
Part 2

MANUFACTURE OF CHEMICALS

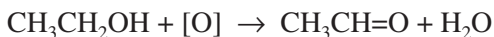
ACETALDEHYDE

Acetaldehyde (ethanal, $\text{CH}_3\text{CH}=\text{O}$, melting point -123.5°C , boiling point: 20.1°C , density: 0.7780, flash point: -38°C , ignition temperature: 165°C) is a colorless, odorous liquid.

Acetaldehyde has a pungent, suffocating odor that is somewhat fruity and quite pleasant in dilute concentrations. Acetaldehyde is miscible in all proportions with water and most common organic solvents, e.g., acetone, benzene, ethyl alcohol, ether, gasoline, toluene, xylenes, turpentine, and acetic acid.

Because of its versatile chemical reactivity, acetaldehyde is widely used as a commencing material in organic syntheses, including the production of resins, dyestuffs, and explosives. It is also used as a reducing agent, preservative, and medium for silvering mirrors. In resin manufacture, paraldehyde $[(\text{CH}_3\text{CHO})_3]$ sometimes is preferred because of its higher boiling and flash points.

Acetaldehyde was first prepared by Scheele in 1774, by the action of manganese dioxide (MnO_2) and sulfuric acid (H_2SO_4) on ethyl alcohol (ethanol, $\text{CH}_3\text{CH}_2\text{OH}$).



Commercially, passing alcohol vapors and preheated air over a silver catalyst at 480°C carries out the oxidation. With a multitubular reactor, conversions of 74 to 82 percent per pass can be obtained while generating steam to be used elsewhere in the process.

The formation of acetaldehyde by the addition of water to acetylene was observed by Kutscherow in 1881.



In this hydration process, high-purity acetylene under a pressure of 15 psi (103.4 kPa) is passed into a vertical reactor containing a mercury catalyst dissolved in 18 to 25% sulfuric acid at 70 to 90°C . Fresh catalyst is fed to the reactor periodically; the catalyst may be added in the mercurous (Hg^+)

form, but the catalytic species has been shown to be a mercuric ion complex. The excess acetylene sweeps out the dissolved acetaldehyde, which is condensed by water and refrigerated brine and then scrubbed with water; this crude acetaldehyde is purified by distillation; the unreacted acetylene is recycled. The catalytic mercuric ion is reduced to catalytically inactive mercurous sulfate (Hg_2SO_4) and metallic mercury. Sludge, consisting of reduced catalyst and tars, is drained from the reactor at intervals and resulfated. The rate of catalyst depletion can be reduced by adding ferric or other suitable ions to the reaction solution. These ions reoxidize the mercurous ion to the mercuric ion; consequently, the quantity of sludge that must be recovered is reduced.

In one variation of the process, acetylene is completely hydrated with water in a single operation at 68 to 73°C using the mercuric-iron salt catalyst. The acetaldehyde is partially removed by vacuum distillation and the mother liquor recycled to the reactor. The aldehyde vapors are cooled to about 35°C, compressed to 37 psi (253 kPa), and condensed. It is claimed that this combination of vacuum and pressure operations substantially reduces heating and refrigeration costs.

The commercial process of choice for acetaldehyde production is the direct oxidation of ethylene.



There are two variations for this commercial production route: the two-stage process and the one-stage process.

In the one-stage process (Fig. 1), ethylene, oxygen, and recycle gas are directed to a vertical reactor for contact with the catalyst solution under

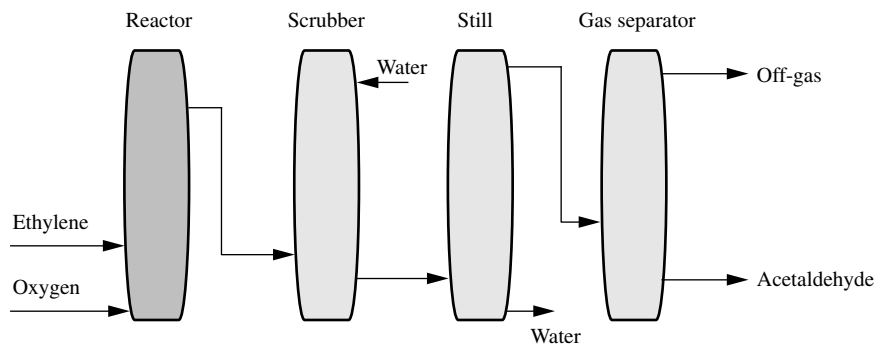


FIGURE 1 Acetaldehyde manufacture by the single-stage process.

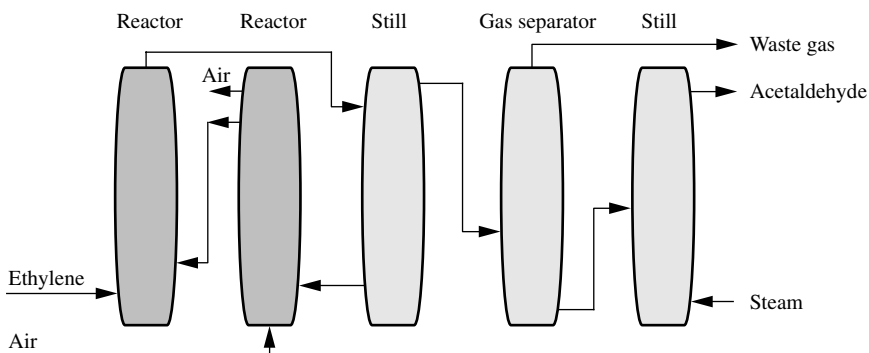


FIGURE 2 Acetaldehyde manufacture by the two-stage process.

slight pressure. The water evaporated during the reaction absorbs the heat evolved, and makeup water is fed as necessary to maintain the desired catalyst concentration. The gases are water scrubbed, and the resulting acetaldehyde solution is fed to a distillation column. The tail gas from the scrubber is recycled to the reactor. Inert materials are eliminated from the recycle gas in a bleed stream that flows to an auxiliary reactor for additional ethylene conversion.

In the two-stage process (Fig. 2), ethylene is almost completely oxidized by air to acetaldehyde in one pass in a tubular plug-flow reactor made of titanium. The reaction is conducted at 125 to 130°C and 150 psi (1.03 MPa) with the palladium and cupric chloride catalysts. Acetaldehyde produced in the first reactor is removed from the reaction loop by adiabatic flashing in a tower. The flash step also removes the heat of reaction. The catalyst solution is recycled from the flash-tower base to the second stage (or oxidation reactor), where the cuprous salt is oxidized to the cupric state with air. The high-pressure off-gas from the oxidation reactor, mostly nitrogen, is separated from the liquid catalyst solution and scrubbed to remove acetaldehyde before venting. A small portion of the catalyst stream is heated in the catalyst regenerator to destroy any undesirable copper oxalate. The flasher overhead is fed to a distillation system where water is removed for recycle to the reactor system and organic impurities, including chlorinated aldehydes, are separated from the purified acetaldehyde product. Synthesis techniques purported to reduce the quantity of chlorinated by-products generated have been patented.

Acetaldehyde was first used extensively during World War I as a starting material for making acetone (CH_3COCH_3) from acetic acid

($\text{CH}_3\text{CO}_2\text{H}$) and is currently an important intermediate in the production of acetic acid, acetic anhydride ($\text{CH}_3\text{CO-O-OCCH}_3$), ethyl acetate ($\text{CH}_3\text{CO-OC}_2\text{H}_5$), peracetic acid ($\text{CH}_3\text{CO-O-OH}$), and a variety of other chemicals such as pentaerythritol, chloral, glyoxal, alkylamines, and pyridines.

In aqueous solutions, acetaldehyde exists in equilibrium with the acetaldehyde hydrate [$\text{CH}_3\text{CH}(\text{OH})_2$]. The enol form, vinyl alcohol ($\text{CH}_2=\text{CHOH}$) exists in equilibrium with acetaldehyde to the extent of 0.003% (1 molecule in approximately 30,000) and can be acetylated with ketene ($\text{CH}_2=\text{C=O}$) to form vinyl acetate ($\text{CH}_2=\text{CHOCOCH}_3$).

ACETAL RESINS

Acetal resins are those homopolymers (melting point: ca. 175°C, density: ca. 1.41) and copolymers (melting point: ca. 165°C, density: ca. 1.42) where the backbone or main structural chain is completely or essentially composed of repeating oxymethylene units $(-\text{CH}_2\text{O}-)_n$. The polymers are derived chiefly from formaldehyde (methanal, $\text{CH}_2=\text{O}$), either directly or through its cyclic trimer, trioxane or 1,3,5-trioxacyclohexane.

Formaldehyde polymerizes by both anionic and cationic mechanisms. Strong acids are needed to initiate cationic polymerization and anionic polymerization is initiated by relatively weak bases (e.g., pyridine). Boron trifluoride (BF_3) or other Lewis acids are used to promote polymerization where trioxane is the raw material.

In the process, anhydrous formaldehyde is continuously fed to a reactor containing well-agitated inert solvent, especially a hydrocarbon, in which monomer is sparingly soluble. Initiator, especially amine, and chain-transfer agent are also fed to the reactor. The reaction is quite exothermic and polymerization temperature is maintained below 75°C (typically near 40°C) by evaporation of the solvent. The product polymer is not soluble in the solvent and precipitates early in the reaction.

The polymer is separated from the polymerization slurry and slurried with acetic anhydride and sodium acetate catalyst. Acetylation of polymer end groups is carried out in a series of stirred tank reactors at temperatures up to 140°C. End-capped polymer is separated by filtration and washed at least twice, once with acetone and then with water.

The copolymerization of trioxane with cyclic ethers or formals is accomplished with cationic initiators such as boron trifluoride dibutyl etherate. Polymerization by ring opening of the six-membered ring to form high molecular weight polymer does not commence immediately upon mixing monomer and initiator. Usually, an induction period is observed during which an equilibrium concentration of formaldehyde is produced.

When the equilibrium formaldehyde concentration is reached, the polymer begins to precipitate and further polymerization takes place in trioxane

solution, and more comonomer is exhausted at relatively low conversion, but a random copolymer is nevertheless obtained.

In the process, molten trioxane, initiator, and comonomer are fed to the reactor; a chain-transfer agent is included if desired. Polymerization proceeds in bulk with precipitation of polymer, and the reactor must supply enough shearing to continually break up the polymer bed, reduce particle size, and provide good heat transfer. Raw copolymer is obtained as fine crumb or flake containing imbibed formaldehyde and trioxane that are substantially removed in subsequent treatments which may be combined with removal of unstable end groups.

Acetal copolymer may be end capped in a process completely analogous to that used for homopolymer. However, the presence of comonomer units (e.g., $\text{-O-CH}_2\text{-CH}_2\text{-O-}$) in the backbone and the relative instability to base of hemiacetal end groups allow for another convenient route to a polymer with stable end groups. The hemiacetal end groups may be subjected to base-catalyzed (especially amine) hydrolysis in the melt or in solution or suspension, and the chain segments between the end group and the nearest comonomer unit deliberately depolymerized until the depropagating chain encounters the comonomer unit. If ethylene oxide or dioxolane is used as comonomer, a stable hydroxyethyl ether end group results ($\text{-O-CH}_2\text{CH}_2\text{-OH}$). Some formate end groups, which are intermediate in thermal stability between hemiacetal and ether end groups, may also be removed by this process.

The product from the melt or suspension treatment is obtained directly as crumb or powder. The polymer recovered from solution treatment is obtained by precipitative cooling or spray drying. The polymer with now stable end groups may be washed and dried to remove impurities, especially acids or their precursors, prior to finishing operations.

The average molecular weight MW of acetal copolymers may be estimated from their melt index (MI, expressed in g/10 min):

$$\text{MI} = 3.3 \times 10^{18} \text{MW}^{-3.55}$$

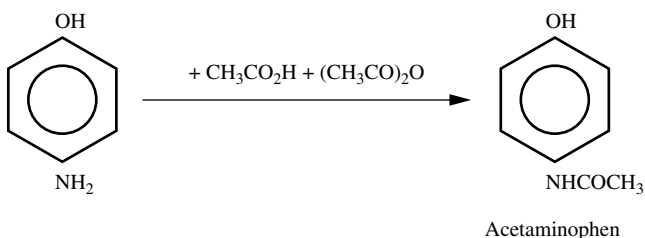
Stiffness, resistance to deformation under constant applied load (creep resistance), resistance to damage by cyclical loading (fatigue resistance), and excellent lubricity are mechanical properties for which acetal resins are perhaps best known and which have contributed significantly to their excellent commercial success. General-purpose acetal resins are substantially stiffer than general-purpose polyamides (nylon-6 or -6,6 types) when the latter have reached equilibrium water content.

Acetal resins are generally stable in mildly alkaline environments. However, bases can catalyze hydrolysis of ester end groups, resulting in a less thermally stable polymer.

Acetals provide excellent resistance to most organic compounds except when exposed for long periods at elevated temperatures. The resins have limited resistance to strong acids and oxidizing agents. The copolymers and some of the homopolymers are resistant to the action of weak bases. Normally, where resistance to burning, weathering, and radiation are required, acetals are not specified. The resins are used for cams, gears, bearings, springs, sprockets, and other mechanical parts, as well as for electrical parts, housings, and hardware.

ACETAMINOPHEN

Acetaminophen, sold under the trade name Tylenol, is a widely used analgesic and antipyretic that is an over-the-counter drug. Combined with codeine it is one of the top five prescription drugs. Acetaminophen is prepared by treating *p*-aminophenol with a mixture of glacial acetic acid and acetic anhydride.



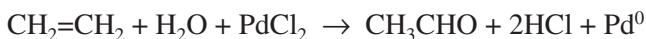
ACETIC ACID

Acetic acid (ethanoic acid, vinegar acid, $\text{CH}_3\text{CO}_2\text{H}$, melting point 16.6°C , boiling point: 117.9°C , density: 1.0490, flash point: 43°C , ignition temperature 465°C) is a colorless, pungent liquid that is miscible with water, alcohol, and ether in all proportions.

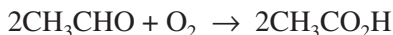
Acetic acid is available commercially in several concentrations: (1) glacial acetic is approximately 99.7% glacial acetic acid with water the principal impurity, (2) reagent grade acetic acid generally contains 36% acetic acid by weight, and (3) commercial aqueous solutions are usually 28, 56, 70, 80, 85, and 90% acetic acid.

Acetic acid is the active ingredient in vinegar, in which the content ranges from 4 to 5% acetic acid. Acetic acid is classified as a weak, monobasic acid ($-\text{CO}_2\text{H}$) but the three hydrogen atoms linked to the carbon atom (CH_3) are not replaceable by metals.

Acetic acid is manufactured by three processes: acetaldehyde oxidation, *n*-butane oxidation, and methanol carbonylation. Ethylene is the exclusive organic raw material for making acetaldehyde, 70 percent of which is further oxidized to acetic acid or acetic anhydride. The single-stage (Wacker) process for making acetaldehyde involves cupric chloride and a small amount of palladium chloride in aqueous solution as a catalyst.



The yield is 95 percent and further oxidation of the acetaldehyde produces acetic acid (Fig. 1).



A manganese or cobalt acetate catalyst is used with air as the oxidizing agent in the temperature and pressure ranges of 55 to 80°C and 15 to 75 psi; the yield is 95 percent.

The second manufacturing method for acetic acid utilizes butane from the C_4 petroleum stream rather than ethylene. A variety of products is formed but conditions can be controlled to allow a large percentage of acetic acid to be formed. Cobalt, manganese, or chromium acetates are cat-

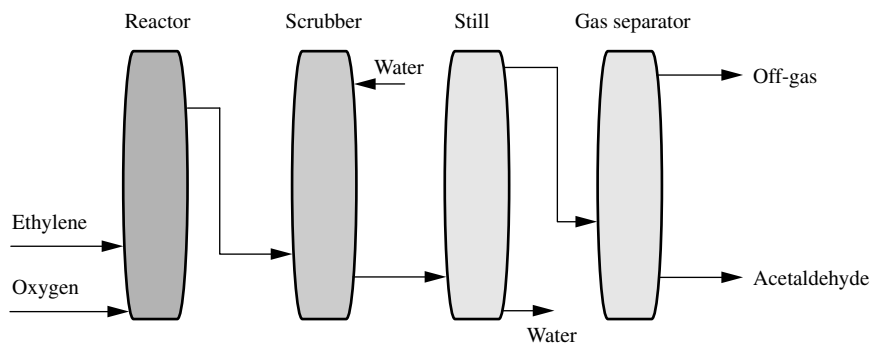
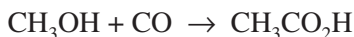


FIGURE 1 Acetaldehyde manufacture by the single-stage (Wacker) process.

alysts with temperatures of 50 to -250°C and a pressure of 800 psi.



The third and preferred method of acetic acid manufacture is the carbonylation of methanol, involving reaction of methanol and carbon monoxide (both derived from methane) with rhodium and iodine as catalysts at 175°C and 1 atm (Fig. 2).



The yield of acetic acid is 99 percent based on methanol and 90 percent based on carbon monoxide.

Acetic acid is used for the manufacture of methyl acetate (Fig. 3) and acetic anhydride (Fig. 4), vinyl acetate, ethyl acetate, terephthalic acid, cellulose acetate, and a variety of acetic esters.

Vinyl acetate is used mainly as a fiber in clothing. Ethyl acetate is a com-

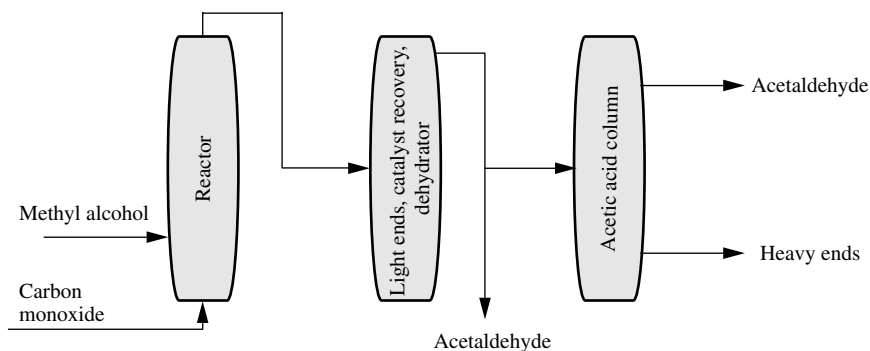


FIGURE 2 Acetaldehyde manufacture by carbonylation of methyl alcohol (methanol).

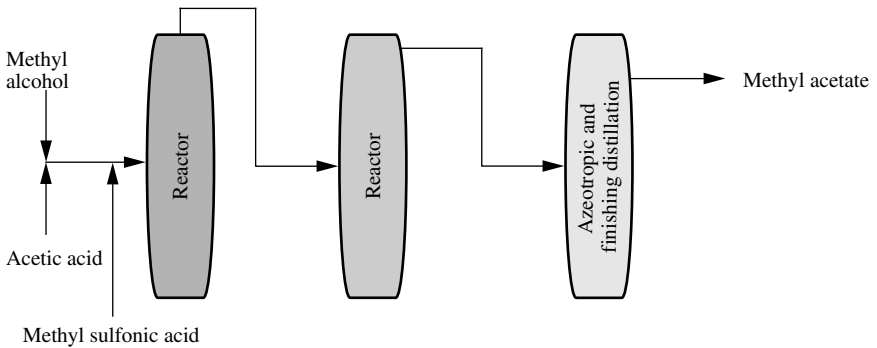


FIGURE 3 Methyl acetate manufacture from methyl alcohol (methanol).

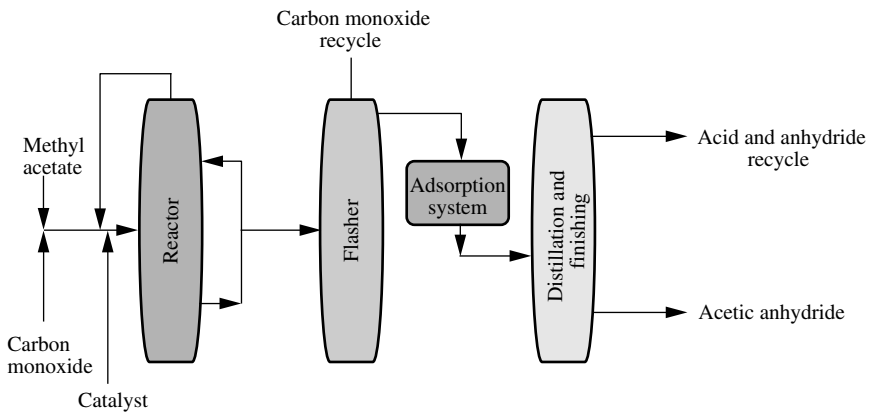
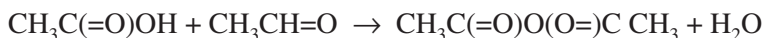
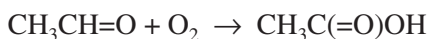


FIGURE 4 Acetic anhydride manufacture by carbonylation of from methyl acetate.

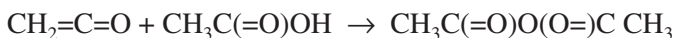
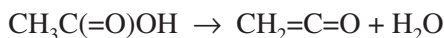
mon organic solvent. Acetic acid is used in the manufacture of terephthalic acid, which is a monomer for the synthesis of poly (ethylene terephthalate), the *polyester* of the textile industry.

ACETIC ANHYDRIDE

Acetic anhydride (boiling point: 139.5, density: 1.0820) may be produced by three different methods. The first procedure involves the in situ production from acetaldehyde of peracetic acid, which in turn reacts with more acetaldehyde to yield the anhydride.



In the preferred process, acetic acid (or acetone) is pyrolyzed to ketene, which reacts with acetic acid to form acetic anhydride.



Another process to make acetic anhydride involves carbon monoxide insertion into methyl acetate (Fig. 1).

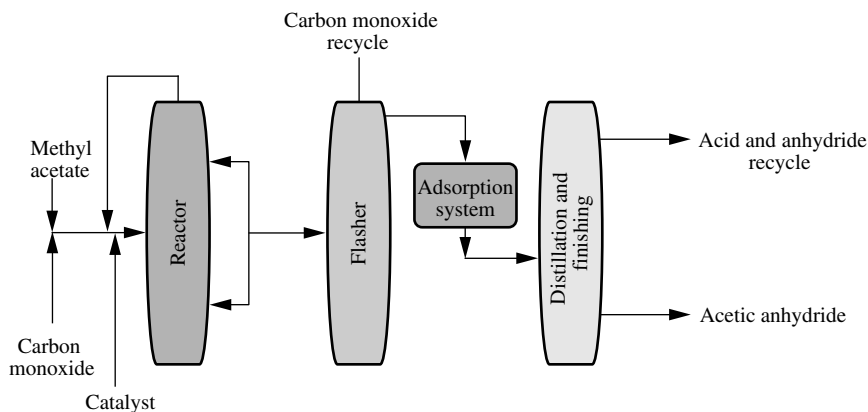


FIGURE 1 Acetic anhydride manufacture by carbonylation of methyl acetate



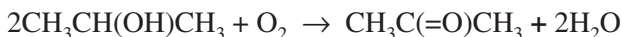
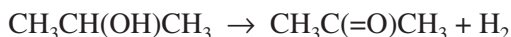
Approximately 80 percent of acetic anhydride is used as a raw material in the manufacture of cellulose acetate.

ACETONE

Acetone (dimethyl ketone, 2-propanone, CH_3COCH_3 , melting point: -94.6°C , boiling point: 56.3°C , density: 0.783) is the simplest ketone and is a colorless liquid that is miscible in all proportions with water, alcohol, or ether.

There are two major processes for the production of acetone (2-propanone). The feedstock for these is either *iso*-propyl alcohol [$(\text{CH}_3)_2\text{CHOH}$] or cumene [*iso*-propyl benzene, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$]. In the last few years there has been a steady trend away from *iso*-propyl alcohol and toward cumene, but *iso*-propyl alcohol should continue as a precursor since manufacture of acetone from only cumene would require a balancing of the market with the coproduct phenol from this process.

Acetone is made from *iso*-propyl alcohol by either dehydrogenation (preferred) or air oxidation. These are catalytic processes at 500°C and 40 to 50 psi. The acetone is purified by distillation, boiling point 56°C and the conversion per pass is 70 to 85 percent, with the overall yield being in excess of 90 percent.



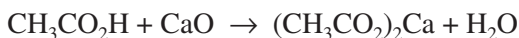
Cumene is also used as a feedstock for the production of acetone. In this process, cumene first is oxidized to cumene hydroperoxide followed by the decomposition of the cumene hydroperoxide into acetone and phenol.

The hydroperoxide is made by reaction of cumene with oxygen at 110 to 115°C until 20 to 25 percent of the hydroperoxide is formed. Concentration of the hydroperoxide to 80% is followed by catalyzed rearrangement under moderate pressure at 70 to 100°C . During the reaction, the palladium chloride (PdCl_2) catalyst is reduced to elemental palladium to produce hydrogen chloride that catalyzes the rearrangement, and reoxidation of the palladium is brought about by use of cupric chloride (CuCl_2) that is converted to cuprous chloride (CuCl). The cuprous chloride is reoxidized during the catalyst regeneration cycle.

The overall yield is 90 to 92 percent. By-products are acetophenone, 2-phenylpropan-2-ol, and α -methylstyrene. Acetone is distilled first at boiling point 56°C.

Vacuum distillation recovers the unreacted cumene and yields α -methylstyrene, which can be hydrogenated back to cumene and recycled. Further distillation separates phenol, boiling point 181°C, and acetophenone, boiling point 202°C.

In older industrial processes, acetone is prepared (1) by passing the vapors of acetic acid over heated lime. Calcium acetate is produced in the first step followed by a breakdown of the acetate into acetone and calcium carbonate:



and (2) by fermentation of starches, such as maize, which produce acetone along with butyl alcohol.

Acetone is a very important solvent and is widely used in the manufacture of plastics and lacquers. For storage purposes, acetone may be used as a solvent for acetylene. Acetone is the starting ingredient or intermediate for numerous organic syntheses. Closely related, industrially important compounds are diacetone alcohol [$\text{CH}_3\text{COCH}_2\text{COH}(\text{CH}_3)_2$], which is used as a solvent for cellulose acetate and nitrocellulose, as well as for various resins and gums, and as a thinner for lacquers and inking materials.

Acetone is used for the production of methyl methacrylate, solvents, bisphenol A, aldol chemicals, and pharmaceuticals.

Methyl methacrylate is manufactured and then polymerized to poly(methyl methacrylate), an important plastic known for its clarity and used as a glass substitute.

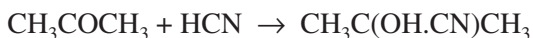
Aldol chemicals refer to a variety of substances desired from acetone involving an aldol condensation in a portion of their synthesis. The most important of these chemicals is methyl *iso*-butyl ketone (MIBK), a common solvent for many plastics, pesticides, adhesives, and pharmaceuticals.

Bisphenol A is manufactured by a reaction between phenol and acetone, the two products from the cumene hydroperoxide rearrangement. Bisphenol A is an important diol monomer used in the synthesis of polycarbonates and epoxy resins.

A product known as synthetic methyl acetone is prepared by mixing acetone (50%), methyl acetate (30%), and methyl alcohol (20%) and is used widely for coagulating latex and in paint removers and lacquers.

ACETONE CYANOHYDRIN

Acetone cyanohydrin is manufactured by the direct reaction of hydrogen cyanide with acetone catalyzed by base, generally in a continuous process.



Acetone cyanohydrin is an intermediate in the manufacture of methyl methacrylate.

ACETOPHENETIDINE

Acetophenetidine (phenacetin), an analgesic and antipyretic, is the ethyl ether of acetaminophen and is prepared from *p*-ethoxyaniline.

ACETYLENE

Acetylene ($\text{CH}\equiv\text{CH}$, ethyne or ethine, melting point -81.5°C , boiling point -84°C) is an extremely reactive hydrocarbon that is moderately soluble in water or alcohol and is markedly soluble in acetone (300 volumes of acetylene dissolve in 1 volume of acetone at 176 psi, 1216 kPa).

Acetylene burns when ignited in air with a luminous sooty flame, requiring a specially devised burner for illumination purposes. An explosive mixture is formed with air over a wide range (about 3 to 80% acetylene), but safe handling is improved when the gas is dissolved in acetone.

Acetylene is still manufactured by the action of calcium carbide, a product of the electric furnace.



and there are two principal methods for generating acetylene from calcium carbide.

The batch carbide-to-water, or wet, method takes place in a cylindrical water shell surmounted by a housing with hopper and feed facilities. The carbide is fed to the water at a measured rate until exhausted. The calcium hydroxide is discharged in the form of a lime slurry containing about 90% by weight water.

For large-scale industrial applications, dry generation, a continuous process featuring automatic feed, is used, in which 1 kg of water is used, per kilogram of carbide. The heat of the reaction is largely dissipated by water vaporization, leaving the by-product lime in a dry state, and part of this can be recycled to the carbide furnaces. Continuous agitation is necessary to prevent overheating, since the temperature should be kept below 150°C and the pressure lower than 204 kPa.

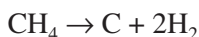
The newest methods of manufacturing acetylene are through the *pyrolysis*, or *cracking*, of *natural gas* or liquid hydrocarbon feeds. The processes of most interest include partial oxidation, using oxygen, thermal cracking, and an electric arc to supply both the high temperature and the energy. Acetylene is produced from the pyrolysis of naphtha in a two-stage crack-

ing process in which both acetylene and ethylene are end products. Varying the naphtha feed rate can change the ratio of the two products. Acetylene also has been produced by a submerged-flame process from crude oil.

At 1327°C and higher, acetylene is more stable than other hydrocarbons but decomposes into its elements. Hence conversion, or splitting, time must be incredibly short (milliseconds). The amount of energy needed is very large and in the region of the favorable free energy.



However, the decomposition of methane (CH_4) into its elements starts at 578°C, hence competes with its degradation to acetylene.



To lessen this degradation after raising the methane (or other hydrocarbon) to a high temperature of about 1500°C for milliseconds, the reaction mass must be water quenched almost instantaneously.

The partial combustion (partial oxidation) of natural gas (Fig. 1) is probably the most widely used method of producing acetylene. The overall reaction of the methane (combustion and splitting) is 90 to 95 percent whereas the oxygen is 100 percent converted. The residence time is 0.001 to 0.01 seconds. The acetylene and gases are cooled rapidly by quench oil or water sprays to 38°C and have the following typical composition (percent by volume: acetylene, 8 to 10; hydrogen, 50 to 60; methane, 5; carbon monoxide, 20 to 25; and carbon dioxide, <5. The soot is removed in a carbon filter and the clean gases are compressed to 165 psi (1.14 MPa).

Acetylene is removed in a column (packed) by a selective solvent such as dimethylformamide. Carbon dioxide is flashed and stripped overhead out

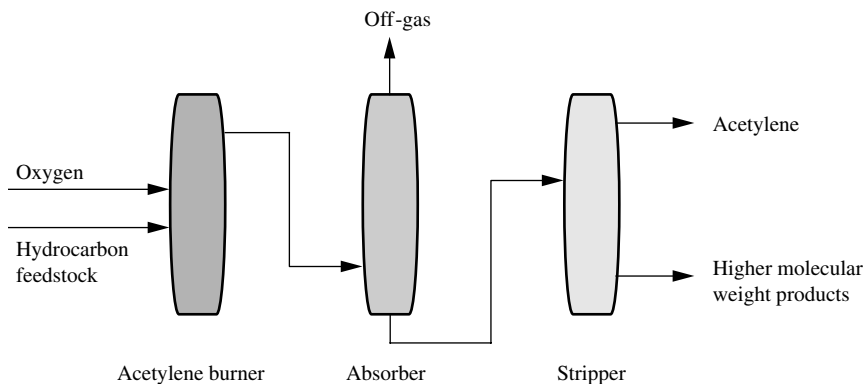


FIGURE 1 Acetylene manufacture by partial oxidation of hydrocarbons.

of the rich solvent in a column (packed), where the acetylene is fractionated out, giving a >99% by volume pure product with a 30 to 40 percent yield from the carbon in the natural gas.

Acetylene is principally used as a chemical intermediate. Acetylene reacts:

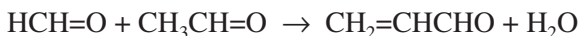
1. With chlorine, to form acetylene tetrachloride ($\text{CHCl}_2\text{CHCl}_2$) or acetylene dichloride ($\text{CHCl}=\text{CHCl}$)
2. With bromine, to form acetylene tetrabromide ($\text{CHBr}_2\text{CHBr}_2$) or acetylene dibromide ($\text{CHBr}=\text{CHBr}$)
3. With hydrogen chloride (hydrogen bromide or hydrogen iodide), to form ethylene monochloride ($\text{CH}_2=\text{CHCl}$) (monobromide, monoiodide), and 1,1-dichloroethane (ethylidene chloride (CH_3CHCl_2) (dibromide, diiodide))
4. With water in the presence of a catalyst such as mercuric sulfate (HgSO_4) to form acetaldehyde (CH_3CHO)
5. With hydrogen, in the presence of a catalyst such as finely divided nickel (Ni) heated, to form ethylene ($\text{CH}_2=\text{CH}_2$) or ethane (CH_3CH_3)
6. With metals, such as copper (Cu) nickel (Ni), when moist, also lead (Pb) or zinc (Zn), when moist and unpurified; tin (Sn) is not attacked but sodium yields, upon heating, sodium acetylide ($\text{CH}\equiv\text{CNa}$) and disodium acetylide ($\text{NaC}\equiv\text{CNa}$)
7. With ammoniocuprous (or silver) salt solution, to form cuprous (or silver) acetylide ($\text{HC}\equiv\text{CCu}$ or $\text{HC}\equiv\text{CAg}$) which is explosive when dry and yields acetylene by treatment with acid
8. With mercuric chloride (HgCl_2) solution, to form trichloromercuric acetaldehyde [$\text{C}(\text{HgCl})_3\cdot\text{CHO}$], which yields acetaldehyde (CH_3CHO) plus mercuric chloride when treated with hydrogen chloride

ACROLEIN

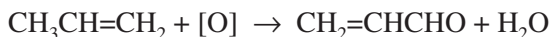
Acrolein (2-propenal, $\text{CH}_2=\text{CHCHO}$, freezing point: -87°C , boiling point: 52.7°C , density: 0.8427, flash point: -18°C) is the simplest unsaturated aldehyde. The primary characteristic of acrolein is its high reactivity due to conjugation of the carbonyl group with a vinyl group.

Acrolein is a highly toxic material with extreme lachrymatory properties. At room temperature acrolein is a liquid with volatility and flammability somewhat similar to those of acetone, but, unlike acetone, its solubility in water is limited. Commercially, acrolein is always stored with hydroquinone and acetic acid as inhibitors.

The first commercial process for manufacturing acrolein was based on the vaporphase condensation of acetaldehyde and formaldehyde.



Catalyst developments led to a vapor-phase processes for the production of acrolein in which propylene was the starting material.



The catalytic vapor-phase oxidation of propylene (Fig. 1) is generally carried out in a fixed-bed multitube reactor at near atmospheric pressures and elevated temperatures (ca 350°C); molten salt is used for temperature control. Air is commonly used as the oxygen source and steam is added to suppress the formation of flammable gas mixtures. Operation can be single pass or a recycle stream may be employed.

The reactor effluent gases are cooled to condense and separate the acrolein from unreacted propylene, oxygen, and other low-boiling components (predominantly nitrogen). This is commonly accomplished in two absorption steps where (1) aqueous acrylic acid ($\text{CH}_2=\text{CHCO}_2\text{H}$) is condensed from the reaction effluent and absorbed in a water-based stream and (2) acrolein is condensed and absorbed in water to separate it from the propylene, nitrogen, oxygen, and carbon oxides. Acrylic acid may be recovered from the aqueous product stream if desired. Subsequent distilla-

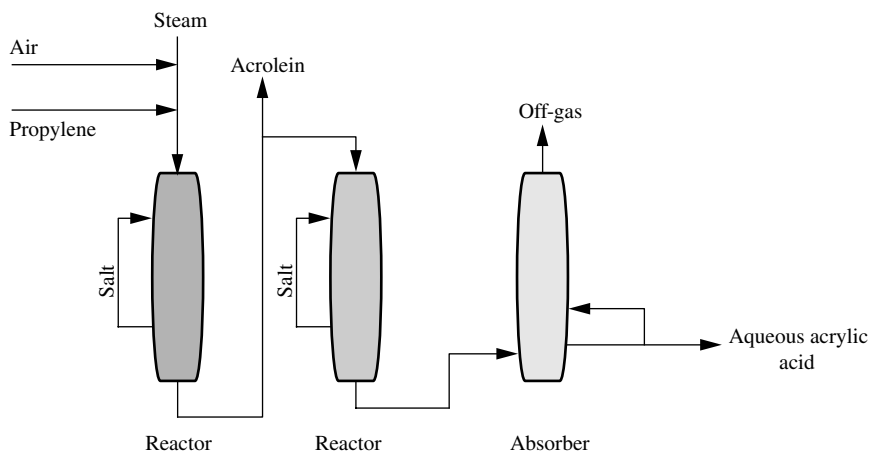


FIGURE 1 Manufacture of acrolein and acrylic acid by oxidation of propylene.

tion refining steps separate water and acetaldehyde (CH_3CHO) from the crude acrolein. In another distillation column, refined acrolein is recovered as an azeotrope with water.

The principal side reactions produce acrylic acid, acetaldehyde, acetic acid, carbon monoxide, and carbon dioxide, and a variety of other aldehydes and acids are also formed in small amounts.

ACRYLIC ACID

Acrylic acid ($\text{CH}_2=\text{CHCO}_2\text{H}$, melting point: 13.5°C , boiling point: 141°C , density: 1.045, flash point: 68°C) and acrylates were once prepared by reaction of acetylene and carbon monoxide with water or an alcohol, with nickel carbonyl as catalyst.



In the presence of such catalysts as a solution of cuprous and ammonium chlorides, hydrogen cyanide adds to acetylene to give acrylonitrile ($\text{CH}_2=\text{CHCN}$). However, this process has been replaced by processes involving ammoxidation of propylene. Similarly, the process for the manufacture of acrylic acid has been superseded by processes involving oxidation of propylene (Fig. 1) although, for some countries, acetylene may still be used in acrylate manufacture.

Thus, acrylic acid is made by the oxidation of propylene to acrolein and further oxidation to acrylic acid.

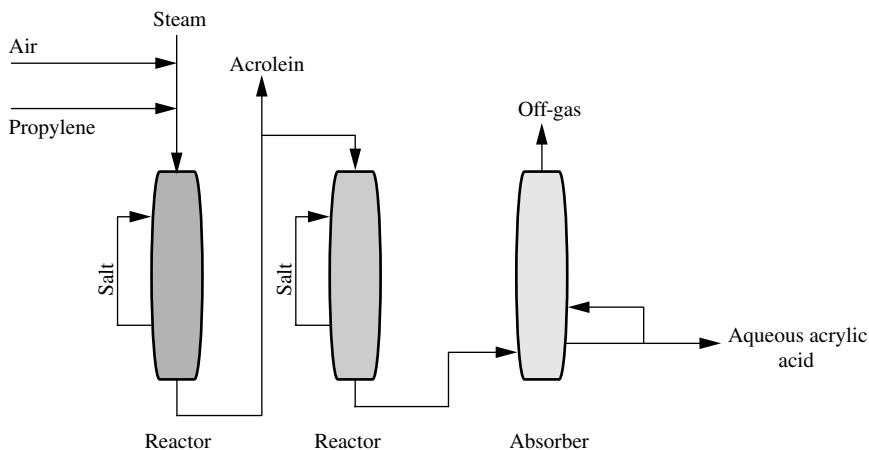
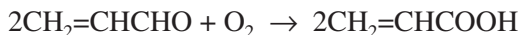
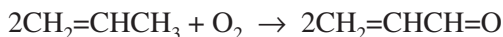
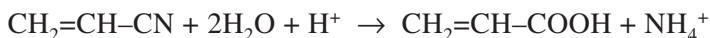


FIGURE 1 Manufacture of acrylic acid by the oxidation of propylene.



Another method of acrylic acid production is by the hydrolysis of acrylonitrile:



Acrylic acid and its salts are raw materials for an important range of esters, including methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate. The acid and its esters are used in polyacrylic acid and salts (including superabsorbent polymers, detergents, water treatment chemicals, and dispersants), surface coatings, adhesives and sealants, textiles, and plastic modifiers.

ACRYLIC RESINS

The methyl, ethyl, and butyl esters of acrylic and methacrylic acids are polymerized under the influence of heat, light, and peroxides. The polymerization reaction is exothermic and may be carried out in bulk for castings, or by emulsion, or in solution. The molecular weight decreases as the temperature and catalyst concentration are increased. The polymers are noncrystalline and thus very clear. Such resins are widely used because of their clarity, brilliance, ease of forming, and light weight. They have excellent optical properties and are used for camera, instrument, and spectacle lenses.

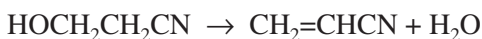
Because of their excellent dielectric strength they are often used for high-voltage line spacers and cable clamps. Emulsions are widely applied as textile finishes and paints.

ACRYLONITRILE

Acrylonitrile (2-propenenitrile, propene nitrile, vinyl cyanide, $\text{CH}_2=\text{CHCN}$; freezing point: -83.5°C , boiling point: 77.3°C , density: 0.806) used to be manufactured completely from acetylene by reaction with hydrogen cyanide.



There was also a process using ethylene oxide as the starting material through addition of hydrogen cyanide (HCN) and elimination of water.



The presently used process focuses on the ammoxidation (ammonoxidation or oxyamination) of propylene that involves reaction of propylene, ammonia, and oxygen at 400 to 450°C and 7 to 29 psi (48 to 200 kPa) in a fluidized bed $\text{Bi}_2\text{O}_3 \cdot n\text{MnO}_3$ catalyst (Fig.1).



The effluent is scrubbed in a countercurrent absorber and the acrylonitrile is purified by fractionation.

In one version of this process, the starting ingredients are mixed with steam and preheated before being fed to the reactor. There are two main by-products, acetonitrile (CH_3CN) and hydrogen cyanide (HCN), with accompanying formation of small quantities of acrolein ($\text{CH}_2=\text{CHCHO}$), acetone (CH_3COCH_3), and acetaldehyde (CH_3CHO). The acrylonitrile is separated from the other materials in a series of fractionation and absorption operations. A number of catalysts have been used, including phosphorus, molybdenum, bismuth, antimony, tin, and cobalt.

The most important uses of acrylonitrile are in the polymerization to polyacrylonitrile. This substance and its copolymers make good synthetic fibers for the textile industry. Acrylic is the fourth-largest synthetic fiber

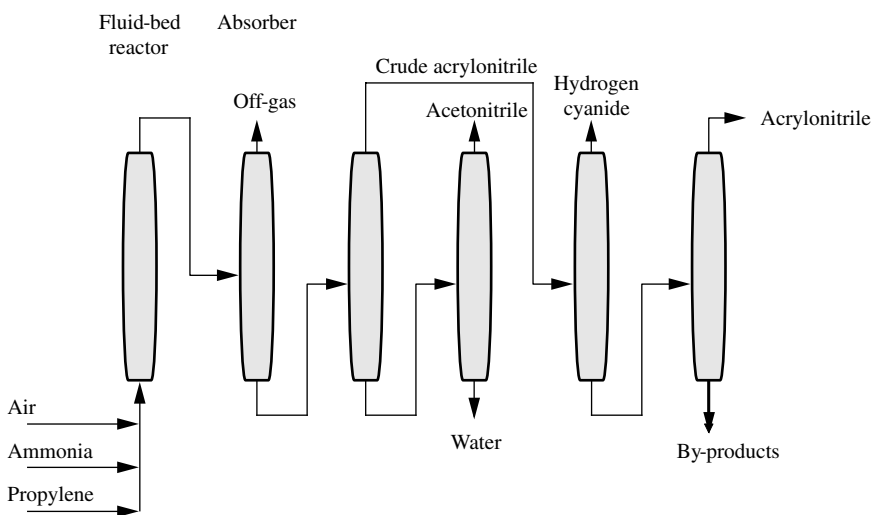


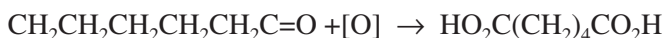
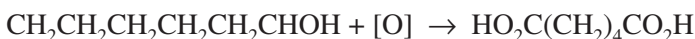
FIGURE 1 Manufacture of acrylonitrile by the ammoxidation of propylene.

produced, behind polyester, nylon, and polyolefin. It is known primarily for its warmth, similar to that natural and very expensive fiber, wool. Acrylonitrile is also used to produce plastics, including the copolymer of styrene-acrylonitrile (SA) and the terpolymer of acrylonitrile, butadiene, and styrene (ABS).

Hydrogen cyanide, a by-product of acrylonitrile manufacture, has its primary use in the manufacture of methyl methacrylate by reaction with acetone.

ADIPIC ACID

Adipic acid (melting point: 152.1°C, density: 1.344) is manufactured predominantly by the oxidation of cyclohexane followed by oxidation of the cyclohexanol/cyclohexanone mixture with nitric acid (Figs. 1 and 2):



There is no need to separate the cyclohexanol/cyclohexanone mixture into its individual components; oxidation of the mixture is carried out directly.

Adipic acid can also be made by hydrogenation of phenol with a palladium or nickel catalyst (150°C, 50 psi) to the mixed oil, then nitric acid oxidation to adipic acid. If palladium is used, more cyclohexanone is formed.

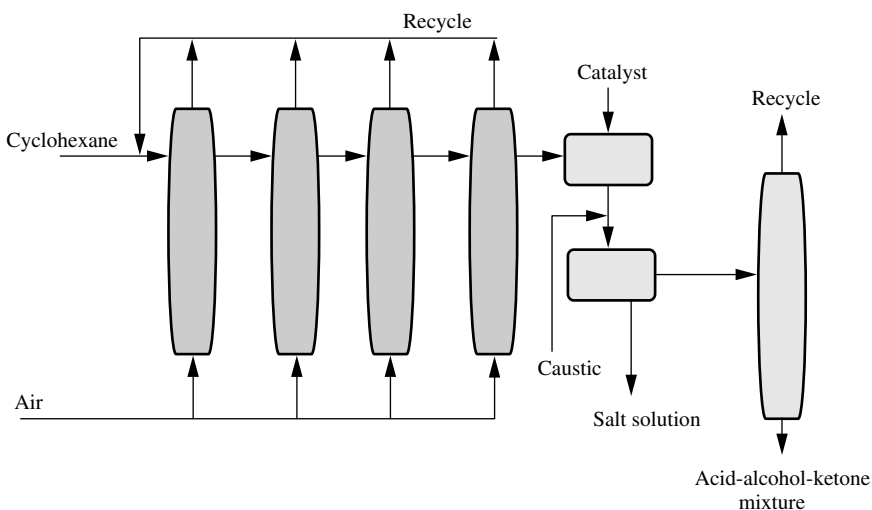


FIGURE 1 Manufacture of adipic acid by aerial oxidation of cyclohexane.

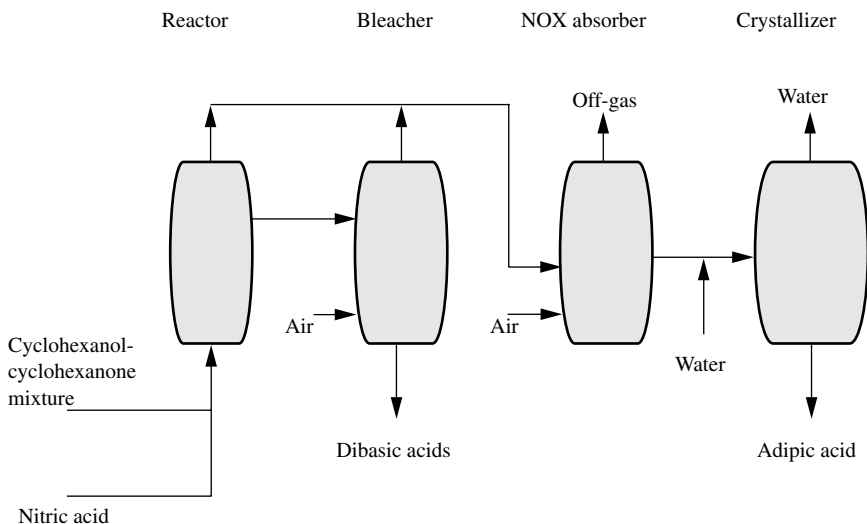


FIGURE 2 Adipic acid manufacture by nitric acid oxidation of cyclohexane

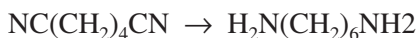
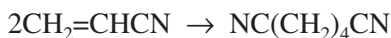
Although the phenol route for making adipic acid is not economically advantageous because phenol is more expensive than benzene, the phenol conversion to greater cyclohexanone percentages can be used successfully for caprolactam manufacture, where cyclohexanone is necessary.

Adipic acid is used to make nylon 6,6 fibers and nylon 6,6 resins; it is also used in the manufacture of polyurethanes and plasticizers.

Other starting materials for adipic acid include butadiene and 1,4-disubstituted-2-butene, which involves dicarbonylation with palladium chloride. Polar, aprotic, and nonbasic solvents are preferred for this reaction to avoid unwanted side products from hydrogenolysis or isomerization.

ADIPONITRILE

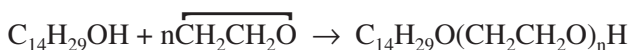
Adiponitrile is made by two different methods. One method is by the electrohydrodimerization of acrylonitrile. It is converted into hexamethylenediamine (HMDA) that is used to make nylon.



In the electrodimmerization of acrylonitrile, a two-phase system containing a phase transfer catalyst tetrabutylammonium tosylate is used.

ALCOHOLS, LINEAR, ETHOXYLATED

Ethoxylated linear alcohols can be made by the reaction of straight-chain alcohols, usually C_{12} to C_{14} , with three to seven moles of ethylene oxide.



The resulting alcohols are one type of many alcohols used for detergents. The linear alcohols can be produced from *n*-paraffins by way of alpha olefins or by way of the chloroparaffins. Or they can be made from alpha olefins formed from Ziegler oligomerization of ethylene.

Sulfonation and sodium salt formation of these alcohols converts them into detergents for shampoos and for dishwashing.

ALKANOLAMINES

Alkanolamines are compounds that contain both the hydroxyl (alcoholic) function (-OH) and the amino function (-NH₂).

Ethylene oxide, propylene oxide, or butylene oxide react with ammonia to produce alkanolamines. The more popular ethanolamines [NH_{3-n}(C₂H₄OH)_n, where $n = 1, 2, 3$: monoethanolamine, diethanolamine, and triethanolamine], are derived from the reaction of ammonia with ethylene oxide.

Alkanolamines are manufactured from the corresponding oxide and ammonia. Anhydrous or aqueous ammonia may be used, although anhydrous ammonia is typically used to favor monoalkanolamine production and requires high temperature and pressure (Fig. 1).

Isopropanolamines, NH_{3-n}(CH₂CHOHCH₃), result from the reaction of ammonia with propylene oxide. Secondary butanolamines, NH_{3-n}(CH₂CHOHCH₂CH₃), are the result of the reaction of ammonia with butylene oxide. Mixed alkanolamines can be produced from a mix-

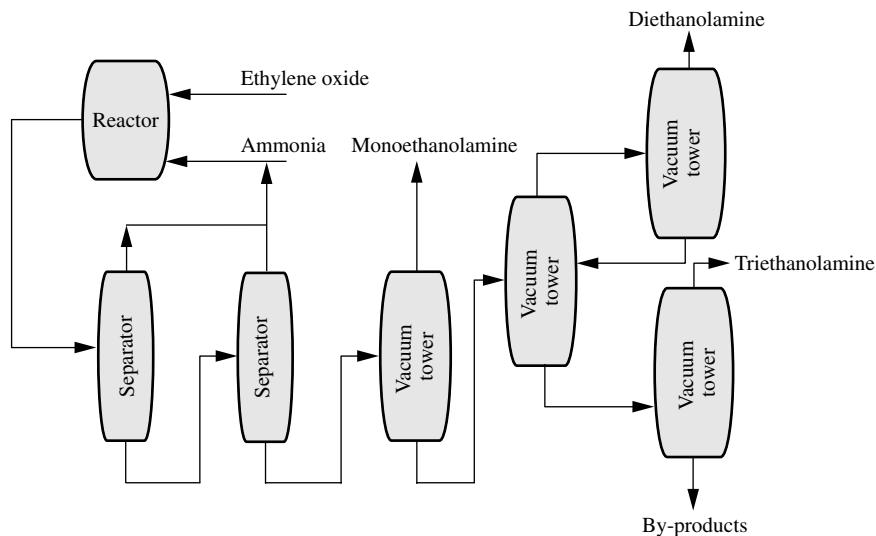


FIGURE 1 Manufacture of ethanolamines from ethylene oxide and ammonia.

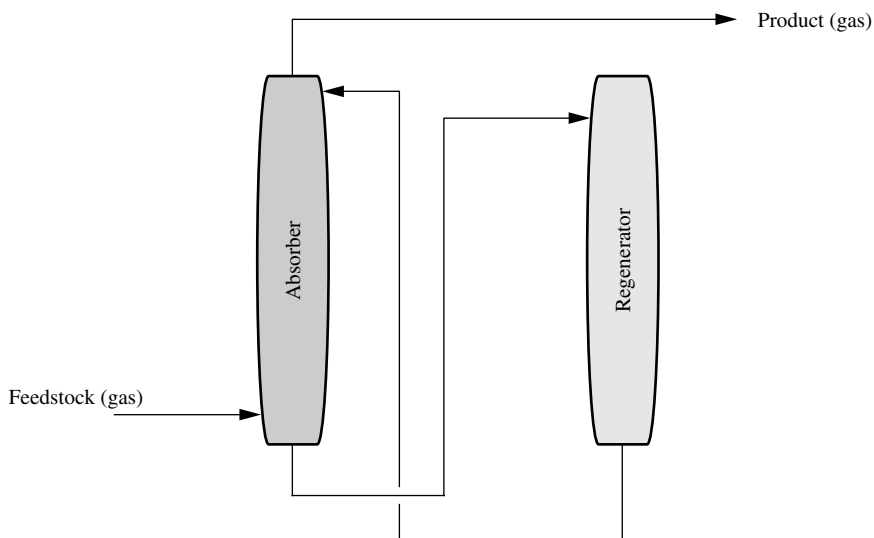


FIGURE 2 Gas cleaning using an aqueous alkanolamine.

ture of oxides reacting with ammonia. A variety of substituted alkanolamines can also be made by reaction of oxide with the appropriate amine.

Alkanolamines are used for gas cleaning (i.e., to remove carbon dioxide and hydrogen sulfide from gas streams) (Fig. 2), particularly in the petroleum and natural gas industries.

ALKYD RESINS

The term *alkyd resins* represents a broad class of compounds commonly used in coatings and is a particular type of polyester formed by the reaction of polyhydric alcohols and polybasic acids.

Alkyd resins are available in several forms of which the major forms are: (1) fibrous, in which the resins are compounded with long glass fibers (about $\frac{1}{2}$ inch; 12 mm) and have medium strength; (2) rope, which is a medium-impact material and conveniently handled and processed; and (3) granular, in which the resins are compounded with other fibers, such as glass, asbestos, and cellulose (length about $\frac{1}{16}$ inch; 2 mm). A commonly used member of the alkyd resin family is made from phthalic anhydride and glycerol. These resins are hard and possess very good stability. Where maleic acid is used as a starting ingredient, the resin has a higher melting point. Use of azelaic acid produces a softer and less brittle resin. Very tough and stable alkyds result from the use of adipic and other long-chain dibasic acids. Pentaerythritol may be substituted for glycerol as a starting ingredient.

The most common method of preparation of alkyd resins is the *fatty acid* method in which a glyceride oil is catalytically treated with glycerol at 225 to 250°C. The glyceride oil is simultaneously esterified and deesterified to a monoglyceride.

The esterification of a polybasic acid with a polyhydric alcohol yields a thermosetting hydroxycarboxylic resin, commonly referred to as an *alkyd resin*.

Alkyd resins are also polyesters containing unsaturation that can be cross-linked in the presence of an initiator known traditionally as a *drier*. A common example is the alkyd formed from phthalic anhydride and a glyceride of linolenic acid obtained from various plants. Cross-linking of the multiple bonds in the long unsaturated chain produces the thermoset polymer.

The processing equipment (reaction kettle and blending tank) used for unsaturated polyesters can also be used for manufacturing alkyd resins.

Alkyd resins are extensively used in paints and coatings. Some advan-

tages include good gloss retention and fast drying characteristics. However, most unmodified alkyds have low chemical and alkali resistance. Modification with esterified rosin and phenolic resins improves hardness and chemical resistance. Styrene and vinyl toluene improve hardness and toughness. For high-temperature coatings (up to about 230°C), copolymers of silicones and alkyds are used. Such coatings include stove and heating equipment finishes. To obtain a good initial gloss, improved adhesion, and exterior durability, acrylic monomers can be copolymerized with oils to modify alkyd resins.

ALKYLBENZENES, LINEAR

Linear alkylbenzenes are made from *n*-paraffins (C_{10} to C_{14}) by either partial dehydrogenation to olefins and addition to benzene with hydrogen fluoride (HF) as catalyst or by chlorination of the paraffins and Friedel-Crafts reaction with benzene and an aluminum chloride catalyst.

In one process (Fig.1), linear paraffins are dehydrogenated to linear olefins that are then reacted with benzene over a solid heterogeneous catalyst to produce the linear alkyl benzenes. Usually, the paraffins are of the C_{10} to C_{14} chain length.

The major uses of linear alkylbenzenes are in the manufacture of linear alkyl sulfonates that are used for manufacture of household detergents and industrial cleaners.

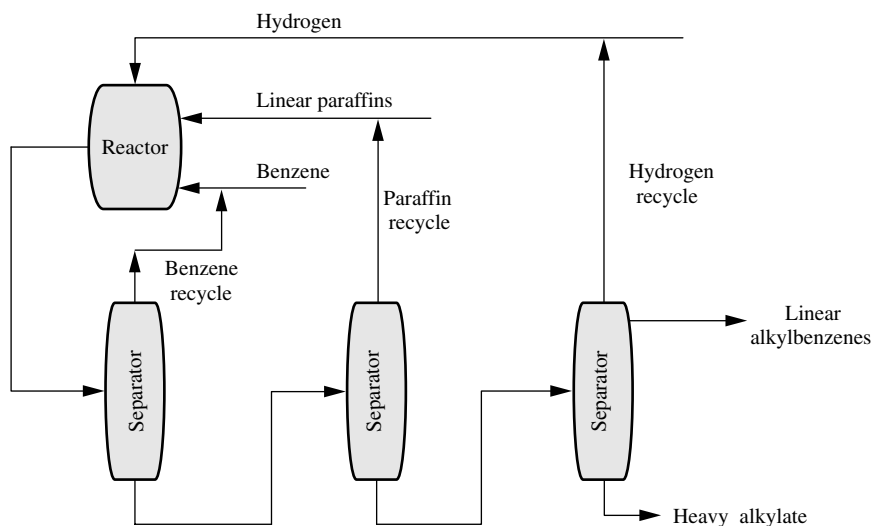
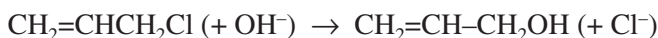


FIGURE 1 Manufacture of linear alkylbenzenes.

ALLYL ALCOHOL

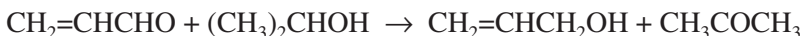
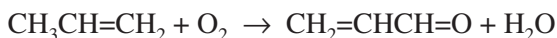
Allyl alcohol (2-propen-1-ol, $\text{CH}_2=\text{CHCH}_2\text{OH}$, boiling point: 96.9° , density: 0.8520, flash point: 25°C) is the simplest unsaturated alcohol and is a colorless corrosive liquid with a pungent odor. The vapor can cause severe irritation and injury to eyes, nose, throat, and lungs. Allyl alcohol is miscible with water and miscible with many polar organic solvents and aromatic hydrocarbons, but is not miscible with *n*-hexane. It forms an azeotropic mixture with water and a ternary azeotropic mixture with water and organic solvents.

There are four processes for industrial production of allyl alcohol. One involves the alkaline hydrolysis of allyl chloride.

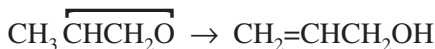


In this process, the amount of allyl chloride, 20 wt % aqueous sodium hydroxide (NaOH) solution, water, and steam are controlled as they are added to the reactor and the hydrolysis is carried out at 150°C , 200 psi (1.4 MPa) and pH 10 to 12. Under these conditions, conversion of allyl chloride is near quantitative (97 to 98 percent), and allyl alcohol is selectively produced in 92 to 93 percent yield. The main by-product is diallyl ether ($\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}=\text{CH}_2$). At high alkali concentrations, the amount of by-product, diallyl ether, increases, and at low concentrations, conversion of allyl chloride does not increase.

A second process has two steps. The first step is oxidation of propylene to acrolein and the second step is reduction of acrolein to allyl alcohol by a hydrogen transfer reaction, using isopropyl alcohol.

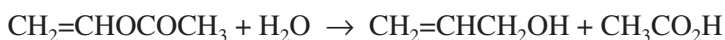
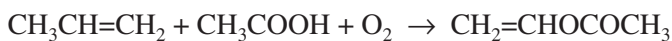


Another process is isomerization of propylene oxide in the presence of a catalyst (lithium phosphate, Li_3PO_4).



In this process, the fine powder of lithium phosphate used as catalyst is dispersed, and propylene oxide is fed at 300°C to the reactor, and the product, allyl alcohol, together with unreacted propylene oxide is removed by distillation. By-products such as acetone and propionaldehyde, which are isomers of propylene oxide, are formed, but the conversion of propylene oxide is 40 percent and the selectivity to allyl alcohol reaches more than 90 percent. Allyl alcohol obtained by this process may contain small amounts (<1%) of propanol.

The fourth process for the production of allyl alcohol was developed partly for the purpose of producing epichlorohydrin via allyl alcohol as the intermediate, using a palladium catalyst.



In the first step of the process (Fig. 1), the acetoxylation of propylene is carried out in the gas phase, using solid catalyst containing palladium as the main catalyst at 160 to 180°C and 70 to 140 psi (0.49 to 0.98 MPa). The reactor effluents from the reactor are separated into liquid components and gas components. The liquid components containing allyl acetate are sent to the hydrolysis process. The gas components contain unreacted gases and

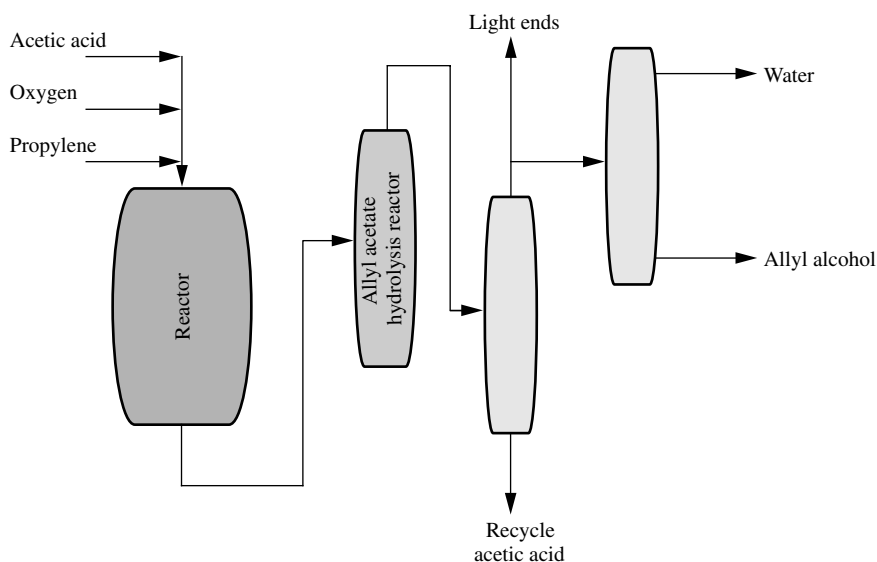


FIGURE 1 Manufacture of allyl alcohol (via allyl acetate) from propylene and acetic acid.

carbon dioxide and, after removal of the carbon dioxide, the unreacted gases are recycled to the reactor.

In the second step, the hydrolysis, which is an equilibrium reaction of allyl acetate, an acid catalyst is used and the reaction takes place at 60 to 80°C and allyl alcohol is selectively produced in almost 100 percent yield. Acetic acid recovered from the hydrolysis process, is reused in the first step.

Allyl alcohol forms an azeotropic mixture with water, and the mixture is a homogeneous liquid. Therefore, to obtain dry allyl alcohol, ternary azeotropic distillation and dehydration are required.

Allyl alcohol exhibits both bacterial and fungicidal effects and has been used as such or as a source for derivatives with these effects.

ALUMINA

Pure alumina (Al_2O_3) is a dry, snow-white, free-flowing crystalline powder and may be obtained in a wide range of particle sizes.

There are two main types of alumina (bauxite) ores used as the primary sources for aluminum metal and aluminum chemicals: aluminum hydroxide [$\text{Al}(\text{OH})_3$] (gibbsite) and a mixed aluminum oxide hydroxide [$\text{AlO}(\text{OH})$] (boehmite). Thus, *bauxite* is a term for a family of ores rather than a substance of one definite composition. An average composition of the ores used by industry today would be: alumina (Al_2O_3), 35 to 60%; silica (SiO_2), 1 to 15%; ferric oxide (Fe_2O_3), 5 to 40%; and titanium dioxide (TiO_2), 1 to 4%.

In the process to produce alumina (Fig. 1), bauxite is crushed and wet ground to 100-mesh, dissolved under pressure and heated in digesters with concentrated spent caustic soda solution from a previous cycle and sufficient lime and soda ash. Sodium aluminate is formed, and the dissolved silica is precipitated as sodium aluminum silicate. The undissolved residue (red mud) is separated from the alumina solution by filtration and washing and sent to recovery. Thickeners and Kelly or drum filters are used. The filtered solution of sodium aluminate is hydrolyzed to precipitate aluminum hydroxide by cooling. The precipitate is filtered from the liquor, washed, and heated to 980°C in a rotary kiln to calcine the aluminum hydroxide.

Several other processes for producing alumina based on ores other than bauxite have been announced. One process uses alunite, a hydrous sulfate of aluminum and potassium. It is claimed to be capable of producing 99% pure alumina from alunite containing only 10 to 15% alumina, compared with bauxite that assays 50% alumina. The alunite is crushed, dehydroxylated by heating to 750°C , ground, and treated with aqueous ammonia. Filtration removes the alumina hydrate, and potassium and aluminum sulfates are recovered from the filtrate (to be used as fertilizer constituents). The alumina hydrate is treated with sulfur dioxide gas, and the resulting aluminum sulfate is converted to alumina by heating in a kiln.

Another process for alumina manufacture involves treatment of clay and shale with concentrated sulfuric acid. Hydrochloric acid is added dur-

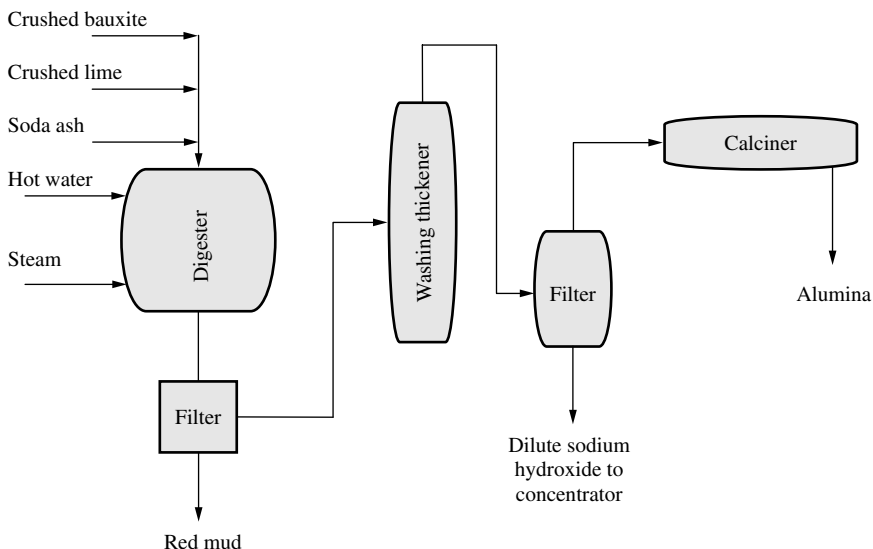


FIGURE 1 Manufacture of alumina.

ing the crystallization step to form aluminum chloride which crystallizes readily.

Other processes involve the treatment of clay with nitric acid and the continuous electrolysis of aluminum chloride.

Alumina is used to produce aluminum by the electrolytic process, and the purity of the aluminum is determined mainly by the purity of the alumina used. Thus, commercial grades of alumina are 99 to 99.5% pure with traces of water, silica (SiO_2), ferric oxide (Fe_2O_3), titanium dioxide (TiO_2), and (ZnO), and very minute quantities of other metal oxides.

Other uses include manufacture of a variety of aluminum salts water purification, glassmaking, production of steel alloys, waterproofing of textiles, coatings for ceramics, abrasives and refractory materials, cosmetics, electronics, drying gases and dehydrating liquids (such as alcohol, benzol, carbon tetrachloride, ethyl acetate, gasoline, toluol, and vegetable and animal oils), filter aids in the manufacture of lubricating and other oil products, catalysts for numerous reactions, polishing compounds, and linings for high-temperature furnaces.

ALUMINUM

Aluminum (melting point: 660°C , boiling point: 2494°C) is the most abundant metal in the world and makes up 7 to 10% by weight of the earth's crust.

Aluminum is manufactured by the electrolytic reduction of pure alumina (Al_2O_3) in a bath of fused cryolite (Na_3AlF_6). It is not possible to reduce alumina with carbon because aluminum carbide (Al_4C_3) is formed and a back-reaction between aluminum vapor and carbon dioxide in the condenser quickly reforms the original aluminum oxide again.

The electrolytic cells are large containers (usually steel), and each is a cathode compartment lined with either a mixture of pitch and anthracite coal or coke baked in place by the passage of electric current or prebaked cathode blocks cemented together.

Two types of cells are used in the Hall-Heroult process: those with multiple prebaked anodes (Fig. 1), and those with a self-baking, or Soderberg, anode. In both types of cell, the anodes are suspended from above and are connected to a movable anode bus so that their vertical position can be adjusted. The prebaked anode blocks are manufactured from a mixture of low-ash calcined petroleum coke and pitch or tar formed in hydraulic presses, and baked at up to 1100°C .

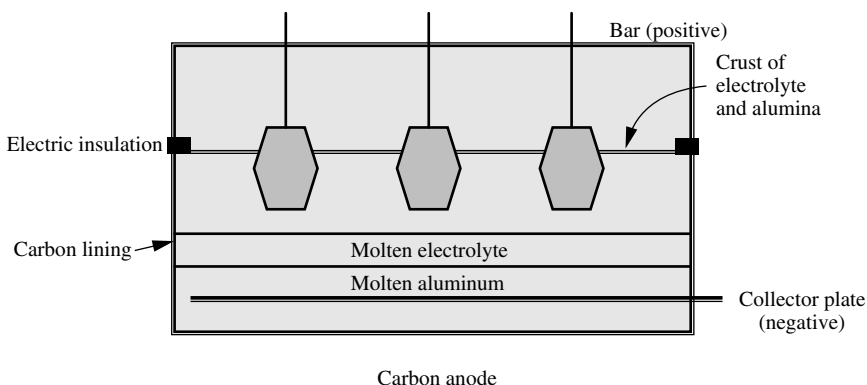
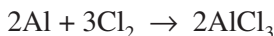


FIGURE 1 Manufacture of aluminum.

ALUMINUM CHLORIDE

Aluminum chloride (AlCl_3) is a white solid when pure that sublimes on heating and, in the presence of moisture, decomposes with the evolution of hydrogen chloride.

Anhydrous aluminum chloride is manufactured primarily by the reaction of chlorine vapor on molten aluminum.

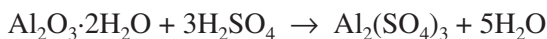


In the process, chlorine is fed in below the surface of the aluminum, and the product sublimes and is collected by condensing. These air-cooled condensers are thin-walled, vertical steel cylinders with conical bottoms. Aluminum chloride crystals form on the condenser walls and are periodically removed, crushed, screened, and packaged in steel containers.

Aluminum chloride is used in the petroleum industries and various aspects of organic chemistry technology. For example, aluminum chloride is a catalyst in the alkylation of paraffins and aromatic hydrocarbons by olefins and also in the formation of complex ketones, aldehydes, and carboxylic acid derivatives.

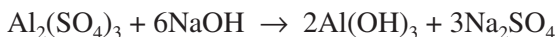
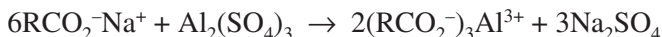
ALUMINUM SULFATE

Aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3$, alum, filter alum, papermaker's alum] is manufactured from aluminum oxide (Al_2O_3 , alumina, bauxite). A mixture of the crude ore and sulfuric acid is heated at 105 to 110°C for 15 to 20 hours.



Filtration of the aqueous solution is followed by evaporation of the water to give the product, which is processed into a white powder.

Alum has two prime uses. It is bought by the pulp and paper industry for coagulating and coating pulp fibers into a hard paper surface by reacting with small amounts of sodium carboxylates (soap) present. Aluminum salts of carboxylic acids are very gelatinous. In water purification it serves as a coagulant, pH conditioner, and phosphate and bacteria remover. It reacts with alkali to give an aluminum hydroxide floc that drags down such impurities in the water. For this reason it also helps the taste of water.



Pharmaceutically, aluminum sulfate is employed in dilute solution as a mild astringent and antiseptic for the skin. The most important single application of aluminum sulfate is in clarifying water; sodium aluminate, which is basic, is sometimes used with aluminum sulfate, which is acid, to produce the aluminum hydroxide.

Aluminum sulfate is also used in sizing of paper, as a mordant in the dye industry, chemical manufacturing, concrete modification, soaps, greases, fire extinguishing solutions, tanning, cellulosic insulation, and in some baking powders.

AMITRIPTYLINE

Amitriptyline hydrochloride and imipramine hydrochloride are similar in structure, with the exception of the nitrogen in the center ring, and belong to the family of phenothiazine compounds. Finally, the two-carbon bridge linking the aromatic rings may be ethyl ($-\text{CH}_2\text{CH}_2-$) or ethylene ($-\text{CH}=\text{CH}-$).

These compounds are central nervous system stimulants or antidepressants although such activity is usually restricted to compounds having a two- or three-carbon side chain and methyl-substituted or unsubstituted amino groups in the side chain although derivatives with substituents on the aromatic ring may have pharmacological activity.

The synthesis of amitriptyline starts from the key intermediate dibenzosuberone (manufactured from phthalic anhydride) and can proceed by two pathways (Fig. 1). Treatment of dibenzosuberone with cyclopropylmagnesium bromide gives the tertiary alcohol after hydrolysis. Reaction of the alco-

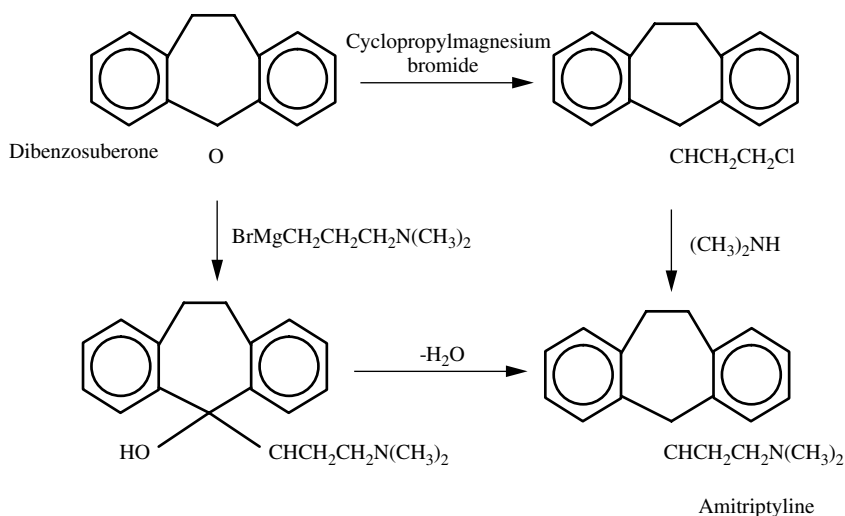


FIGURE 1 Manufacture of amitriptyline.

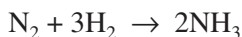
hol with hydrochloric acid proceeds with rearrangement and opening of the strained cyclopropane to give a chloride. Reaction and displacement of the chlorine atom with dimethylamine forms amitriptyline. Alternatively, dibenzosuberone can be reacted with dimethylaminopropyl Grignard to form an alcohol, which upon dehydration forms amitriptyline.

Amitriptyline is recommended for the treatment of mental depression, with improvement in mood seen in 2 to 3 weeks after the start of medication.

AMMONIA

Ammonia (NH₃, melting point -77.7°C , boiling point -33.4°C , and density 0.817 at -79°C and 0.617 at 15°C) is a colorless gas with a penetrating, pungent-sharp odor in small concentrations that, in heavy concentrations, produces a smothering sensation when inhaled. Ammonia is soluble in water and a saturated solution contains approximately 45% ammonia by weight at the freezing temperature of the solution and about 30% ammonia by weight at standard conditions. Ammonia dissolved in water forms a strongly alkaline solution of ammonium hydroxide (NH₄OH) and the aqueous solution is called *ammonia water*, *aqua ammonia*, or sometimes *ammonia* (although this is misleading). Ammonia burns with a greenish-yellow flame.

The first breakthrough in the large-scale synthesis of ammonia resulted from the development of the Haber process in 1913 in which ammonia was produced by the direct combination of two elements, nitrogen and hydrogen, in the presence of a catalyst (iron oxide with small quantities of cerium and chromium) at a relatively high temperature (550°C) and under a pressure of about 2940 psi (20.3 MPa).



In the Haber process (Fig. 1), the reaction of nitrogen and hydrogen gases is accomplished by feeding the gases to the reactor at 400 to 600°C . The reactor contains an iron oxide catalyst that reduces to a porous iron metal in the nitrogen/hydrogen mixture. Exit gases are cooled to -0 to -20°C , and part of the ammonia liquefies; the remaining gases are recycled.

The process for ammonia manufacture will vary somewhat with the source of hydrogen, but the majority of ammonia plants generate the hydrogen by steam reforming natural gas or hydrocarbons such as naphtha (Fig. 2).

If the hydrogen is made by steam reforming, air is introduced at the secondary reformer stage to provide nitrogen for the ammonia reaction. The

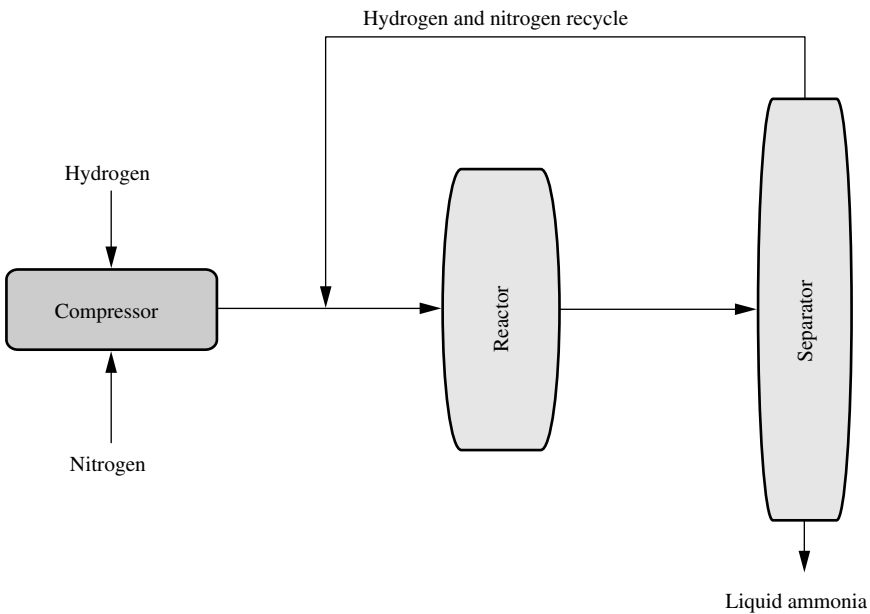


FIGURE 1 Ammonia manufacture from hydrogen and nitrogen by the Haber process.

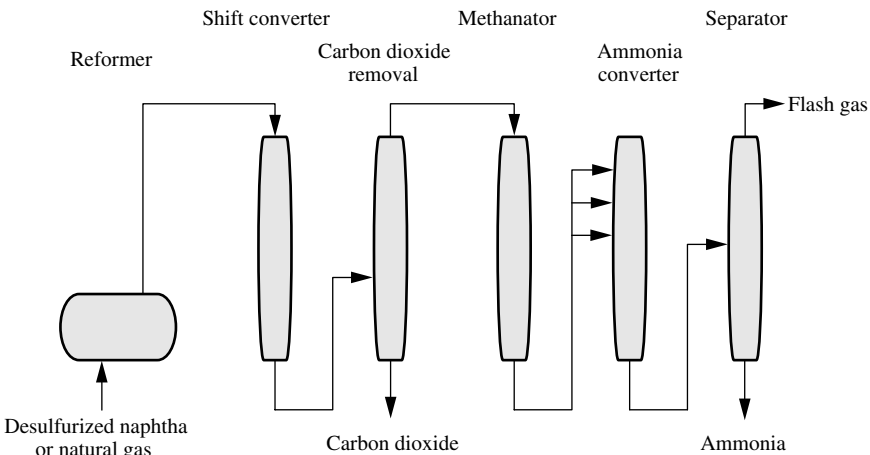


FIGURE 2 Ammonia manufacture from natural gas or naphtha.

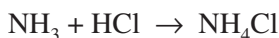
oxygen of the air reacts with the hydrocarbon feedstock in combustion and helps to elevate the temperature of the reformer. Otherwise nitrogen can be added from liquefaction of air. In either case a hydrogen-nitrogen mixture is furnished for ammonia manufacture.

Ammonia is used for the manufacture of fertilizers or for the manufacture of other nitrogen-containing compounds used for fertilizer or, to a lesser extent, explosives, plastics, and fibers. Explosives made from ammonia are ammonium nitrate and (via nitric acid) the nitroglycerin used in dynamite. Plastics include (via urea) urea-formaldehyde and melamine-formaldehyde resins. Some ammonia ends up in fibers, since it is used to make hexamethylenediamine (HMDA), adipic acid, or caprolactam, all nylon precursors.

AMMONIUM CHLORIDE

Ammonium chloride (NH_4Cl , density 1.52) is a white crystalline solid that decomposes at 350°C and sublimates at 520°C under controlled conditions. It is also known as *sal ammoniac* and is soluble in water and in aqueous solutions of ammonia; it is slightly soluble in methyl alcohol.

Ammonium chloride is produced by neutralizing hydrochloric acid (HCl) with ammonia gas or with liquid ammonium hydroxide, and evaporating the excess water, followed by drying, crystallizing, and screening operations.



Ammonium chloride can also be produced in the gaseous phase by reacting hydrogen chloride gas with ammonia.

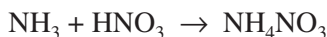
Ammonium chloride is used as an ingredient of dry cell batteries, as a soldering flux, as a processing ingredient in textile printing and hide tanning, and as a starting material for the manufacture of other ammonium chemicals.

AMMONIUM NITRATE

Ammonium nitrate (NH_4NO_3), a colorless crystalline solid, occurs in two forms: (1) α -ammonium nitrate (tetragonal crystals, stable between -16°C and 32°C ; melting point: 169.9°C ; density: 1.66) and (2) β -ammonium nitrate (rhombic or monoclinic crystals, stable between 32°C and 84°C with decomposition occurring above 210°C ; density: 1.725).

When heated, ammonium nitrate yields nitrous oxide (N_2O) gas and can be used as an industrial source of that gas. Ammonium nitrate is soluble in water, slightly soluble in ethyl alcohol, moderately soluble in methyl alcohol, and soluble in acetic acid solutions containing ammonia.

Ammonium nitrate is manufactured from ammonia and nitric acid.



In the process (Figs. 1 and 2), the gases are fed to the reactor in which the heat of neutralization boils the mixture, concentrating it to 85% nitrate. Vacuum evaporation at 125 to 140°C further concentrates the solution to 95%. The last water of this hygroscopic material is very difficult to remove. The hot solution is pumped to the top of a spray tower 60 to 70 m high, where it is discharged through a spray head and solidifies as it falls in the air to form small spherical pellets, prills, of 2 mm diameter that are screened, further dried, and dusted with clay to minimize sticking.

If properly proportioned and preheated, the reaction can be run continuously to produce molten ammonium nitrate containing very little water (1 to 5%), which can be formed into small spheres (prills) by dropping the reaction product through a shot tower or into flakes by cooling it on belts or drums. By fluidized bed treatment, it is possible to obtain a dry granular material as product; batch processes have also been used.

Ammonium nitrate finds major applications in explosives and fertilizers, and additional uses in pyrotechnics, freezing mixtures (for obtaining low temperatures), as a slow-burning propellant for missiles (when formulated with other materials, including burning-rate catalysts), as an ingredient in rust inhibitors (especially for vapor-phase corrosion), and as a component of insecticides.

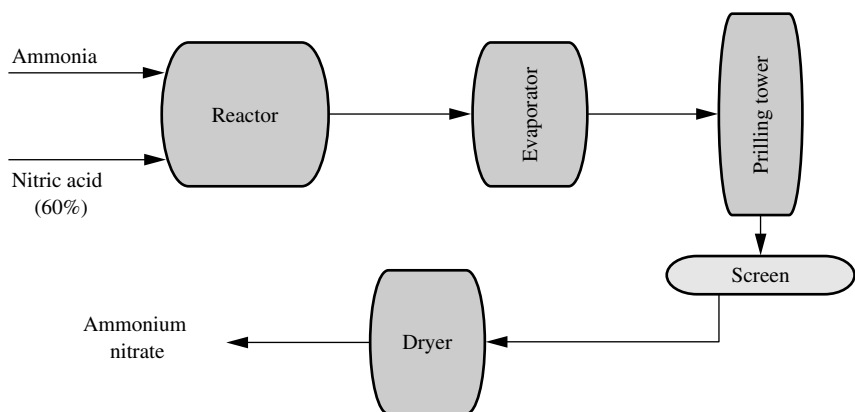


FIGURE 1 Manufacture of ammonium nitrate.

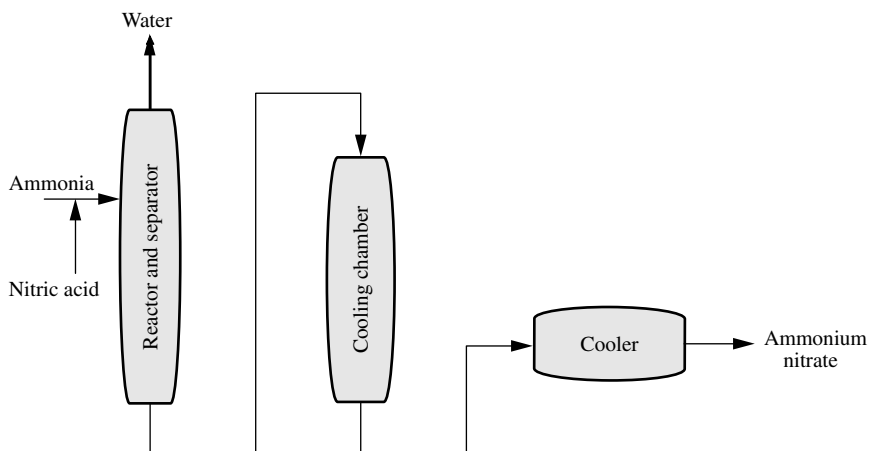


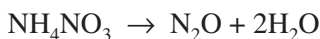
FIGURE 2 Ammonium nitrate by the Stengel process.

Ammonium nitrate is used in explosives, and many commercial and military explosives contain ammonium nitrate as the major explosive ingredient. Ammonium nitrate is difficult to detonate, but, when sensitized with oil or mixed with other explosive materials, it can be detonated with a large booster-primer. Amatol is a mixture of trinitrotoluene (TNT) and granular ammonium nitrate and is a major conventional military explosive. The explosive ANFO is a mixture of ammonium nitrate and fuel oil.

Explosive decomposition causes ammonium nitrate to rapidly and violently decompose to form elemental nitrogen.



However, under different conditions, i.e., at 200 to 260°C, ammonium nitrate is safely decomposed to form the anesthetic nitrous oxide, and this reaction is used for the commercial manufacture of nitrous oxide.



Slurry explosives consist of oxidizers (NH_4NO_3 and NaNO_3), fuels (coals, oils, aluminum, other carbonaceous materials), sensitizers (trinitrotoluene, nitrostarch, and smokeless powder), and water mixed with a gelling agent to form a thick, viscous explosive with excellent water-resistant properties. Slurry explosives may be manufactured as cartridge units, or mixed on site.

As a fertilizer, ammonium nitrate contains 35% nitrogen and, because of the explosive nature of the compound, precautions in handling are required. This danger can be minimized by introducing calcium carbonate into the mixture, reducing the effective nitrogen content of the product to 26% by weight.

Ammonium nitrate is hygroscopic; clay coatings and moisture-proof bags are used to preclude spoilage in storage and transportation.

AMMONIUM PHOSPHATE

There are three possible ammonium orthophosphates, only two of which are manufactured on any scale.

Monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, white crystals, density: 1.803) is readily made by reacting ammonia with phosphoric acid, centrifuging, and drying in a rotary dryer. It is used in quick-dissolving fertilizers and as a fire-retarding agent for wood, paper, and cloth. Diammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$, white crystals, density: 1.619] requires a two-stage reactor system in order to prevent loss of ammonia. A granulation process follows with completion of the reaction in a rotary drum. Both compounds are soluble in water and insoluble in alcohol or ether.

A third compound, triammonium phosphate $[(\text{NH}_4)_3\text{PO}_4]$ does not exist under normal conditions because, upon formation, it immediately decomposes, losing ammonia (NH_3) and reverts to one of the less alkaline forms.

Ammonium phosphates usually are manufactured by neutralizing phosphoric acid with ammonia in which control of the pH (acidity/alkalinity) determines which of the ammonium phosphates will be produced.

Pure grades of a particular ammonium phosphate can be produced by crystallization of solutions obtained from furnace-grade phosphoric acid.

There has been a trend toward the production of ammonium phosphates in powder form by a process in which concentrated phosphoric acid is neutralized under pressure, and the heat of neutralization is used to remove the water in a spray tower. The powdered product then is collected at the bottom of the tower. Ammonium nitrate/ammonium phosphate combination products can be obtained either by neutralizing mixed nitric acid and phosphoric acid or by the addition of ammonium phosphate to an ammonium nitrate melt.

Large quantities of the ammonium phosphates are used as fertilizers and in fertilizer formulations as well as fire retardants in wood building materials, paper and fabric products, and in matches to prevent afterglow. Solutions of the ammonium phosphates sometimes are air-dropped to retard forest fires, serving the double purpose of fire fighting and fertilizing the soil to accelerate new plant growth.

Ammonium phosphates are also used in baking powder formulations, as nutrients in the production of yeast, as nutritional supplements in animal feeds, for controlling the acidity of dye baths, and as a source of phosphorus in certain kinds of ceramics.

AMMONIUM PICRATE

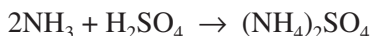
Ammonium picrate (explosive D) is manufactured by the neutralization of a hot aqueous solution of picric acid (2,4,6-trinitrophenol) with aqueous ammonia.

It is used in armor-piercing shells as a bursting charge. Ammonium picrate is a salt and does not melt, so it must be loaded by compression.

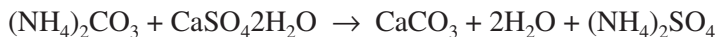
AMMONIUM SULFATE

Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, density: 1.769] is a colorless crystalline solid that decomposes above 513°C and is soluble in water but insoluble in alcohol.

Ammonium sulfate was originally manufactured by using sulfuric acid to scrub by-product ammonia from coke-oven gas, and much is still produced in this manner. Most of the ammonium sulfate produced is now made by reaction between synthetic ammonia and sulfuric acid.



Where sulfur for sulfuric acid is at a premium, a process based on gypsum and carbon dioxide from combustion can be used:



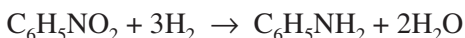
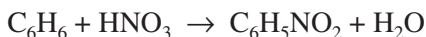
Water is removed by evaporation, and the product is crystallized to large, white uniform crystals, melting point 513°C , with decomposition. Anhydrite (CaSO_4) can also be used in this process.

Large quantities of ammonium sulfate are produced by a variety of industrial neutralization operations required for alleviation of stream pollution by free sulfuric acid (H_2SO_4) as well as in the manufacture of caprolactam. Ammonium sulfate also is a byproduct of coke oven operations where the excess ammonia formed is neutralized with sulfuric acid to form the ammonium sulfate.

Ammonium sulfate is used predominantly as a fertilizer. As a fertilizer, $(\text{NH}_4)_2\text{SO}_4$ has the advantage of adding sulfur to the soil as well as nitrogen, as it contains 21% by weight nitrogen and 24% by weight sulfur. Ammonium sulfate also is used in electric dry cell batteries, as a soldering liquid, as a fire retardant for fabrics and other products, and as a source of certain ammonium chemicals. Other uses include water treatment, fermentation processes, fireproofing agents, and leather tanning.

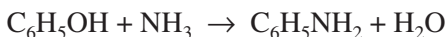
ANILINE

Aniline is an important derivative of benzene that can be made in two steps by nitration to nitrobenzene and either catalytic hydrogenation or acidic metal reduction to aniline.



Both steps occur in excellent yield.

The reaction of ammonia and phenol is also being used for aniline production.



Major uses of aniline include the manufacture of *p,p'*-methylene diphenyl diisocyanate (MDI), which is polymerized with a diol (HO-R-OH) to give a polyurethane. Two moles of aniline react with formaldehyde to give *p,p'*-methylenedianiline (MDA), which reacts with phosgene to give *p,p'*-methylene diphenyl diisocyanate. Toluene diisocyanate (TDI) also reacts with a diol to give a polyurethane, but polyurethanes derived from *p,p'*-methylene diphenyl diisocyanate are more rigid than those from toluene diisocyanate.

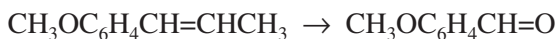
Aniline is used in the rubber industry for the manufacture of various vulcanization accelerators and age resistors. Aniline is also used in the production of herbicides, dyes and pigments, and specialty fibers.

See Amination.

ANISALDEHYDE

Anisaldehyde is a colorless oily liquid with an agreeable odor resembling that of coumarin, which is developed only after dilution and in mixtures.

It is made by the oxidation of anethole (the chief constituent of anise, star anise, and fennel oils).



Anethole is obtained from the higher-boiling fractions of pine oil.

ANTIBIOTICS

The term *antibiotic* is broad and is defined as a substance produced by microorganisms that has the capacity of inhibiting the growth of and even of destroying other microorganisms by the action of very small amounts of the substance.

Penicillin, erythromycin, tetracycline, and cephalosporins are among the most widely used. Synthetic modifications of the naturally occurring antibiotic compounds have produced many variations that have the necessary clinical properties.

Many antibiotics are now manufactured (Fig. 1) and caution is often required during production because of the instability of these compounds to heat, variation in the pH, and chemical action, and they may even decompose in solution.

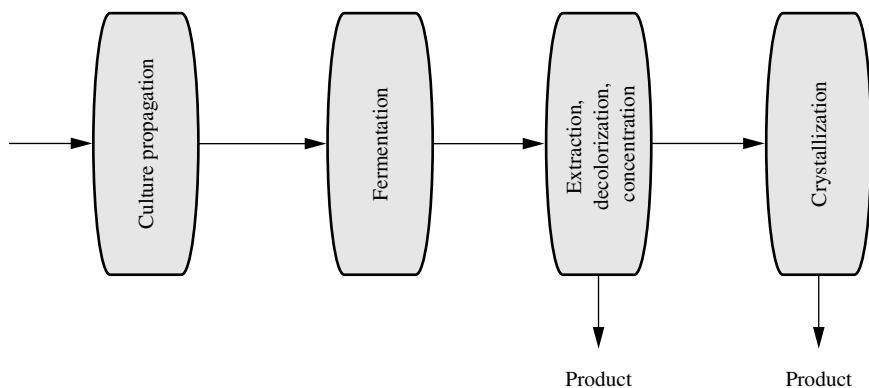


FIGURE 1 Schematic for the manufacture of antibiotics.

ANTI HISTAMINES

Antihistamines are sold under such trade names as Dimetapp[®], Actifed[®], and Benadryl[®]. They have a structure including the group R-X-C-C-N=, where X can be nitrogen, oxygen, or carbon (Fig. 1).

Antihistamines are produced by certain key steps, such as the synthesis of diphenhydramine from diphenylmethane (Fig. 2).

Antihistamines are used to alleviate allergic conditions such as rashes and runny eyes and nose and are decongestants that are used for swelled sinuses and nasal passages during the common cold. These symptoms are caused by histamine and hence the drugs that get rid of them are antihistamines. Antihistamines are also sleep inducers.

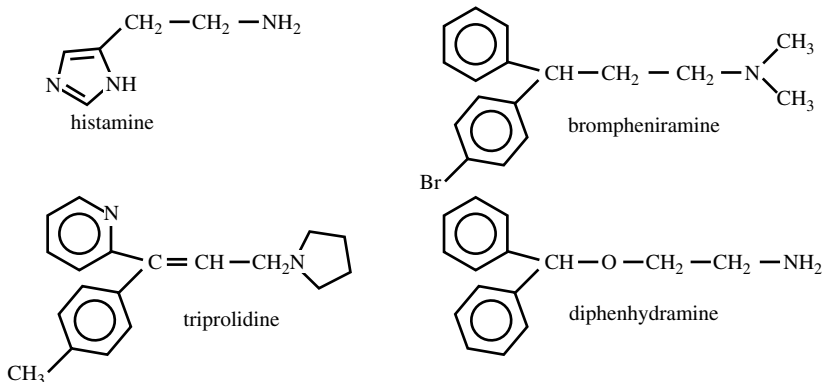


FIGURE 1 Examples of antihistamines.

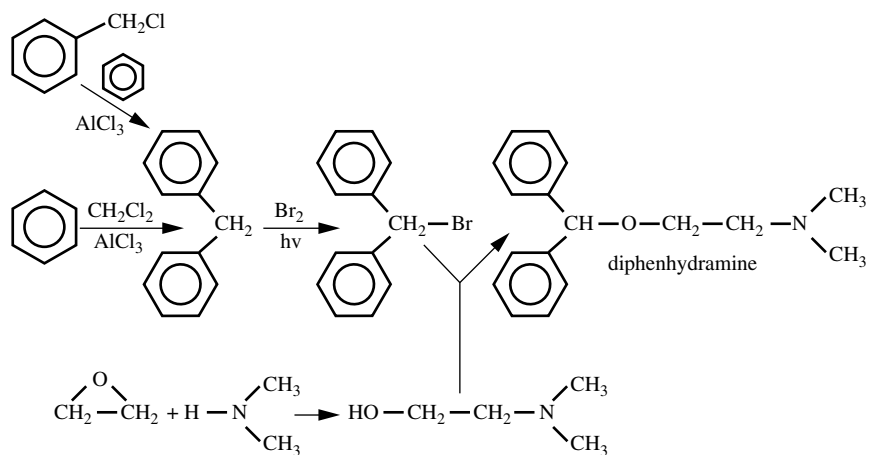


FIGURE 2 Manufacture of diphenylhydramine.

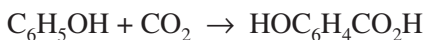
ARGON

See Rare Gases.

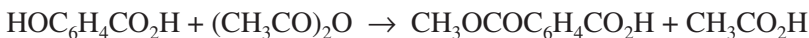
ASPIRIN

Aspirin (acetylsalicylic acid) is by far the most common type of analgesic, an important class of compounds that relieve pain, and it also lowers abnormally high body temperatures. Aspirin also finds use in reducing inflammation caused by rheumatic fever and rheumatoid arthritis.

The manufacture of aspirin is based on the synthesis of salicylic acid from phenol. Reaction of carbon dioxide with sodium phenoxide is an electrophilic aromatic substitution on the ortho, para-directing phenoxy ring. The ortho isomer is steam distilled away from the para isomer.



Salicylic acid reacts easily with acetic anhydride to give aspirin.



In this process, a 500-gallon glass-lined reactor is needed to heat the salicylic acid and acetic anhydride for 2 to 3 hours. The mixture is transferred to a crystallizing kettle and cooled to 3°C. Centrifuging and drying of the crystals yields the bulk aspirin. The excess solution is stored and the acetic acid is recovered to make more acetic anhydride.

The irritation of the stomach lining caused by aspirin can be alleviated with the use of mild bases such as sodium bicarbonate, aluminum glycinate, sodium citrate, aluminum hydroxide, or magnesium trisilicate (a trademark for this type of aspirin is Bufferin®).

Both phenacetin and the newer replacement acetaminophen are derivatives of *p*-aminophenol. Although these latter two are analgesics and antipyretics, the aniline-phenol derivatives show little if any antiinflammatory activity. *p*-Aminophenol itself is toxic, but acylation of the amino group makes it a convenient drug.

A trademark for acetaminophen is Tylenol®. Excedrin® is acetaminophen, aspirin, and caffeine. Acetaminophen is easily synthesized from phenol.

See Salicylic Acid.