

BARBITAL

Barbital[®], diethylbarbituric acid, is sold under the trade name Veronal[®]. It is the oldest of the long-acting barbiturates and is derived through diethyl malonate.

BARBITURATES

Barbiturates are sedative drugs that are derived from barbituric acid and have the ability to depress the central nervous system and act especially on the sleep center in the brain, thus their sedative and sometimes hypnotic effects.

The method of synthesis for thousands of barbital analogs involves the reaction of urea with various derivatives of malonic acid, usually a diethyl ester of a dialkyl-substituted malonic acid.

The barbiturates are usually administered as the sodium salts. The N-H bonds are acidic and although barbituric acid itself is inactive, a range of activities is obtained that varies with the groups at R and R¹. Activity and toxicity both increase with the size of the groups. Branching and unsaturation decrease the duration of action.

Barbiturates have been used in sleeping pills, but in recent years several other compounds also have been introduced for this purpose. Barbiturates induce a feeling of relaxation, usually followed by sleep, and have been used to provide temporary respite in times of unusual emotional stress, but they will only prolong the stress and patient reliance on the drugs is common.

The maximum therapeutic index (tolerated dose/minimum effective dose) is highest when the two groups have a total of 6 to 10 carbons. Major drawbacks of their use are their habit formation and their high toxicity when alcohol is present in the bloodstream.

BARIUM CARBONATE

See Barium Salts.

BARIUM SALTS

The most common naturally occurring barium compounds are the mineral carbonate (witherite, BaCO_3) and the sulfate (barite, BaSO_4).

The manufacture of soluble barium salts involves treatment of the mineral (usually barite) with the relevant acid, filtration to remove insoluble impurities, and crystallization of the salt.

The high-temperature reduction of barium sulfate with coke yields the water-soluble barium sulfide (BaS), which is subsequently leached out. Treatment of barium sulfide with the relevant chemical yields the desired barium salt. Purification of the product is complicated by the impurities introduced in the coke. Pure barium carbonate and barium sulfate are made by precipitation from solutions of water-soluble barium salts.

Barite is ground, acid-washed, and dried to produce a cheap pigment or paper or rubber filler, or changed to *blanc fixe*.

The applications of barium compounds are varied and include use as oil-drilling mud. Barium carbonate is sometimes employed as a neutralizing agent for sulfuric acid and, because both barium carbonate and barium sulfate are insoluble, no contaminating barium ions are introduced. The foregoing application is found in the synthetic dyestuff industry.

Barium carbonate is used in the glass industry and in the brick and clay industry. When barium carbonate is added to the clay used in making bricks, it immobilizes the calcium sulfate and prevents it from migrating to the surface of the bricks and producing a whitish surface discoloration.

Barium sulfate is a useful white pigment, particularly in the precipitated form, *blanc fixe*. It is used as a filler for paper, rubber, linoleum, and oil-cloth. Because of its opacity to x-rays, barium sulfate, in a purified form, is important in contour photographs of the digestive tract.

The paint industry is the largest single consumer of barium compounds. Barium sulfide and zinc sulfate solutions are mixed to give a precipitate of barium sulfate and zinc sulfide, which is heat treated to yield the pigment *lithopone*. Barium chlorate and nitrate are used in pyrotechnics to impart a green flame. Barium chloride is applied where a soluble barium compound is needed.

BARIUM SULFATE

Barium sulfate (BaSO_4 , melting point 1580°C with decomposition) occurs as colorless rhombic crystals. It is soluble in concentrated sulfuric acid, forming an acid sulfate; dilution with water reprecipitates barium sulfate. Precipitated barium sulfate, known as *blanc fixe*, is prepared from the reaction of aqueous solutions of barium sulfide (BaS) and sodium sulfate (Na_2SO_4).

Barium sulfate, often prepared by grinding the ore barite, is not usually used alone as a white pigment because of its poor covering power, but is widely used as a pigment extender. It also contributes to gloss. Its principal use (over 90 percent) is in oil-drilling muds. *Blanc fixe* is made by precipitation of a soluble barium compound, such as barium sulfide or barium chloride, by a sulfate. This form has finer particles than the ground barite and is often used in printing inks to impart transparency.

See also Barium Salts, Lithopone.

BARIUM SULFIDE

See Barium Salts, Lithopone.

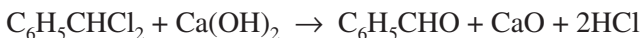
BAUXITE

See Alumina.

BENZALDEHYDE

Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$, melting point: -26°C , boiling point: 179°C , density: 1.046) is a colorless liquid that is sometimes referred to as *artificial almond oil* or *oil of bitter almonds* because of the characteristic nutlike odor. Benzaldehyde is slightly soluble in water but is miscible in all proportions with alcohol or ether. On standing in air, benzaldehyde oxidizes readily to benzoic acid.

Commercially, benzaldehyde may be produced (1) by heating benzal chloride ($\text{C}_6\text{H}_5\text{CHCl}_2$) with calcium hydroxide:



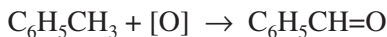
(2) by heating calcium benzoate and calcium formate:



or (3) by boiling glucoside amygdalin of bitter almonds with a dilute acid.

Benzaldehyde is manufactured in two grades, technical and refined. The technical grade is largely used as an intermediate in the synthesis of other chemicals, such as benzyl benzoate, cinnamic aldehyde, and dyes.

Most of the technical grade is made by direct vapor-phase oxidation of toluene, although some is made by chlorinating toluene to benzal chloride, followed by alkaline or acid hydrolysis. For perfume and flavoring use, the refined, chlorine-free grade is required, which is economically produced by the direct vapor-phase oxidation of toluene with air at 500°C .



It is claimed that a catalyst mixture of 93% uranium oxide and 7% molybdenum oxide gives relatively high yields. The oxidation is sometimes carried out in the liquid phase by using manganese dioxide/sulfuric acid at 40°C .

Benzaldehyde is used as a flavoring material, in the production of cinnamic acid, in the manufacture of malachite green dye, as an ingredient in pharmaceuticals, and as an intermediate in chemical syntheses.

BENZENE

Benzene (C_6H_6 , boiling point: $80^\circ C$, density: 0.8789, flash point: $-11^\circ C$, ignition temperature: $538^\circ C$), is a volatile, colorless, and flammable liquid aromatic hydrocarbon possessing a distinct, characteristic odor. Benzene is practically insoluble in water (0.07 part in 100 parts at $22^\circ C$); and fully miscible with alcohol, ether, and numerous organic liquids.

For many years benzene (benzol) was made from coal tar, but new processes that consist of catalytic reforming of naphtha and hydrodealkylation of toluene are more appropriate. Benzene is a natural component of petroleum, but it cannot be separated from crude oil by simple distillation because of azeotrope formation with various other hydrocarbons. Recovery is more economical if the petroleum fraction is subjected to a thermal or catalytic process that increases the concentration of benzene.

Petroleum-derived benzene is commercially produced by reforming and separation, thermal or catalytic dealkylation of toluene, and disproportionation. Benzene is also obtained from pyrolysis gasoline formed in the steam cracking of olefins.

If benzene is the main product desired, a narrow light naphtha fraction boiling over the range 70 to $104^\circ C$ is fed to the reformer, which contains a noble metal catalyst consisting of, for example, platinum-rhenium on a high-surface-area alumina support. The reformer operating conditions and type of feedstock determine the amount of benzene that can be produced. The benzene product is most often recovered from the reformate by solvent extraction techniques.

In the platforming process (Fig. 1), the feedstock is usually a straight-run, thermally cracked, catalytically cracked, or hydrocracked C_6 to $200^\circ C$ naphtha. The feed is first hydrotreated to remove sulfur, nitrogen, or oxygen compounds that would foul the catalyst, and also to remove olefins present in cracked naphthas. The hydrotreated feed is then mixed with recycled hydrogen and preheated to 495 to $525^\circ C$ at pressures of 116 to 725 psi (0.8 to 5 MPa). Typical hydrogen charge ratios of 4000 to 8000 standard cubic feet per barrel (scf/bbl) of feed are necessary.

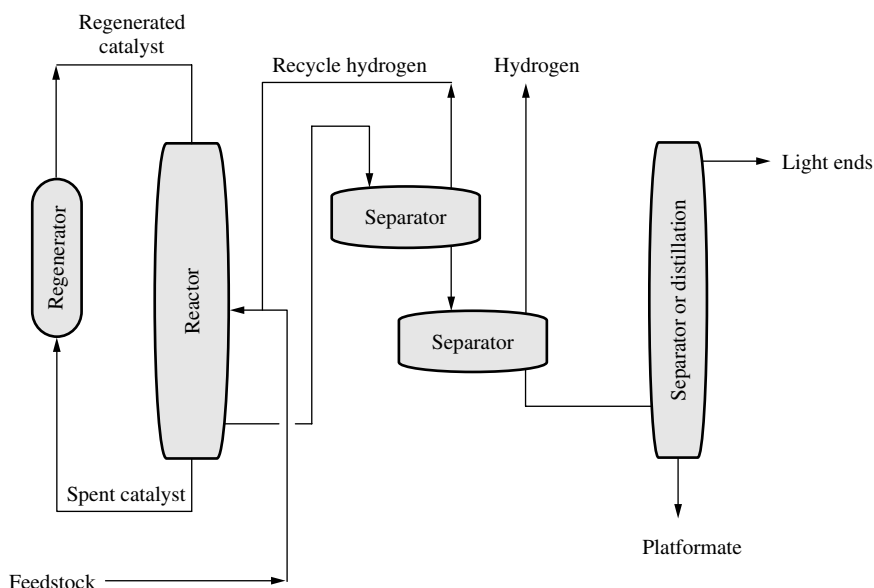


FIGURE 1 Benzene manufacture by the platforming process.

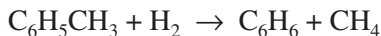
The feed is then passed through a stacked series of three or four reactors containing the catalyst (platinum chloride or rhenium chloride supported on silica or silica-alumina). The catalyst pellets are generally supported on a bed of ceramic spheres.

The product coming out of the reactor consists of excess hydrogen and a reformate rich in aromatics. The liquid product from the separator goes to a stabilizer where light hydrocarbons are removed and sent to a debutanizer. The debutanized platformate is then sent to a splitter where C_8 and C_9 aromatics are removed. The platformate splitter overhead, consisting of benzene, toluene, and nonaromatics, is then solvent extracted.

Solvents used to extract the benzene include tetramethylene sulfone (Fig. 2), diethylene glycol, *N*-methylpyrrolidinone process, dimethylformamide, liquid sulfur dioxide, and tetraethylene glycol.

Benzene is also produced by the hydrodemethylation of toluene under catalytic or thermal conditions.

In the catalytic hydrodealkylation of toluene (Fig. 3):



toluene is mixed with a hydrogen stream and passed through a vessel packed with a catalyst, usually supported chromium or molybdenum oxides, platinum or platinum oxides, on silica or alumina. The operating temperatures range from 500 to 595°C and pressures are usually 580 to 870 psi

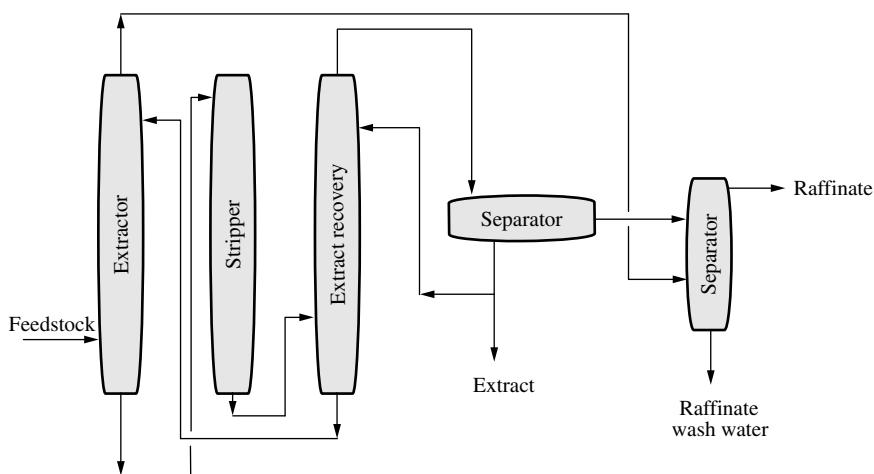


FIGURE 2 Benzene manufacture by sulfolane extraction.

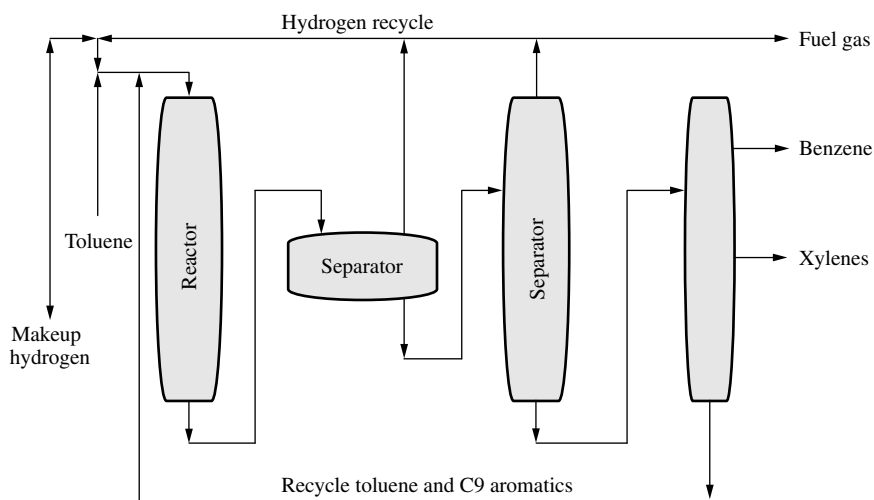


FIGURE 3 Benzene manufacture by toluene hydrodealkylation.

(4 to 6 MPa). The reaction is exothermic and temperature control (by injection of quench hydrogen) is necessary at several places along the reaction sequence. Conversions per pass typically reach 90 percent and selectivity to benzene is often greater than 95 percent. The catalytic process occurs at lower temperatures and offers higher selectivity but requires frequent regeneration of the catalyst. Products leaving the reactor pass through a separator where unreacted hydrogen is removed and recycled to the feed. Further fractionation separates methane from the benzene product.

Benzene is also produced by the transalkylation of toluene in which two molecules of toluene are converted into one molecule of benzene and one molecule of mixed xylene isomers.

In the process (Fig. 4), toluene and C₉ aromatics are mixed with liquid recycle and recycle hydrogen, heated to 350 to 530°C at 150 to 737 psi (1 to 5 MPa), and charged to a reactor containing a fixed bed of noble metal or rare earth catalyst with hydrogen-to-feedstock mole ratios of 5:1 to 12:1. Following removal of gases, the separator liquid is freed of light ends and the bottoms are then clay treated and fractionated to produce high-purity benzene and xylenes. The yield of benzene and xylene obtained from this procedure is about 92 percent of the theoretical.

Other sources of benzene include processes for steam cracking heavy naphtha or light hydrocarbons such as propane or butane to produce a liquid product (pyrolysis gasoline) rich in aromatics that contains up to about 65 percent aromatics, about 50 percent of which is benzene. Benzene can be recovered by solvent extraction and subsequent distillation.

Benzene can also be recovered from coal tar. The lowest-boiling fraction of the tar is extracted with caustic soda to remove tar acids, and the base oil is then distilled and further purified by hydrodealkylation.

Benzene is used as a chemical intermediate for the production of many important industrial compounds, such as styrene (polystyrene and synthetic rubber), phenol (phenolic resins), cyclohexane (nylon), aniline (dyes), alkylbenzenes (detergents), and chlorobenzenes. These intermedi-

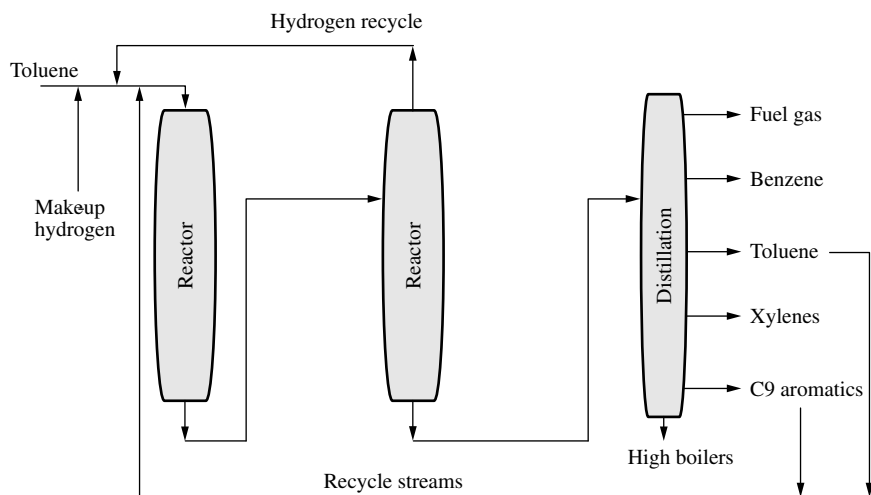


FIGURE 4 Benzene manufacture by the transalkylation of toluene.

ates, in turn, supply numerous sectors of the chemical industry producing pharmaceuticals, specialty chemicals, plastics, resins, dyes, and pesticides. In the past, benzene has been used in the shoe and garment industry as a solvent for natural rubber. Benzene has also found limited application in medicine for the treatment of certain blood disorders and in veterinary medicine as a disinfectant.

Benzene, along with other light high-octane aromatic hydrocarbons such as toluene and xylene, is used as a component of motor gasoline. Benzene is used in the manufacture of styrene, ethylbenzene, cumene, phenol, cyclohexane, nitrobenzene, and aniline. It is no longer used in appreciable quantity as a solvent because of the health hazards associated with it.

Ethylbenzene is made from ethylene and benzene and then dehydrogenated to styrene, which is polymerized for various plastics applications. Cumene is manufactured from propylene and benzene and then made into phenol and acetone. Cyclohexane, a starting material for some nylon, is made by hydrogenation of benzene. Nitration of benzene followed by reduction gives aniline, important in the manufacture of polyurethanes.

BENZINE

Benzine is a product of petroleum (boiling between 49 and 66°C) and is composed of aliphatic hydrocarbons.

Benzine should not be confused with benzene, which is a single chemical compound and an aromatic hydrocarbon.

BENZODIAZEPINES

Benzodiazepines are a series of compounds that have a benzene ring fused to a seven-membered ring containing two nitrogen atoms. The two most successful members of the group are diazepam (Valium[®]) and chlor-diazepoxide (Librium[®]); Flurazepam (Dalmane[®]) is a hypnotic.

The production of diazepam (Fig. 1) starts from *p*-chloroaniline prepared from benzene by nitration, reduction of the nitro group to an amine, and chlorination of the *o,p*-directing aniline) followed by reaction with benzoyl chloride (from toluene by oxidation to benzoic acid, followed by acid chloride formation) in a Friedel-Crafts acylation. Acylation occurs at the *o*-position, and formation of the oxime derivative is followed by methylation and then acylation of the amino group with chloroacetyl chloride. Heating with base eliminates hydrogen chloride to form the ring and reduction of the amine oxide with hydrogen gives diazepam.

Diazepam is used for the control of anxiety and tension, the relief of muscle spasms, and the management of acute agitation during alcohol withdrawal, but it may be habit forming.

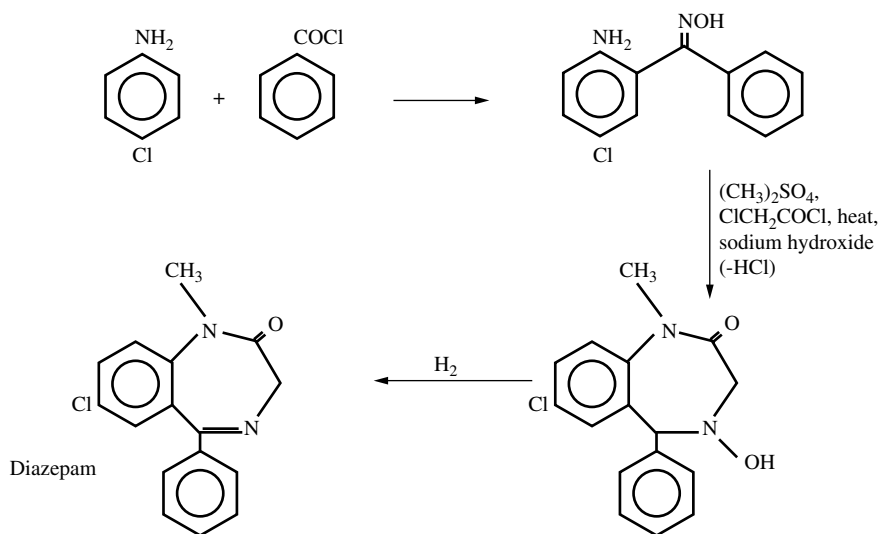
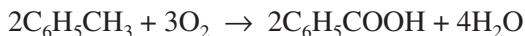


FIGURE 1 Manufacture of diazepam (Valium).

BENZOIC ACID

Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, phenyl formic acid, melting point: 121.7°C , boiling point: 249.2°C , density: 1.266) is a white crystalline solid that sublimates readily at 100°C and is volatile in steam. Benzoic acid is insoluble in cold water but is readily soluble in hot water or in alcohol or ether.

Although benzoic acid occurs naturally in some substances, such as gum benzoin, dragon's blood resin, balsams, cranberries, and the urine of the ox and horse, the product is made on a large scale by synthesis from other materials. Benzoic acid can be manufactured by the liquid-phase oxidation of toluene by air in a continuous oxidation reactor operated at moderate pressure and temperature:



Benzoic acid also can be obtained as a by-product of the manufacture of benzaldehyde from benzal chloride or benzyl chloride.

Benzoic acid is used as a starting or intermediate material in various industrial organic syntheses, especially in the manufacture of terephthalic acid. Benzoic acid forms benzoates; e.g., sodium benzoate and calcium benzoate which, when heated with calcium oxide, yields benzene and calcium. With phosphorus trichloride, benzoic acid forms benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$), an agent for the transfer of the benzoyl group ($\text{C}_6\text{H}_5\text{CO}-$). Benzoic acid reacts with chlorine to form *m*-chlorobenzoic acid and reacts with nitric acid to form *m*-nitrobenzoic acid. Benzoic acid forms a number of useful esters such as methyl benzoate, ethyl benzoate, glycol dibenzoate, and glyceryl tribenzoate.

BENZYL ACETATE

Benzyl acetate ($\text{C}_6\text{H}_5\text{CH}_2\text{OCOCH}_3$) is a widely used ester because of its floral odor.

It is prepared by esterification of benzyl alcohol, by heating with either an excess of acetic anhydride or acetic acid with mineral acids.

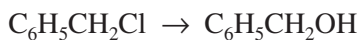


The product is purified by treatment with boric acid and distilled to a purity in excess of 98%.

BENZYL ALCOHOL

Benzyl alcohol is employed in pharmaceuticals and lacquers. This alcohol has a much weaker odor than its esters.

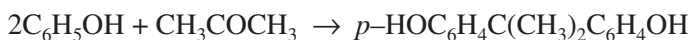
Benzyl alcohol is manufactured by hydrolysis of benzyl chloride.



*See **Benzyl Acetate***

BISPHENOL A

Bisphenol A is made by reacting phenol with acetone in the presence of an acid catalyst (Fig. 1). The temperature of the reaction is maintained at 50°C (120°F) for about 8 to 12 hours. A slurry of bisphenol A is formed, which is neutralized and distilled to remove excess phenol.



Bisphenol A is used in the production of epoxy resins and polycarbonate resins.

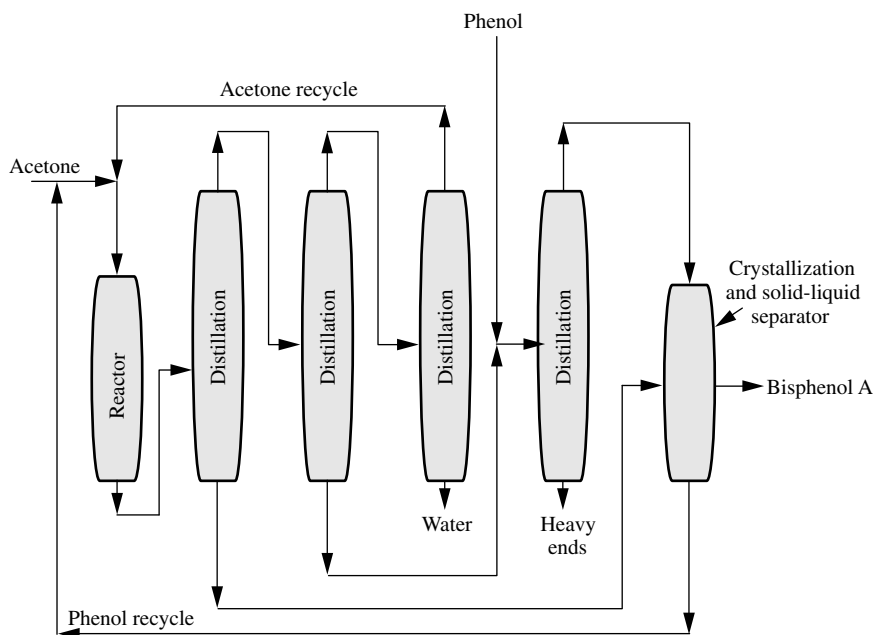


FIGURE 1 Manufacture of Bisphenol A.

BORAX

Borax is a hydrated sodium borate mineral ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, density: 1.715). It crystallizes in the monoclinic system, usually in short prismatic crystals. Borax ranges from colorless through gray, blue to greenish and has a vitreous to resinous luster of translucent to opaque character. Borax is a product of evaporation from shallow lakes.

Borax is used in antiseptics and medicines, as a flux in smelting, soldering, and welding operations; as a deoxidizer in nonferrous metals; as a neutron absorber for atomic energy shields; in rocket fuels; and as extremely hard, abrasive boron carbide (harder than corundum).

BORON COMPOUNDS

The important naturally occurring ores of boron are colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), tincal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), and boracite ($2\text{Mg}_3\text{B}_8\text{O}_{15} \cdot \text{MgCl}_2$). Boron-containing brines and kernite, or rasorite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), are also sources of boron compounds.

Crude and refined hydrated sodium borates and hydrous boric acid are produced from kernite and tincal. The ore is fed to the dissolving plant and mixed with hot recycle liquor. Liquor and fine insolubles are fed to a primary thickener. The strong liquors are crystallized in a continuous vacuum crystallizer.

Another process involves the use of an organic solvent to extract the borax brines. Boric acid is extracted with kerosene, carrying a chelating agent. In a second mixer-settler system, dilute sulfuric acid strips the borates from the chelate. The aqueous phase with boric acid, potassium sulfate, and sodium sulfate is purified by carbon treatment and evaporated in two evaporator-crystallizers. From the first, pure boric acid is separated, and from the other, a mixture of sodium and potassium sulfates.

Borax (tincal, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), is the most important industrial compound of boron. The largest single use is in the manufacture of glass-fiber insulation. Boric acid (H_3BO_3) is a weak acid that is used in the manufacture of glazes and enamels for pottery. Its main uses are as a fire retardant for cellulosic insulation and in the manufacture of borosilicate glasses and textile-grade glass fibers.

BROMAL

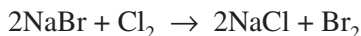
See Chloral.

BROMINE

Bromine (freezing point: -7.3°C , boiling point: 58.8°C , density: 3.1226) is a member of the halogen family and is a heavy, dark-red liquid.

Bromine is produced from seawater, in which bromine occurs in concentrations of 60 to 70 ppm, and from natural brine, where the concentration of bromine may be as high as 1300 ppm. It can also be produced from waste liquors resulting from the extraction of potash salts from carnallite deposits.

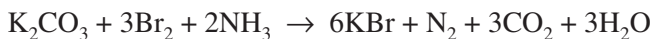
Bromine is isolated from sea water by air-blowing it out of chlorinated seawater.



In ocean water, where the concentration of bromine is relatively dilute, air has proved to be the most economical blowing-out agent. However, in the treatment of relatively rich bromine sources such as brines, *steaming out* the bromine vapor is more satisfactory.

The steaming-out process (Fig. 1) process involves preheating the brine to 90°C in a heat exchanger and passing it down a chlorinator tower. After partial chlorination, the brine flows into a steaming-out tower, where steam is injected at the bottom and the remaining chlorine is introduced. The halogen-containing vapor is condensed and gravity separated. The top water-halogen layer is returned to the steaming-out tower, and the crude halogen (predominantly bromine) bottom layer is separated and purified. Crude bromine is purified by redistillation or by passing the vapors over iron filings that remove any chlorine impurity.

Bromine is used for the production of alkali bromides that cannot be manufactured by the action of caustic soda on bromine because hypobromites and bromates are also produced. Thus, the van der Meulen process from the production of potassium bromide involves treating bromine with potassium carbonate in the presence of ammonia.



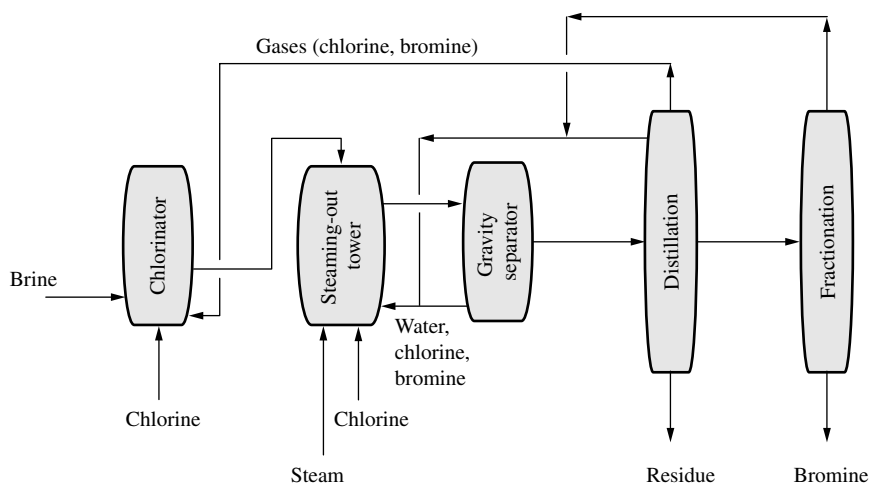


FIGURE 1 Manufacture of bromine from brine.

BROMOACETALDEHYDE

See Chloral.

BTX AROMATICS

BTX (benzene-toluene-xylene) mixtures are an important petroleum refinery stream that is separated by extractive distillation (Fig. 1) from a hydrocarbon stream, usually a reformate, and followed by downstream fractionation for isolation of the pure materials for further treatment and use (Fig. 2).

The BTX stream provides the individual components of the mixture for further use (Fig. 3).

*See **Benzene, Toluene, Xylenes.***

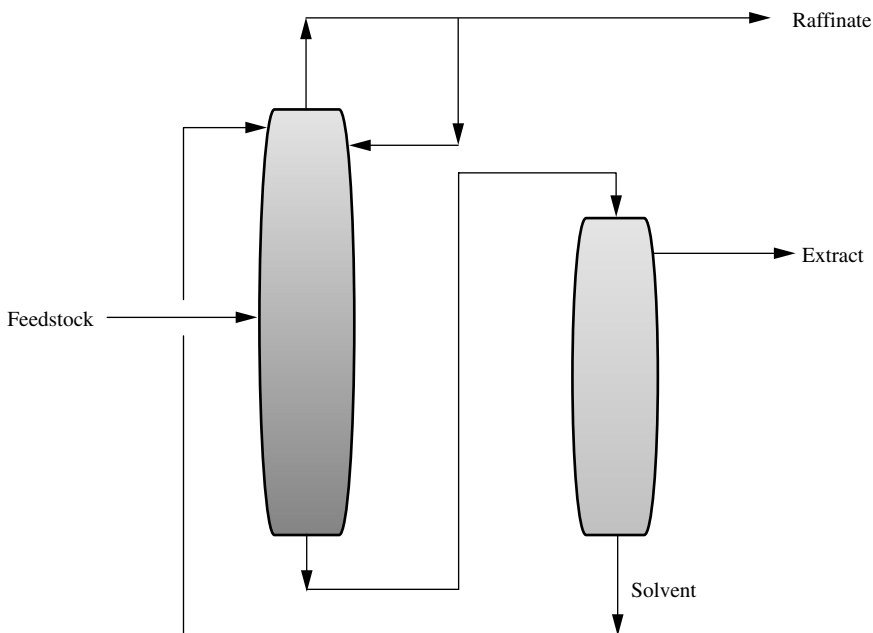


FIGURE 1 Schematic of extractive distillation.

BUTADIENE

Butadiene (1,3-butadiene, boiling point: -4.4°C , density: 0.6211, flash point: -85°C) is made by steam cracking and by the dehydrogenation of butane or the butenes using an iron oxide (Fe_2O_3) catalyst.



In the process (Fig. 1), the crude C_4 fraction is extracted with acetone, furfural, or other solvents to remove alkanes such as *n*-butane, *iso*-butane, and small amounts of pentanes, leaving only 1- and 2-butenes and *iso*-butene. The *isobutene* is removed by extraction with sulfuric acid because it oligomerizes more easily.

The straight-chain 1- and 2-butenes are preheated to 600°C in a furnace, mixed with steam as a diluent to minimize carbon formation, and passed through a 5-m-diameter reactor with a bed of iron oxide pellets (or calcium nickel phosphate) 90 to 120 cm deep (contact time 0.2 second) at 620 to 750°C . The material is cooled and purified by *fractional distillation* and extraction with solvents such as furfural, acetonitrile, dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP) (Fig. 2).

Extractive distillation (Fig. 3) is used where the C_4 compounds other than butadiene are distilled while the butadiene is complexed with the solvent. The solvent and butadiene pass from the bottom of the column and are then separated by distillation.

Butadiene is a colorless, odorless, flammable gas, with a boiling point of -4.7°C and is used for the manufacture of polybutadiene, nitrile rubber, chloroprene, and various other polymers. An important synthetic elastomer is styrene-butadiene rubber (SBR) in the automobile tire industry. Specialty elastomers are polychloroprene and nitrile rubber, and an important plastic is acrylonitrile/butadiene/styrene (ABS) terpolymer. Butadiene is made into adiponitrile, which is converted into hexamethylenediamine (HMDA), one of the monomers for nylon.

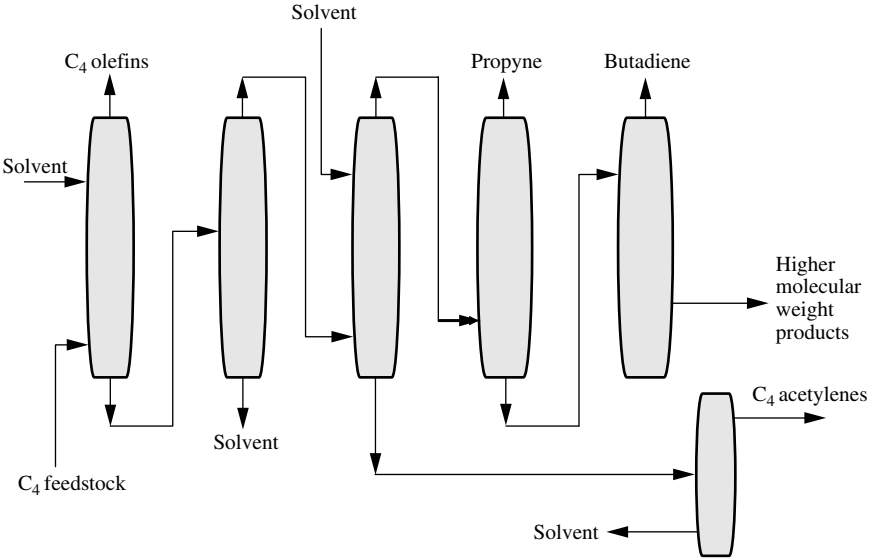


FIGURE 1 Butadiene manufacture from a refinery C₄ stream.

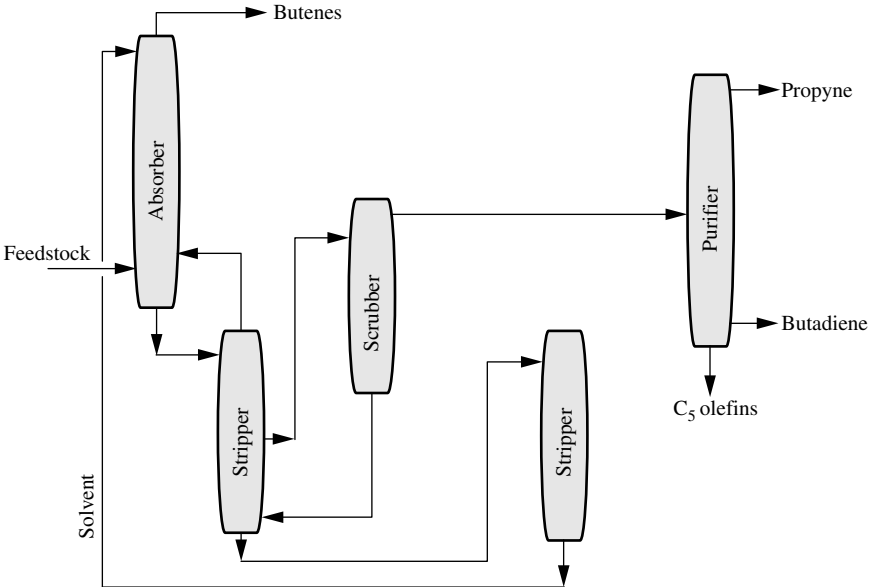


FIGURE 2 Butadiene recovery using *N*-methyl-2-pyrrolidone (NMP).

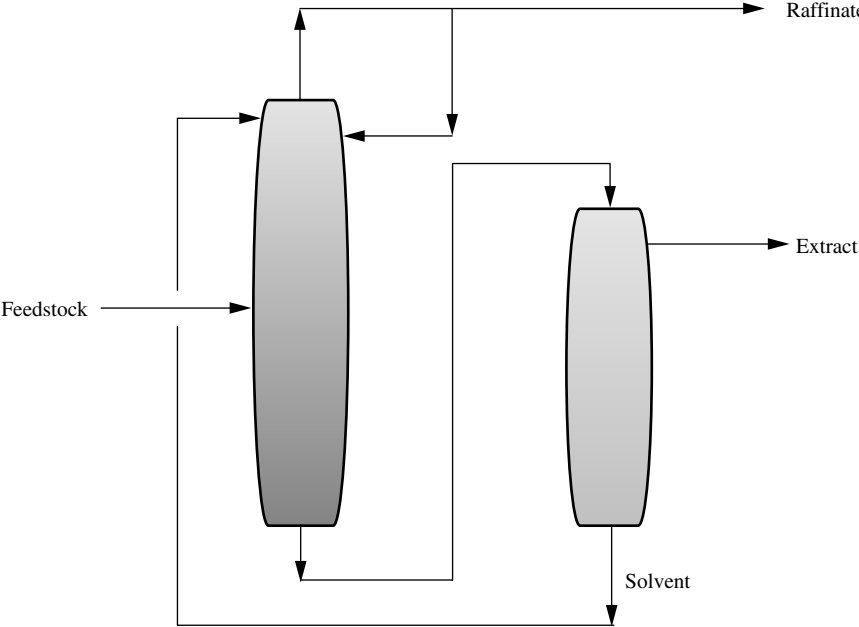


FIGURE 3 Schematic of extractive distillation.

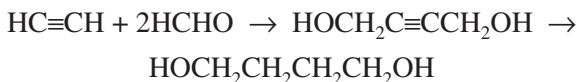
BUTANE

See Liquefied Petroleum Gas.

BUTANEDIOL

1,4-butanediol (tetramethylene glycol, 1,4-butylene glycol; melting point: 20.2°C, boiling point: 228°C, density: 1.017, flash point: 121°C) was first prepared in 1890 by acid hydrolysis of *N,N'*-dinitro-1,4-butanediamine. Other early preparations were by reduction of succinaldehyde or succinic esters and by saponification of the diacetate prepared from 1,4-dihalobutanes. Catalytic hydrogenation of butynediol, now the principal commercial route, was first described in 1910.

Butanediol is manufactured by way of hydrogenation of butynediol (the Reppe process):



An alternative route involving acetoxylation of butadiene and has come on stream, and, more recently, a route based upon hydroformylation of allyl alcohol has also been used. Another process, involving chlorination of butadiene, hydrolysis of the dichlorobutene, and hydrogenation of the resulting butenediol, has been practiced.

A more modern process involves the use of maleic anhydride as the starting material. In the process (Fig. 1), maleic anhydride is first esterified with methanol and the ester is fed to a low-pressure vapor-phase hydrogenation system where it is converted to butanediol.

Butanediol is specified as 99.5% minimum pure, determined by gas chromatography, solidifying at 19.6°C minimum. Moisture is 0.04% maximum, determined by Karl Fischer analysis (directly or by a toluene azeotrope).

Butanediol is much less toxic than its unsaturated analogs and it is neither a primary skin irritant nor a sensitizer. Because of its low vapor pressure, there is ordinarily no inhalation problem but, as with all chemicals, unnecessary exposure should be avoided.

The uses of butanediol are determined by the chemistry of the two primary hydroxyls. Esterification is normal and it is advisable to use nonacidic

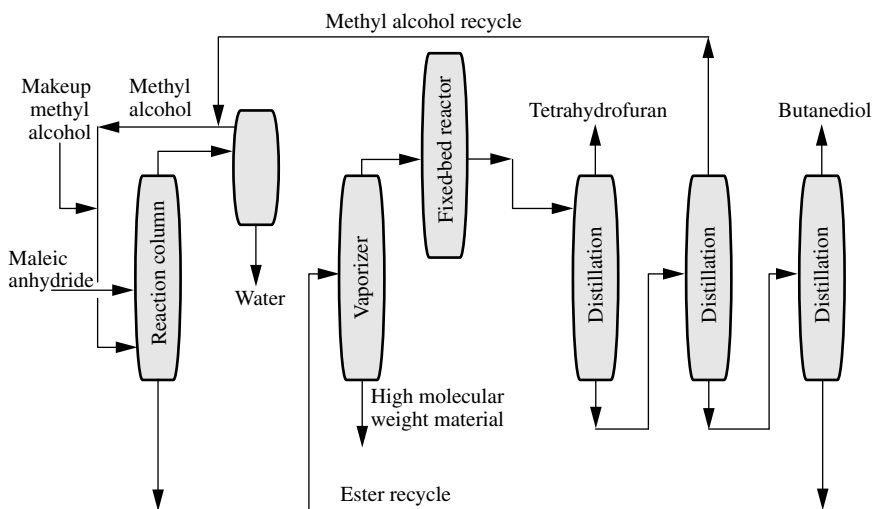


FIGURE 1 Manufacture of 1,4-butanediol from maleic anhydride.

catalysts for esterification and transesterification to avoid cyclic dehydration. When carbonate esters are prepared at high dilutions, some cyclic ester is formed; more concentrated solutions give a polymeric product.

Ethers are formed in the usual way; the *bis*-chloromethyl ether is obtained by using formaldehyde and hydrogen chloride. With aldehydes or their derivatives, butanediol forms acetals, either 7-membered rings (1,3-dioxepanes) or linear polyacetals; the rings and chains are easily intraconverted.

Thionyl chloride readily converts butanediol to 1,4-dichlorobutane and hydrogen bromide gives 1,4-dibromobutane. A procedure using 48% hydrobromic acid with a Dean-Stark water trap gives good yields of 4-bromobutanol, free of diol and dibromo compound.

With various catalysts, butanediol adds carbon monoxide to form adipic acid. Heating with acidic catalysts dehydrates butanediol to tetrahydrofuran. With dehydrogenation catalysts, such as copper chromite, butanediol forms butyrolactone. With certain cobalt catalysts, both dehydration and dehydrogenation occur, giving 2,3-dihydrofuran.

Heating butanediol or tetrahydrofuran with ammonia or an amine in the presence of an acidic heterogeneous catalyst gives pyrrolidines. With a dehydrogenation catalyst, amino groups replace one or both of the hydroxyl groups.

Vapor-phase oxidation over a promoted vanadium pentoxide catalyst gives a 90 percent yield of maleic anhydride. Liquid-phase oxidation with a supported palladium catalyst gives 55 percent of succinic acid.

The largest uses of butanediol are internal consumption in manufacture of tetrahydrofuran and butyrolactone. The largest merchant uses are for poly(butylene terephthalate) resins and in polyurethanes, both as a chain extender and as an ingredient in a hydroxyl-terminated polyester used as a macroglycol. Butanediol is also used as a solvent, as a monomer for various condensation polymers, and as an intermediate in the manufacture of other chemicals.

ISO-BUTANE

Iso-butane [(CH₃)₃CH] can be isolated from the petroleum C₄ fraction or from natural gas by extraction and distillation.

There are two major uses of *iso*-butane. One is dehydrogenation to isobutylene followed by conversion of the isobutylene to the gasoline additive methyl *t*-butyl ether (MTBE). However, current environmental issues may ban this gasoline additive.

Iso-butane is also oxidized to the hydroperoxide and then reacted with propylene to give propylene oxide and *t*-butyl alcohol. The *t*-butyl alcohol can be used as a gasoline additive, or dehydrate to *iso*-butylene.

BUTENE-1

The steam cracking of naphtha and catalytic cracking in the refinery produce the C_4 stream, which includes butane, 1-butene (butylene), *cis*- and *trans*-2-butene, isobutylene, and butadiene.



Extracting the isobutylene with sulfuric acid and distilling the 1-butene away from butane and butadiene is used for separation of the 1-butene. It is also made by Ziegler (or non-Ziegler) oligomerization of ethylene (Fig. 1).

1-butene is used as a comonomer to make polyethylene and is used to make valeraldehyde (pentanal) by the oxo process, polybutene-1, and butylene oxide.

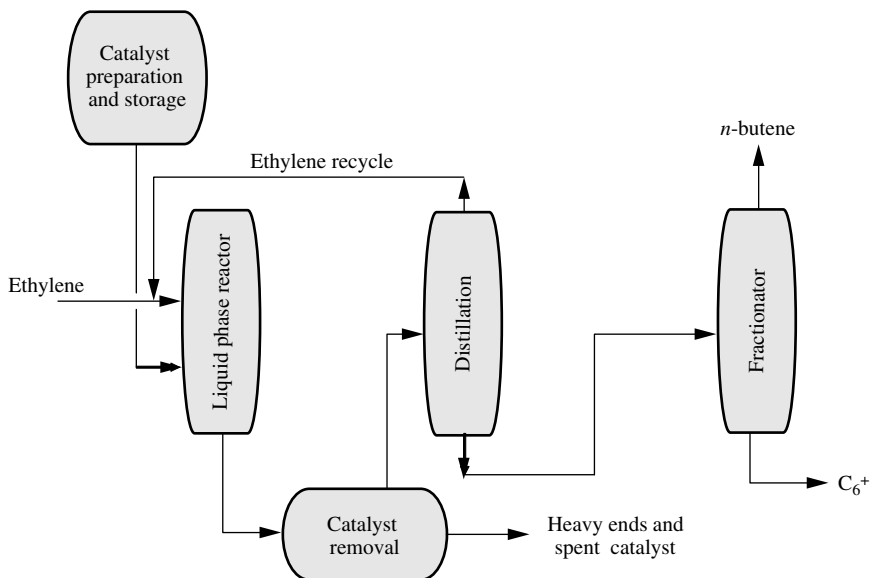


FIGURE 1 Manufacture of butene-1 (*n*-butene) by dimerization of ethylene.

BUTENEDIOL

2-butene-1,4-diol (melting point: 11.8°C, boiling point: 234°C, density: 1.070, flash point: 128°C) is the only commercially available olefinic diol with primary hydroxyl groups. The commercial product consists almost entirely of the *cis* isomer. Butenediol is very soluble in water, lower alcohols, and acetone, but is almost insoluble in aliphatic or aromatic hydrocarbons.

Butenediol is manufactured by partial hydrogenation of butynediol. Although suitable conditions can lead to either *cis* or *trans* isomers, the commercial product contains almost exclusively *cis*-2-butene-1,4-diol. The *trans* isomer, available at one time by hydrolysis of 1,4-dichloro-2-butene, is unsuitable for the major uses of butenediol involving Diels-Alder reactions. The liquid-phase heat of hydrogenation of butynediol to butenediol is 156 kJ/mol (37.28 kcal/mol).

The original German process used either carbonyl iron or electrolytic iron as hydrogenation catalyst. The fixed-bed reactor was maintained at 50 to 100°C and 20.26 MPa (200 atm) of hydrogen pressure, giving a product containing substantial amounts of both butynediol and butanediol. Newer, more selective processes use more active catalysts at lower pressures. In particular, supported palladium, alone or with promoters, has been found useful.

Purity is determined by gas chromatography. Technical grade butenediol, specified at 95% minimum, is typically 96 to 98% butenediol. The *cis* isomer is the predominant constituent; 2 to 4% is *trans*. Principal impurities are butynediol (specified as 2.0% maximum, typically less than 1%), butanediol, and the 4-hydroxybutyraldehyde acetal of butenediol. Moisture is specified at 0.75% maximum (Karl-Fischer titration). Technical-grade butenediol freezes at about 8°C.

Butenediol is noncorrosive and stable under normal handling conditions. It is a primary skin irritant but not a sensitizer; contact with skin and eyes should be avoided. It is much less toxic than butynediol. The LD₅₀ is 1.25 mL/kg for white rats and 1.5 mL/kg for guinea pigs.

Butenediol is used to manufacture the insecticide Endosulfan, other agricultural chemicals, and pyridoxine (vitamin B₆). Small amounts are consumed as a diol by the polymer industry.

In addition to the usual reactions of primary hydroxyl groups and of double bonds, *cis*-butenediol undergoes a number of cyclization reactions.

The hydroxyl groups can be esterified normally: the interesting diacrylate monomer and the biologically active haloacetates have been prepared in this manner. Reactions with dibasic acids have given polymers capable of being cross-linked or suitable for use as soft segments in polyurethanes. Polycarbamic esters are obtained by treatment with a diisocyanate or via the bischloroformate.

The hydroxyl groups can be alkylated in the usual manner. Hydroxyalkyl ethers may be prepared with alkylene oxides and chloromethyl ethers by reaction with formaldehyde and hydrogen chloride. The terminal chlorides can be easily converted to additional ether groups.

ISO-BUTENE

Iso-butylene is made largely by the catalytic and thermal cracking of hydrocarbons. Other four-carbon (C_4) products formed in the reaction include other butenes, butane, *iso*-butane, and traces of butadiene. The most widely used process is the fluid catalytic cracking of gas oil; other methods are delayed coking and flexicoking.



Iso-butene is used as a raw material in the production of methyl *t*-butyl ether (MTBE, gasoline additive) and butylated hydroxytoluene (an antioxidant) as well as for the production of alkylate for gasoline.

N-BUTENE

n-Butylene (butene-1) is manufactured by the dimerization of ethylene obtained from the catalytic and thermal cracking of hydrocarbons (Fig. 1).



n-Butene thus produced is of suitably high purity to be used for various polymerization and copolymerization processes.

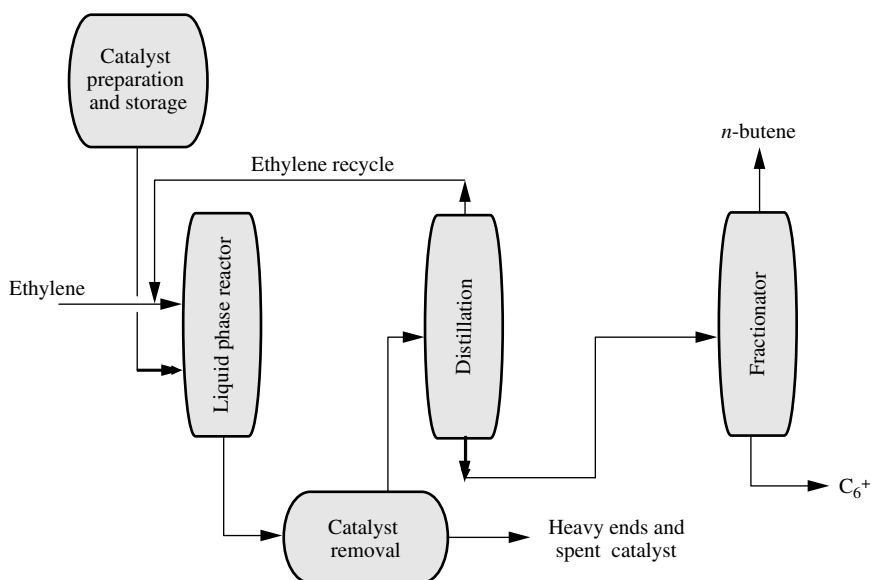


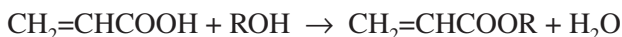
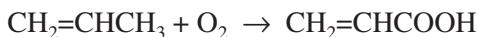
FIGURE 1 Manufacture of *n*-butene by dimerization of ethylene.

BUTYL ACRYLATE

Acrylates are still produced by a modified Reppe process that involves the reaction of acetylene, the appropriate alcohol (in the case of butyl acrylate, butyl alcohol is used), and carbon monoxide in the presence of an acid. The process is continuous, and a small amount of acrylates is made this way.



The most economical method of acrylate production is that of the direct oxidation of propylene to acrylic acid, followed by esterification.



Esters of acrylic acid (acrylates) are used for manufacture of coatings, textiles, fibers, polishes, paper, and leather.

ISO-BUTYL ALCOHOL

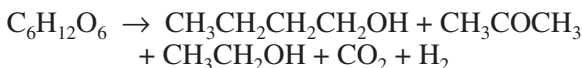
Iso-butyl alcohol (boiling point: 108.1°C, density: 0.8018) is of particular interest in motor fuels because of its high octane rating, which makes it desirable as a gasoline-blending agent.

This alcohol can be reacted with methanol in the presence of a catalyst to produce methyl-*t*-butyl ether. Although it is currently cheaper to make *iso*-butyl alcohol from *iso*-butene (*iso*-butylene), it can be synthesized from syngas with alkali-promoted zinc oxide catalysts at temperatures above 400°C (750°F).

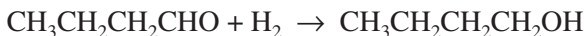
See Iso-Butene, Oxo Reaction, Synthesis Gas.

n-BUTYL ALCOHOL

n-Butanol (*n*-butanol; boiling point: 117.7°C, density: 0.8097, flash point: 28.9°C) can be obtained from carbohydrates (such as molasses and grain) by fermentation. Acetone and ethanol are produced as by-products.



Propylene and synthesis gas give *n*-butyl alcohol; *iso*-butyl alcohol is a by-product.



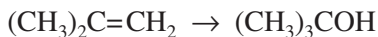
n-Butyl alcohol is used in the manufacture of butyl acrylate and methacrylate, glycol ethers, solvents, butyl acetate, and plasticizers.

See Oxo Reaction, Synthesis Gas.

***t*-BUTYL ALCOHOL**

t-Butyl alcohol (melting point: 25.8°C, boiling point: 82.4°C, density: 0.7866, flash point: 11.1°C) is a low-melting solid that, after melting, exists as a colorless liquid.

t-Butyl alcohol is produced by the hydration of *iso*-butene. The favored tertiary carbocation intermediate limits the possible alcohols produced to only this one.



See Iso-Butene.

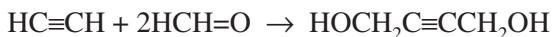
BUTYL VINYL ETHER

See Vinyl Ethers.

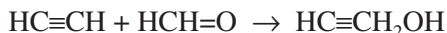
BUTYNEDIOL

Butynediol (2-butyne-1,4-diol; melting point: 58°C, boiling point: 248°C, density: 1.114, flash point: 152°C) is a stable crystalline solid but violent reactions can take place in the presence of certain contaminants, particularly at elevated temperatures. In the presence of certain heavy-metal salts, such as mercuric chloride, dry butynediol can decompose violently. Heating with strongly alkaline materials should be avoided.

Butynediol was first synthesized in 1906 by reaction of acetylene *bis*(magnesium bromide) with paraformaldehyde.



All manufacturers of butynediol use this formaldehyde ethynylation process, and yields of butynediol may be in excess of 90 percent, in addition to 4 to 5% propargyl alcohol.



Most butynediol produced is consumed in the manufacture of butanediol and butenediol. Butynediol is also used for conversion to ethers with ethylene oxide and in the manufacture of brominated derivatives that are useful as flame retardants. Butynediol was formerly used in a wild oat herbicide, Carbyne (Barban), 4-chloro-2-butyne-1-*N*-(3-chlorophenyl)carbamate ($\text{C}_{11}\text{H}_9\text{Cl}_2\text{NO}_2$).

Butynediol undergoes the usual reactions of primary alcohols that contribute to its use as a chemical intermediate. Because of its rigid, linear structure, many reactions forming cyclic products from butanediol or *cis*-butenediol give only polymers with butynediol. Both hydroxyl groups can be esterified normally, and the monoesters are readily prepared as mixtures with diesters and unesterified butynediol, but care must be taken in separating them because the monoesters disproportionate easily.

The hydroxyl groups can be alkylated with the alkylating agents, although a reverse treatment is used to obtain aryl ethers; for example, treatment of butynediol toluene sulfonate or dibromobutyne with a phenol

gives the corresponding ether. Reactions of butynediol with alkylene oxides give ether alcohols.

In the presence of acid catalysts, butynediol and aldehydes or acetals give polymeric acetals, useful intermediates for acetylenic polyurethanes suitable for high-energy solid propellants.



Electrolytic oxidation gives acetylene dicarboxylic acid (2-butyne-dioic acid) in good yields. Butynediol can be hydrogenated partway to butenediol ($\text{HOCH}_2\text{CH}=\text{CHCH}_2\text{OH}$) or completely to butanediol ($\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$).

Addition of halogens proceeds stepwise, sometimes accompanied by oxidation. Iodine forms 2,3-diiodo-2-butene-1,4-diol and, depending on conditions, bromine gives 2,3-dibromo-2-butene-1, 4-diol, 2,2,3,3-tetrabromobutane-1, 4-diol, mucobromic acid, or 2-hydroxy-3,3,4,4-tetrabromotetrahydrofuran. Addition of chlorine is attended by more oxidation, which can be lessened by esterification of the hydroxyl groups.

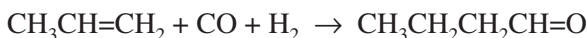
Butynediol is more difficult to polymerize than propargyl alcohol, but it cyclotrimerizes to hexamethylolbenzene (benzenehexamethanol) with a nickel carbonyl-phosphine catalyst or a rhodium chloride-arsine catalyst.

***ISO*-BUTYRALDEHYDE**

See n-Butyraldehyde.

***n*-BUTYRALDEHYDE**

n-butyraldehyde (boiling point: 74.8°C, density: 0.8016) is made by the reaction of propylene (propene-1, CH₃CH=CH₂), carbon monoxide, and hydrogen (synthesis gas) at 130 to 175°C and 3675 psi (25.3 MPa) over a rhodium carbonyl, cobalt carbonyl, or ruthenium carbonyl catalyst (Fig. 1).

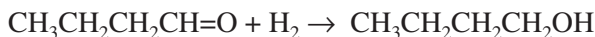


The reaction is referred to as the *oxo process*, and a second product of the reaction is *iso*-butyraldehyde (boiling point: 64.1°C, density: 0.7891).



The ratio of the *normal* to the *iso* product is approximately 4:1. Other catalysts produce different *normal*-to-*iso* product ratios under different conditions. For example, a rhodium catalyst can be used at lower temperatures and pressures and gives a *normal*-to-*iso* product ratio of approximately 16:1.

Butyraldehyde is used for the production of *n*-butyl alcohol.



See Oxo Reaction, Synthesis Gas.

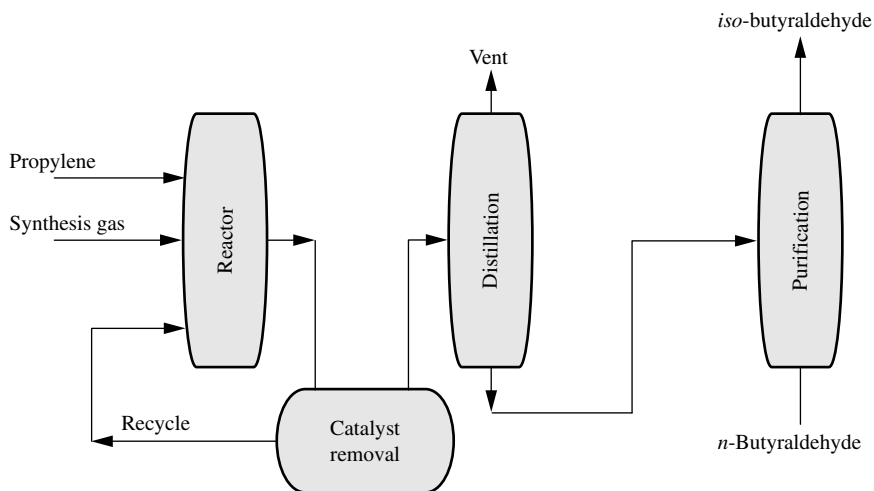


FIGURE 1 Manufacture of butyraldehyde from propylene and synthesis gas.

BUTYROLACTONE

γ -butyrolactone (dihydro-2,3H-furanone, boiling point: 204°C, density: 1.129, flash point: 98°C) was first synthesized in 1884 by an internal esterification of 4-hydroxybutyric acid. The principal commercial source of this material is dehydrogenation of butanediol. The manufacture of butyrolactone by hydrogenation of maleic anhydride is also a viable route.

Butyrolactone is completely miscible with water and most organic solvents. It is only slightly soluble in aliphatic hydrocarbons. It is a good solvent for many gases, for most organic compounds, and for a wide variety of polymers.

Butyrolactone is used to produce *N*-methyl-2-pyrrolidinone and 2-pyrrolidinone, by reaction with methylamine or ammonia, respectively. Considerable amounts are used as a solvent for agricultural chemicals and polymers, in dyeing and printing, and as an intermediate for various chemical syntheses.

Butyrolactone undergoes the reactions typical of γ -lactones. Particularly characteristic are ring openings and reactions in which ring oxygen is replaced by another heteroatom. There is also marked reactivity of the hydrogen atoms alpha to the carbonyl group.

With acid catalysts, butyrolactone reacts with alcohols rapidly even at room temperature to produce esters of 4-hydroxybutyric acid. The esters can be separated by a quick flash distillation at high vacuum.

Butyrolactone reacts rapidly and reversibly with ammonia or an amine forming 4-hydroxybutyramides, which dissociate to the starting materials when heated. At high temperatures and pressures, the hydroxybutyramides slowly and irreversibly dehydrate to pyrrolidinones; this dehydration is accelerated by use of a copper-exchanged Y-zeolite or magnesium silicate.