphoric acid. Solvent precipitation uses a completely miscible solvent plus alkalis or ammonia to precipitate the impurities as phosphate salts. After filtration, the solvent is separated by distillation and recycled.

The majority of the phosphoric acid is made by the *wet process*, which involves reaction of calcium phosphate or the mixed calcium fluoride-calcium phosphate ores with sulfuric acid.



In the wet process (Fig. 1), the phosphate rock is ground and mixed with dilute phosphoric acid in a mill, after which it is transferred to a reactor and sulfuric acid is added. The reactors are heated to  $75$  to  $80^\circ\text{C}$  for 4 to 8 hours. Air cooling carries the hydrogen fluoride and silicon tetrafluoride side products to an adsorber that transforms them into fluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ). Filtration of the solid calcium sulfate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , gypsum) gives a dilute phosphoric acid solution (28 to 35%  $\text{P}_2\text{O}_5$  content) and evaporation of the water to a higher concentration (54%  $\text{P}_2\text{O}_5$  content) is optional. The fluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is formed in the process by reac-



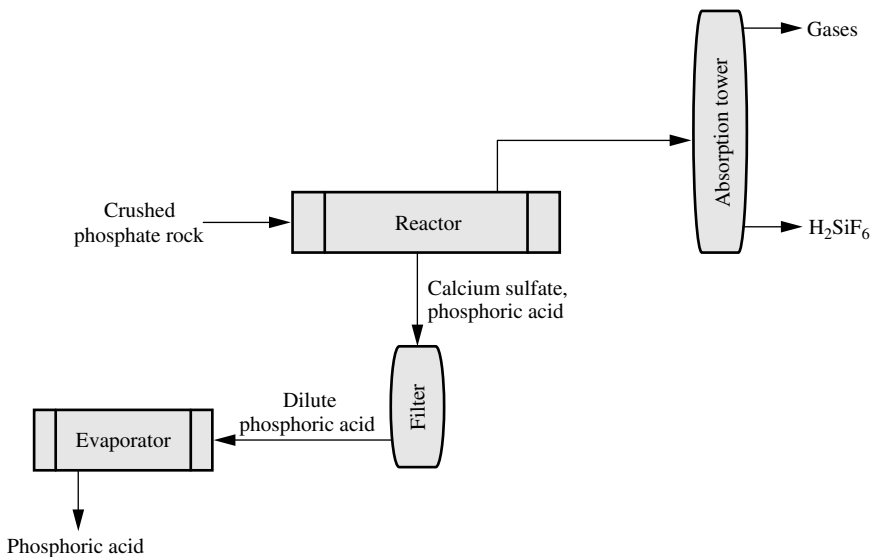
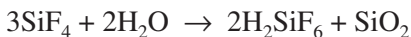
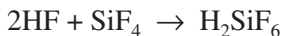
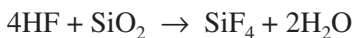


FIGURE 1 Manufacture of phosphoric acid by the wet process.

tion of the hydrogen fluoride with silica ( $\text{SiO}_2$ ) that is present in most phosphate rock.

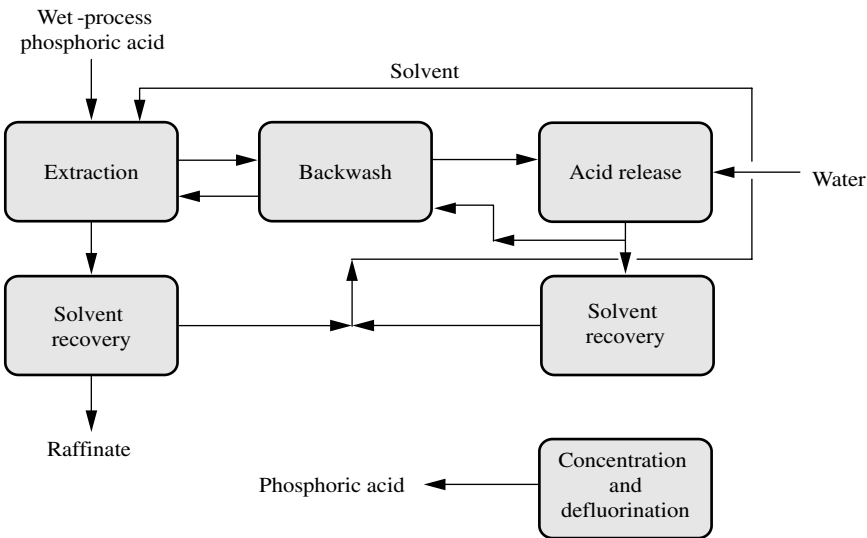


The fluorosilicate acid can be used for fluoridation of drinking water, and fluorosilicate salts find use in ceramics, pesticides, wood preservatives, and concrete hardeners. The phosphoric acid can be purified by a solvent extraction process (Fig. 2).

Another wet process for producing phosphoric acid uses:

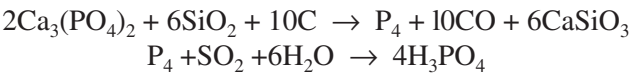
1. Hydrochloric acid to acidulate (in slight excess to prevent formation of monocalcium phosphate)
2. An organic solvent ( $\text{C}_3$  or  $\text{C}_4$  alcohols) to extract the phosphoric acid
3. Water to strip out the phosphoric acid (with a small amount of solvent and hydrochloric acid)
4. Concentration to remove the small amounts of solvent and hydrochloric acid and to yield a high-grade product

The *furnace process* is used only to make concentrated acid (75-85%) and pure product. It is very expensive because of the  $2000^\circ\text{C}$  temperature



**FIGURE 2** Solvent extraction process for purification of phosphoric acid.

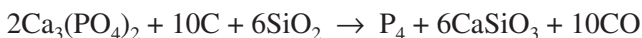
required. In the furnace process, phosphate rock is heated with sand and coke to give elemental phosphorus, which is then oxidized and hydrated to phosphoric acid.



See *Phosphorus*.

# PHOSPHORUS

Yellow phosphorus (known also as *white phosphorus*) is produced by reducing phosphate rock (calcium phosphate or calcium fluorophosphate) with carbon in the presence of silica as flux; an electric arc furnace furnishes heat of reaction (Fig. 1).



The silica is an essential raw material that serves as an acid and a flux. About 20 percent of the fluorine present in the phosphate rock is converted to  $\text{SiF}_4$  and volatilized. In the presence of water vapor this reacts to give silica ( $\text{SiO}_2$ ) and fluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ).

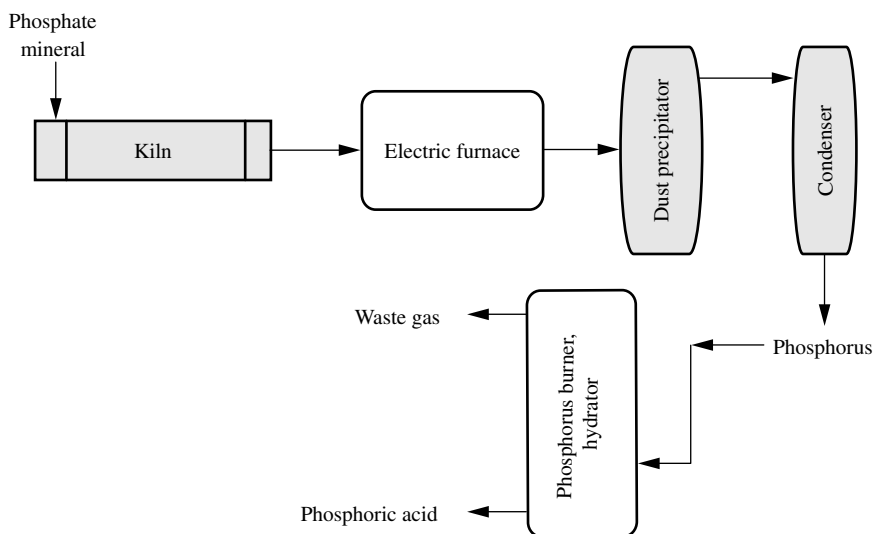
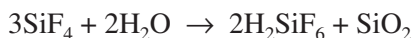


FIGURE 1 Manufacture of phosphorus.

Phosphorus is used for the manufacture of phosphoric acid and other chemicals, including phosphorus trichloride, phosphorus pentasulfide, and phosphorus pentoxide.

*See Phosphoric Acid.*

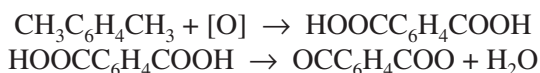
# PHTHALIC ACID

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*See Phthalic Anhydride.*

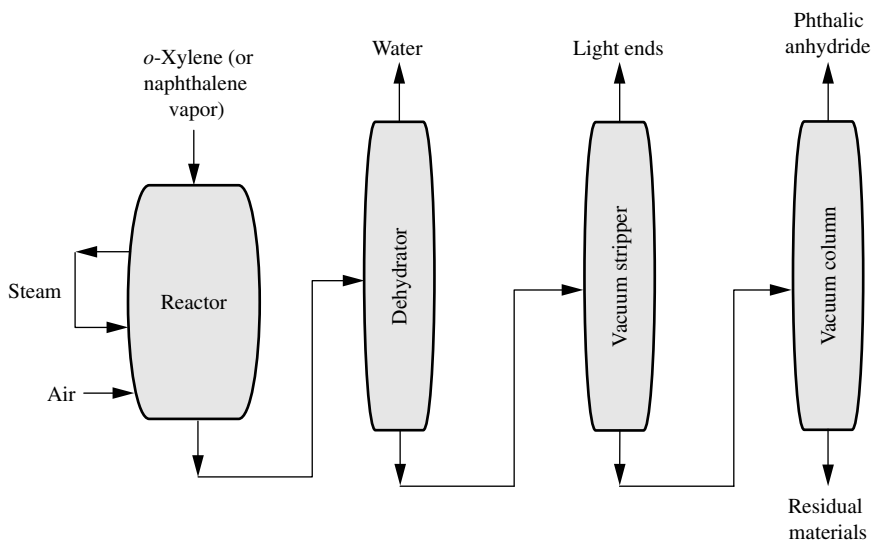
# PHTHALIC ANHYDRIDE

Phthalic anhydride (melting point: 131.6°C, boiling point: 295°C with sublimation) can be made from the reaction of *o*-xylene with air and also from naphthalene (Fig. 1), which is isolated from coal tar and from petroleum.



The use of naphthalene as the source of phthalic anhydride diminished but has become popular once again.

Phthalic anhydride is used for the manufacture of plasticizers, such as dioctyl phthalate, unsaturated polyester resins, and alkyd resins. Phthalic anhydride reacts with alcohols such as 2-ethylhexanol, and the products are often liquids that, when added to plastics, impart flexibility without adversely affecting the strength of the plastic. Most of these plasticizers are used for poly(vinyl chloride) flexibility. Dioctyl phthalate is a common plasticizer.



**FIGURE 1** Manufacture of phthalic anhydride.

# PHTHALOCYANINE BLUE

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The phthalocyanine blues are particularly useful for nitrocellulose lacquers in low concentrations as a pigment highly resistant to alkali, acid, and color change.

As presently produced, they are highly stable pigments, resistant to crystallization in organic solvents, and essentially free from flocculation in coatings. Both the green and the blue dyes have high tinting power and are used in latex paints and in printing inks, as well as all types of interior and exterior coatings. They are prepared by reacting phthalic anhydride with a copper salt with or without ammonia.

# PHTHALOCYANINE GREEN

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The major green pigment is phthalocyanine green. It is a complex copper compound that is suitable for use in both solvent- and water-based paints.



# PICRIC ACID

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Picric acid (2,4,6-trinitrophenol, melting point: 122°C) is manufactured by the nitration of mixed phenolsulfonates with mixed acid. Mixed acid increases the yield of desired products.

The heavy metal salts of picric acid are dangerously sensitive, and its major use is for the manufacture of ammonium picrate (Explosive D).

# PIPERAZINE CITRATE

---

Piperazine citrate is produced from piperazine that is first manufactured by the cyclization of ethylene dibromide with alcoholic ammonia at 100°C. The citrate is formed in aqueous solution and crystallized out.

Piperazine citrate is used as an anthelmintic in the treatment of infections caused by pinworms and roundworms. It is also employed by veterinarians against various worms infecting domestic animals, including chickens.

# POLYACETALDEHYDE

---

Polyacetaldehyde, a rubbery polymer with an acetal poly(oxymethylene) structure, is an unstable solid that depolymerizes to acetaldehyde

Polyacetaldehyde is formed by cationic polymerization using boron trifluoride ( $\text{BF}_3$ ) in liquid ethylene ( $\text{CH}_2=\text{CH}_2$ ). At temperatures below  $-75^\circ\text{C}$  using anionic initiators, such as metal alkyls in a hydrocarbon solvent, a crystalline isotactic polymer is obtained. Molecular weights of the products fall into the range 800,000 to 3,000,000.

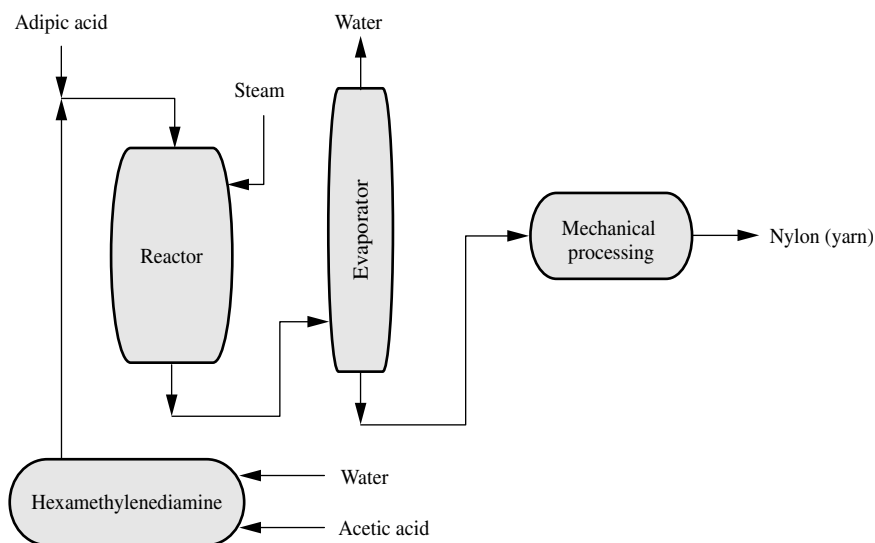
*See Acetaldehyde.*

# POLYAMIDES

Polyamides are polymers that contain the amide group and are produced, by, for example, polymerization reaction of adipic acid and hexamethylenediamine (HMDA). Nylon 6,6 (so-called because each of the raw material chains contains six carbon atoms) was the first all-synthetic fiber made commercially.

Nylon 6 is the homopolymer of caprolactam, and Kevlar is an aromatic polyamide, poly-*p*-phenylene terephthalamide.

The reaction between adipic acid and hexamethylene diamine produces hexamethylenediammonium adipate, commonly called *nylon salt* (Fig. 1) Forming the salt assures the correctly balanced proportions. It is also necessary that the material to be polymerized contain very few impurities if high-quality fibers are to be made by a variety of routes (Fig. 2).



**FIGURE 1** Manufacture of nylon.

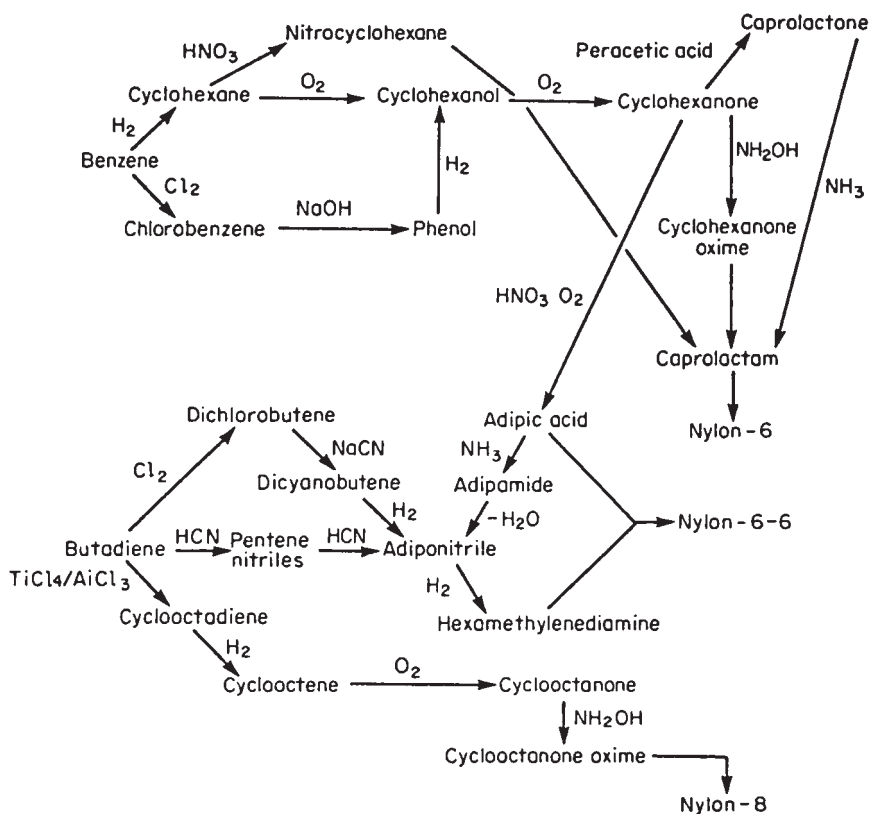


FIGURE 2 Various routes to nylon.

Like all other synthetic fibers that have become competitively popular, nylon in both the filament and staple form must have certain properties that are superior to natural fibers. It is stronger than *any* natural fiber and has a wet strength of 80 to 90 percent of its dry strength. Its good flexing tenacity makes it very desirable for women's hosiery, and it has good stretch recovery. Nylon's high tenacity has made it important in parachute fabrics and related nonapparel items. Nylon can be dyed by all acid and dispersed dyes. It has a low affinity for direct cotton, sulfur, and vat dyes.

Nylon 6, or nylon caprolactam, is a polymeric fiber derived from only one constituent, caprolactam, giving the polymer  $[-(\text{CH}_2)_5\text{CONH}-]_n$ . It has a lower melting point than nylon 6,6, but it is superior to it in resistance to light degradation, elastic recovery, fatigue resistance, and thermal stability.

### See *Caprolactam*.

# POLYCARBONATES

---

Polycarbonate resins are a variety of polyester in which a derivative of carbonic acid is substituted for adipic, phthalic, or other acid and a diphenol is substituted for the more conventional glycols.

A number of methods for the manufacture of polycarbonates are available but the *melt process* and the *phosgenation process* are the most important.

# POLYCHLORINATED BIPHENYLS

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Polychlorinated biphenyls (PCBs, Arochlor<sup>®</sup>, Phenochlor<sup>®</sup>, and Clophen<sup>®</sup>) are chemically similar to the chlorinated insecticides.

Polychlorinated biphenyls are manufactured by chlorination of biphenyl. The conditions determine the degree of chlorination.

They were used to make more flexible and flame-retardant plastics and are still used as insulating fluids in electrical transformers since there is no substitute in the application. Their existence and persistence in the environment is well established, and they are classed as a pollutant.

# POLYESTERS

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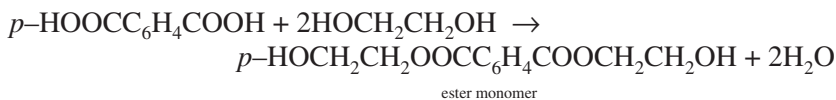
The common polyester fibers are polymers of the ester formed from dimethyl terephthalate and ethylene glycol. The polymer melts at 270°C and has very high strength and elasticity. It is 3 times as strong as cellulose. It is also particularly resistant to hydrolysis (washing) and resists creasing. Hence it has been used in clothing, especially shirts (65/35 polyester/cotton most popular). Its excellent clarity has made it useful in photographic film and overhead transparencies. Poly(ethylene terephthalate) is known commonly by the trademarks Dacron<sup>®</sup>, Terylene<sup>®</sup>, and Fortrel<sup>®</sup> fibers and Mylar<sup>®</sup> for film.

Polyesters are manufactured in one of two ways: by direct reaction of a di-acid and a diol or by ester interchange of a di-ester and a diol. By far the most commercially useful polyester is poly(ethylene terephthalate).

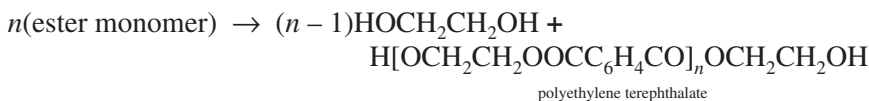
Polymerization is a two-stage process (Fig. 1) in which the monomer is first prepared either by an ester interchange between dimethyl terephthalate and ethylene glycol, or by direct esterification of terephthalic acid.



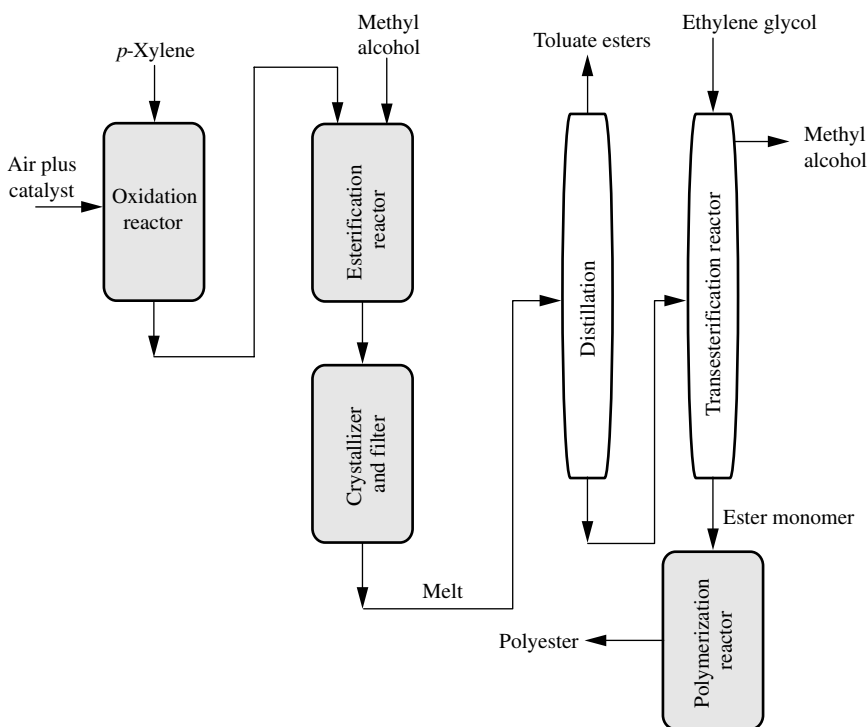
or



The second stage is the polymerization of the monomer by heating at 260°C.







**FIGURE 1** Manufacture of polyesters.

The polymer is extruded from the bottom of the polymerizer through a slot or holes on to the surface of a water-cooled drum. The ribbon is cut to chips and dried before melt spinning in a manner similar to that described for nylon. The filaments are stretched, with the application of heat, to about 3 to 6 times their original length.

Most useful polyesters have need for the strong, rigid aromatic ring in their structure since they lack the hydrogen bonding prevalent in polyamides.

# **POLYESTERS (UNSATURATED)**

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An unsaturated polyester resin consists of a linear polyester whose chain contains double bonds and an unsaturated monomer such as styrene that copolymerizes with the polyester to provide a cross-linked product.

The most common unsaturated polyester is manufactured by step growth polymerization of propylene glycol with phthalic and maleic anhydrides. Subsequent treatment with styrene and a peroxide catalyst leads to a solid, infusible thermosetting product.

Unsaturated polyesters are relatively brittle, and about 70 percent is used with fillers, of which glass fiber is easily the most popular. Glass fiber-reinforced polyester for small boat hulls consumes one-quarter of unsaturated polyesters.

# POLYHYDRIC ALCOHOLS

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*See Pentaerythritol.*

# POLYIMIDES

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Polyimides are compounds that contain two anhydride groups, which will react with primary amines or isocyanates to form polyimide polymers that are very stable linear polymers.

# POLYSULFONES

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Polysulfones are both aliphatic and aromatic polymers that are resistant to high temperatures and are very stable.

Typically, polysulfones are prepared by the reaction of disodium bisphenol A with 4,4'-dichlorodiphenylsulfone.

Their resistance to autoclave sterilization makes them useful for medical instruments and trays. Other uses are microwave cookware, coffee decanters, and corrosion-resistant piping.

# POLYURETHANE FOAMS

---

Polyurethane foams are manufactured from a diisocyanate, such as toluene diisocyanate (TDI), and a low-molecular-weight polyether such as poly(propylene glycol).

In the process, a small amount of water is added to convert some isocyanate functionalities into carbon dioxide and amines. The degree of foaming can be controlled by the amount of water added.

One way of obtaining the more useful cross-linked polyurethanes is by using a trifunctional reagent. Thus either the toluene diisocyanate can react with a triol or the propylene oxide can be polymerized in the presence of a triol.

# POTASSIUM CHLORATE

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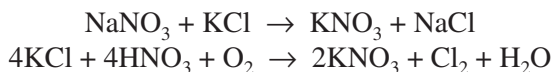
*See Sodium Chlorate.*

# POTASSIUM COMPOUNDS

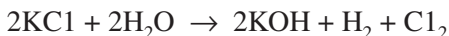
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The industrial term *potash* usually refers to potassium carbonate ( $\text{K}_2\text{CO}_3$ ) but also can be used in reference to potassium hydroxide ( $\text{KOH}$ ), potassium chloride ( $\text{KCl}$ ), potassium sulfate ( $\text{K}_2\text{SO}_4$ ), potassium nitrate ( $\text{KNO}_3$ ), or collectively to all potassium salts and to the oxide ( $\text{K}_2\text{O}$ ). Another term, *caustic potash*, is used in reference to potassium hydroxide, and *muriate of potash* is commonly used in reference to potassium chloride.

Deposits of sylvinite (43% by weight potassium chloride and 57% by weight sodium chloride) account for large amounts of naturally occurring potassium. The potassium chloride can be separated by either fractional crystallization or flotation. Brine is also a valuable source of potassium chloride. A small amount of potassium sulfate is isolated from natural deposits, and potassium nitrate is manufactured by two processes.



Potassium hydroxide is made by electrolysis of potassium chloride solutions in cells that are exactly analogous to those for sodium hydroxide production.

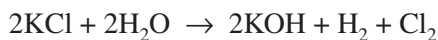




# POTASSIUM HYDROXIDE

---

Potassium hydroxide is produced by the electrolysis of potassium chloride solutions.



Potassium hydroxide is used for the production of potassium carbonate, tetrapotassium pyrophosphate and other potassium phosphates, liquid fertilizers, and soaps.

# POTASSIUM NITRATE

---

Potassium nitrate (saltpeter,  $\text{KNO}_3$ ) is manufactured in two ways: (1) by reacting nitric acid with potassium chloride with a chlorine by-product and (2) by reacting sodium nitrate with potassium chloride and crystallizing out the salt.

Potassium nitrate is used in the manufacture of fertilizers, explosives, ceramics, and heat-treating salts.

# POTASSIUM PERCHLORATE

---

Potassium perchlorate is made by converting sodium chlorate into sodium perchlorate in steel electrolytic cells that have platinum anodes and operate at a temperature of 65°C. Filtered potassium chloride solution is added to the sodium perchlorate, precipitating potassium perchlorate crystals, which are centrifuged, washed, and dried. The mother liquor now contains sodium chloride, which can be used as a cell feed for sodium chlorate manufacture.

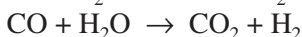
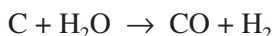
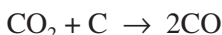
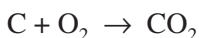
Potassium perchlorate may also be manufactured by electrolysis of potassium chloride solutions.

Potassium perchlorate is used in matches, pharmaceutical products, and pyrotechnic mixtures. Most mixtures of organic substances and chlorates are explosive, so use of any such mixtures should be limited to those expert in their use.

# PRODUCER GAS

---

Producer gas is manufactured by passing air and steam through a bed of hot coal or coke at a temperature of 980 to 1540°C, depending on the fusion points of the fuel ash. The primary purpose of the steam (25 to 30 % of the weight of the coke) is to employ the exothermic energy from the reaction between carbon and oxygen to supply energy (heat) to the endothermic carbon-steam reaction.



The initial reaction is the formation of carbon dioxide, and, as the gases progress up the bed, the carbon dioxide is reduced to carbon monoxide and the water vapor is partly decomposed to yield hydrogen, carbon monoxide, and carbon dioxide. Producer gas has about 15 percent of the heating value of natural gas.

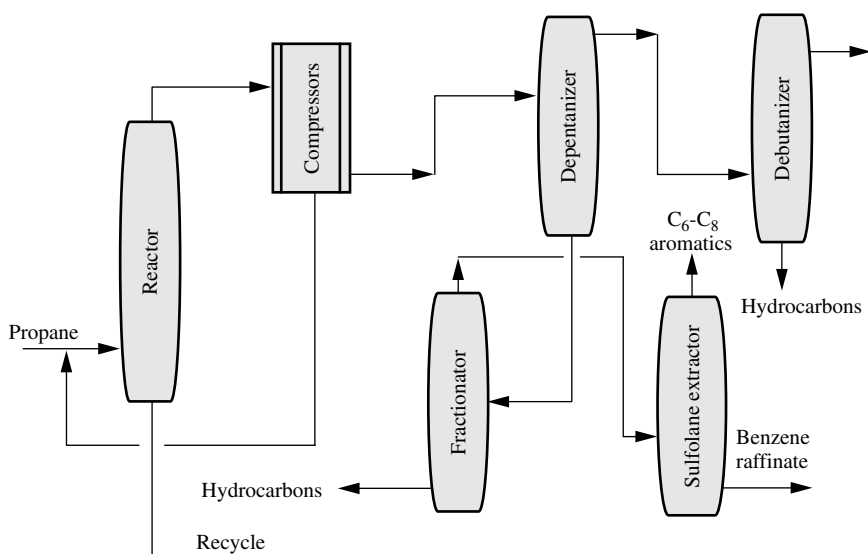
Producer gas was once used for industrial heating, but its use is now diminished and it finds only occasional use in industrial operations.

# PROPANE

Natural gas (predominantly methane,  $\text{CH}_4$ , with ethane, propane, and butane) is a fuel gas, and it is also an important chemical raw material for various syntheses. Natural gas can also be separated into its hydrocarbon constituents thereby producing feedstocks for petrochemical processes.

Propane ( $\text{CH}_3\text{CH}_2\text{CH}_3$ , melting point:  $-189.7^\circ\text{C}$ , boiling point  $-42.1^\circ\text{C}$ , density: 0.5853) is also a constituent of liquefied petroleum gas along with butane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), and propane can be used for the manufacture of aromatics by reforming (Fig. 1).

*See Liquefied Petroleum Gas, Natural Gas.*



**FIGURE 1** Manufacture of aromatics from propane by reforming.

# PROPRANOLOL HYDROCHLORIDE

---

This compound, sold under the trade name Inderal<sup>®</sup>, was the second most widely prescribed drug in the early 1980s. It is used as an antianginal and antihypertensive drug.

Propranolol hydrochloride is prepared from  $\alpha$ -naphthol (1-naphthol) and epichlorohydrin. Subsequent treatment with isopropyl amine opens the epoxy ring to yield propranolol. Treatment with hydrochloric acid yields the hydrochloride.

Propranolol is a type of antihypertensive agent called a  $\beta$ -adrenergic blocking agent because it competes with epinephrine (adrenaline) and norepinephrine at their receptor sites and protects the heart against undue stimulation.

# PROPARGYL ALCOHOL

---

Propargyl alcohol (2-propyn-1-ol, boiling point: 114°C) is a colorless volatile liquid with an unpleasant odor that is the only commercially available acetylenic primary alcohol. It is miscible with water and with many organic solvents. The commercial material is specified as 97% minimum purity, determined by gas chromatography or acetylation. Moisture is specified at 0.05% maximum (Karl-Fischer titration). Formaldehyde content is determined by bisulfite titration.

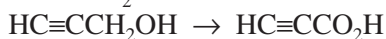
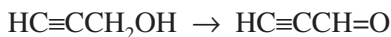
Propargyl alcohol is a by-product of butynediol manufacture. The original high-pressure butynediol processes gave about 5 percent of the by-product; lower-pressure processes give much less. Processes have been described that give much higher proportions of propargyl alcohol.

Although propargyl alcohol is stable, it has a low flash point, and vapor ignition and violent reactions can occur in the presence of contaminants, particularly at elevated temperatures. Heating in undiluted form with bases or strong acids should be avoided. Weak acids have been used to stabilize propargyl alcohol prior to distillation. Propargyl alcohol is a primary skin irritant and a severe eye irritant and is toxic by all means of ingestion; all necessary precautions must be taken to avoid contact with liquid or vapors.

Propargyl alcohol is a component of oil-well acidizing compositions, inhibiting the attack of mineral acids on steel, and is also employed in the pickling and plating of metals.

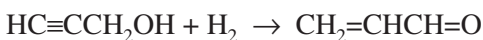
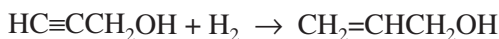
Propargyl alcohol is used as an intermediate in preparation of the miticide Omite® 2-(4'-tert-butylphenoxy)cyclohexyl 2-propynyl sulfite, of sulfadiazine, and of halogenated propargyl carbonate fungicides.

The chemical properties and uses of propargyl alcohol has three potentially reactive sites: (1) a primary hydroxyl group (i.e.,  $\text{CH}_2\text{OH}$ ), (2) a triple bond ( $-\text{C}\equiv\text{C}-$ ), and (3) an acetylenic hydrogen ( $-\text{C}\equiv\text{CH}$ ) that makes the alcohol an extremely versatile chemical intermediate. The hydroxyl group can be esterified with acid chlorides, anhydrides, or carboxylic acids, and it reacts with aldehydes or vinyl ethers in the presence of an acid catalyst to form acetals. At low temperatures, oxidation with chromic acid gives propynal or propynoic acid:



Halogenating agents can be used to replace hydroxyl with chlorine or bromine. Phosphorus trihalides, especially in the presence of pyridine, are particularly suitable, and propargyl iodide is easily prepared from propargyl bromide by halogen exchange.

Hydrogenation gives allyl alcohol, its isomer propanal, or propanol, whereas with acidic mercuric salt catalysts, water adds to give acetol (hydroxyacetone):



In the presence of copper acetylide catalysts, propargyl alcohol and aldehydes give acetylenic glycols. When dialkylamines are also present, dialkylaminobutynols are formed.

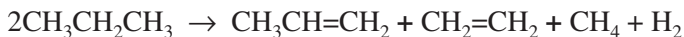
*See Butynediol.*



# PROPENE

Propene (propylene,  $\text{CH}_3\text{CH}=\text{CH}_2$ , boiling point:  $-47.7^\circ\text{C}$ , flash point:  $-107.8^\circ\text{C}$ , ignition temperature:  $497.2^\circ\text{C}$ ) is a colorless, flammable gas with a slightly sweet aroma.

Like ethylene (q.v.), propylene can also be isolated from refinery gas but propylene (propene) is also manufactured by steam cracking of hydrocarbons as for ethylene and the best feedstocks are propane, naphtha, or gas oil (Fig. 1).



Much of the propylene is consumed by the petroleum refining industry for alkylation and polymerization to oligomers that are added to gasoline. A smaller amount is used for chemical manufacture.

Propene is used for the manufacture of a variety of chemicals (Fig. 2), including polypropylene, acrylic acid, *iso*-propyl alcohol, cumene, propy-

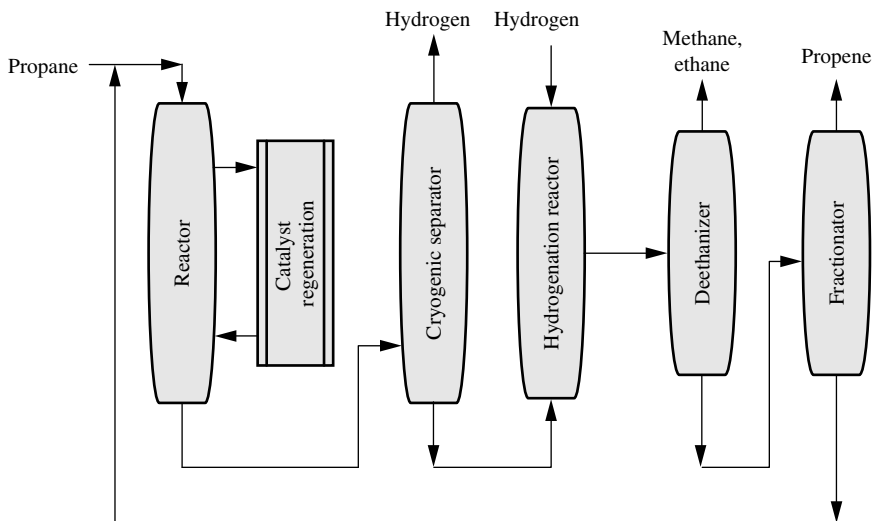


FIGURE 1 Manufacture of propene.

lene, and acrylonitrile. Propylene oxide is used in polyurethane plastic and foam. Cumene is made from propylene and benzene and is an important intermediate in the manufacture of phenol and acetone.

*iso*-propyl alcohol is made from propylene and is a common industrial solvent in coatings, chemical processes, pharmaceuticals, and household and personal products. Oxo chemicals are made by reacting propylene with synthesis gas ( $\text{CO}/\text{H}_2$ ) to form  $\text{C}_4$  alcohols. Small amounts of propylene are made into oligomers, where 3 to 5 propylene units are added to each other for use in the manufacture of soaps and detergents, in addition to being used as *polymer* gasoline.

### See *Iso-Propyl Alcohol*.

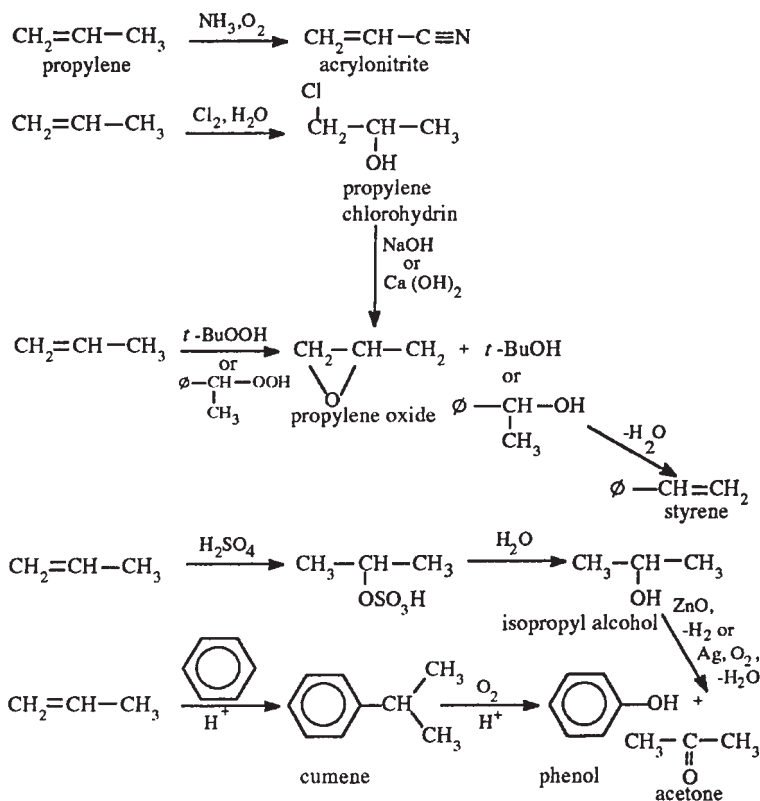


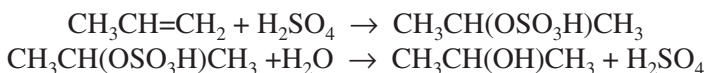
FIGURE 2 Manufacture of chemicals from propene.

# ISO-PROPYL ALCOHOL

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*Iso*-propyl alcohol (2-propanol, *iso*-propanol, rubbing alcohol; boiling point: 82.4°C, melting point: 89.5°C, density: 0.7855) is manufactured by the esterification/hydrolysis of propylene to *iso*-propyl alcohol. Unlike ethanol, for which the esterification/hydrolysis has been replaced by direct hydration, the direct process for *iso*-propyl alcohol is more difficult for crude propylene.

In the esterification process, only the propylene reacts and conditions can be maintained so that ethylene is inert.



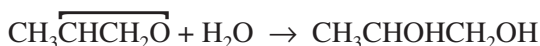
The esterification step occurs with 85% sulfuric acid at 24 to 27°C, and dilution to 20% concentration is done in a separate tank. The *iso*-propyl alcohol is distilled from the dilute acid that is concentrated and returned to the esterification reactor. The *iso*-propyl alcohol is originally distilled as a 91% azeotrope with water. Absolute *iso*-propyl alcohol, boiling point 82.5°C, is obtained by distilling a tertiary azeotrope with *iso*-propyl ether. A 95% yield is realized.

*Iso*-propyl alcohol is used to produce acetone, pharmaceuticals, processing solvents, and coatings. Some of the chemicals derived from *iso*-propyl alcohol are *iso*-propyl ether (an industrial extraction solvent), *iso*-propyl acetate (a solvent for cellulose derivatives), *iso*-propyl myristate (an emollient, lubricant, and blending agent in cosmetics, inks, and plasticizers), *t*-butylperoxy *iso*-propyl carbonate (a polymerization catalyst and curing agent, and *iso*-propylamine and *diiso*-propylamine (low-boiling bases).

# PROPYLENE GLYCOL

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Propylene glycol (boiling point: 189°C, density: 1.0361) is produced by hydration of propylene oxide in a process similar to that for the production of ethylene glycol by hydration of ethylene oxide.



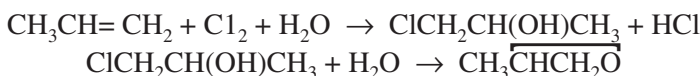
Unsaturated polyester resins account for the majority of the commercial use of propylene glycol. Other uses include food, cosmetics, pharmaceuticals, pet food, and tobacco humectants.

*See Ethylene Glycol, Propylene Oxide.*

# PROPYLENE OXIDE

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There are two important methods for the manufacture of propylene oxide. The older method involves chlorohydrin formation from the reaction of propylene with chlorine water (Fig. 1).



The dilute chlorohydrin solution is mixed with a 10% slurry of lime to form the oxide, which is purified by distillation, boiling point 34°C. The yield is 90 percent.

A new variation of the chlorohydrin process uses *t*-butyl hypochlorite as the chlorinating agent. The waste brine solution can be converted back to chlorine and caustic by a special electrolytic cell to avoid the waste of chlorine.

The second manufacturing method for propylene oxide is via peroxidation of propylene (Halcon process). Oxygen is first used to oxidize *iso*-butane to *t*-butyl hydroperoxide (BHP) over a molybdenum naphthenate catalyst at 90°C and 450 psi (Fig. 2).



The *t*-butyl hydroperoxide is then used to oxidize propylene to the oxide.



The *t*-butyl alcohol can be used to increase the octane number of unleaded gasoline or it can be made into methyl *t*-butyl ether (MTBE) for the same application. The alcohol can also be dehydrated to isobutylene, which in turn is used in alkylation to give highly branched dimers for addition to straight-run gasoline. An alternative reactant in this method is ethylbenzene hydroperoxide. This eventually forms phenylmethylcarbinol along with the propylene oxide, and the alcohol is dehydrated to styrene. Thus, the yield of the by-product can be varied depending on the demand for substances such as *t*-butyl alcohol or styrene.

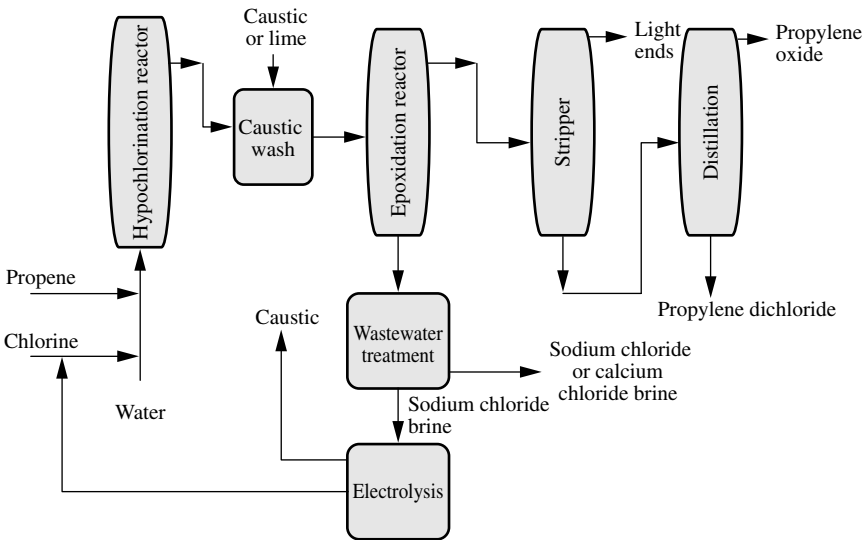


FIGURE 1 Manufacture of propylene oxide by the chlorohydrin process.

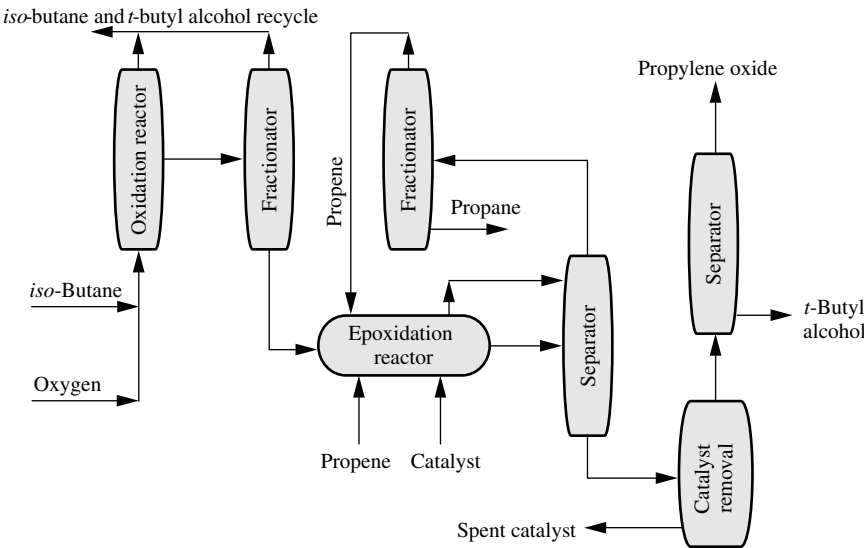


FIGURE 2 Manufacture of propylene oxide by the *t*-butyl hydroperoxide process.

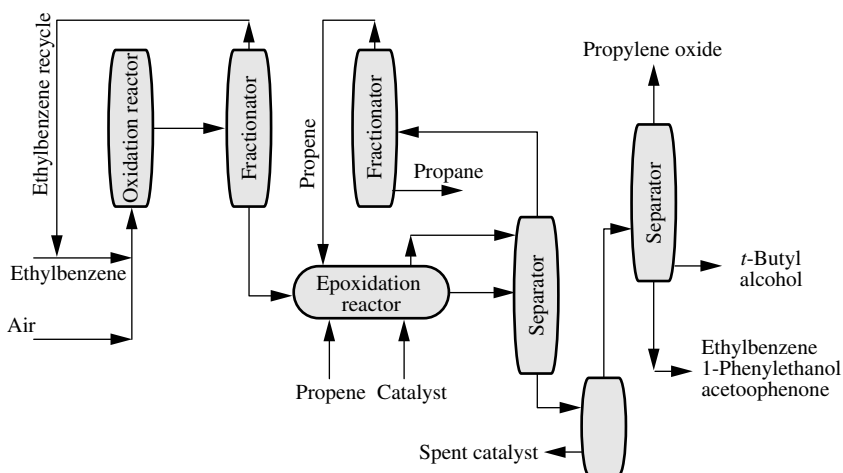


FIGURE 3 Manufacture of propylene oxide from ethylbenzene.

A third process involves the production of propylene oxide from ethylbenzene (Fig. 3); styrene is also produced.

Propylene oxide is used in the manufacture of propylene glycol, polypropylene glycol, dipropylene glycol, and glycol ethers. The polymerization of propylene oxide yields polypropylene glycol, which is actually a polyether, although it has terminal hydroxyl groups. These hydroxyl groups are reacted with an isocyanate such as toluene diisocyanate (TDI) to form the urethane linkages in the high-molecular-weight-polyurethanes.

# PULP AND PAPER CHEMICALS

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Cellulose is not only the most abundant organic substance available, it is a major component of woody plants and is constantly replaceable. Its conversion to paper products is the function of the pulp and paper industries, which manufacture thousands of useful items from cellulose.

Before paper can be made from wood, the cellulose fibers must be freed from the matrix of lignin that cements them together. The fibers may be separated by mechanical procedures or by solution of the lignin by various chemicals. The pulp thus formed has its fibers recemented together to form paper when suitable additives are used.

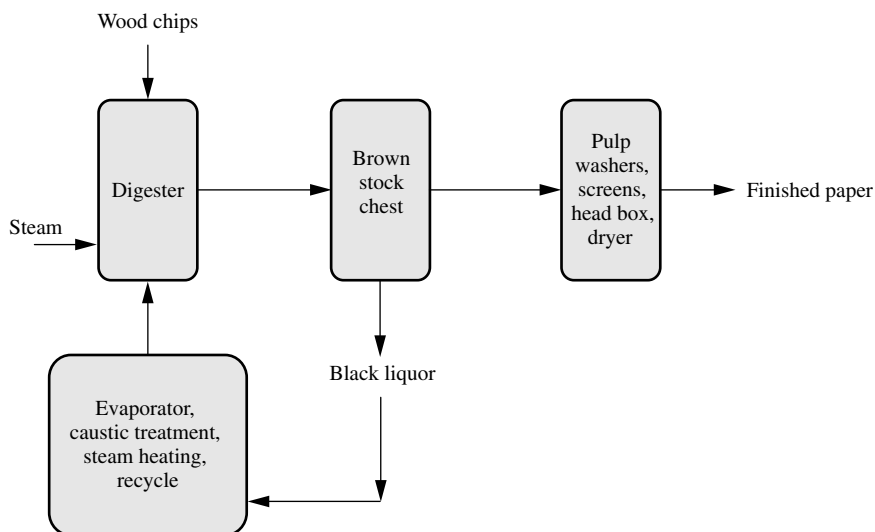
All processes used for pulping have the same goal, and that is the release the fibrous cellulose from its surrounding lignin while keeping the hemicelluloses and celluloses intact, thereby increasing the yield of useful fibers. The fibers thus obtained are naturally colored and must be bleached before they can be used for paper.

There are many processes and variations of basic processes that can be used for making pulp from wood. The major processes are: the *kraft process* (also known as the *sulfate process*), the groundwood and thermo-mechanical process, semichemical process, and the *sulfite process*. The kraft process remains dominant.

The kraft process (Fig. 1) is an alkaline process that is an outgrowth of the obsolete soda process that cooked with a strong (12%) solution of sodium hydroxide and sodium carbonate. The soda process gave low yields and worked well only with short-fibered hardwoods. The material added to the cooking liquor for the kraft process is sodium sulfate ( $\text{Na}_2\text{SO}_4$ , hence the alternative name, the sulfate process). However, the heating is accomplished by using a solution containing sodium sulfide ( $\text{Na}_2\text{S}$ ), sodium hydroxide ( $\text{NaOH}$ ), and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) formed from the sulfate during preparation and recovery of the cooking liquor.

An essential factor in the kraft process has been the recovery of the spent liquor from the cooking process. The black liquor removed from the





**FIGURE 1** The kraft pulping process.

pulp in the pulp washer, or diffuser, contains 95 to 98 percent of the total chemicals charged to the digester. Organic sulfur compounds are present in combination with sodium sulfide. Sodium carbonate is present, as are also small amounts of sodium sulfate, salt, silica, and traces of lime, iron oxide, alumina, and potash. The black liquor is concentrated, burned, and limed to break down any remaining organic compounds. The carbon is burned and the inorganic chemicals melted for reuse or disposal.

# PYRIDINE

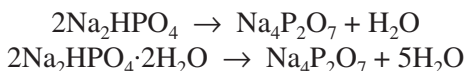
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There are no natural sources of pyridine compounds that are either a single pyridine isomer or just one compound. For instance, coal tar contains a mixture of bases, mostly alkylpyridines, in low concentrations.

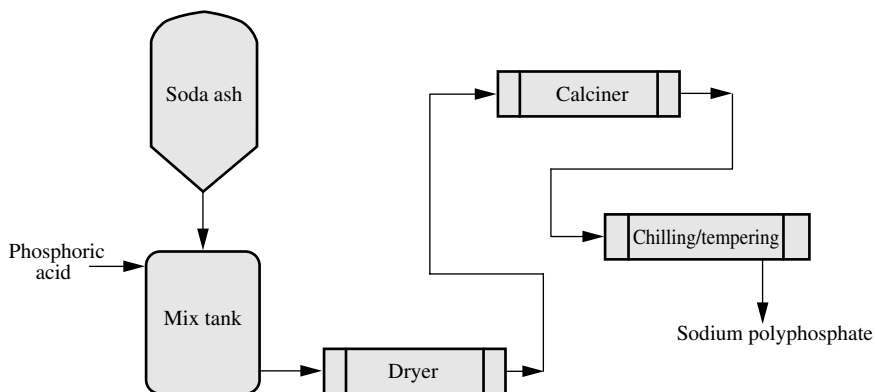
Pyridine (boiling point: 115.5°C, density: 0.9819) is manufactured by reacting formaldehyde, acetaldehyde, and ammonia at 350 to 550°C in the presence of a silica-alumina catalyst ( $\text{SiO}_2\text{-Al}_2\text{O}_3$ ), and the principal products are pyridine (1) and 3-picoline (3-methyl pyridine).

# PYROPHOSPHATES

Tetrasodium pyrophosphate (sodium polyphosphate,  $\text{Na}_4\text{P}_2\text{O}_7$ ) is manufactured by reacting phosphoric acid and soda ash to yield a disodium phosphate solution, which may be dried to give anhydrous disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) or crystallized to give disodium phosphate dihydrate ( $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ) or disodium phosphate heptahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ). These compounds are calcined at a high temperature in an oil-fired or gas-fired rotary kiln to yield tetrasodium pyrophosphate (Fig. 1).



Tetrasodium pyrophosphate is used as a water softener and as a soap and detergent builder.



**FIGURE 3** Manufacture of sodium polyphosphate.