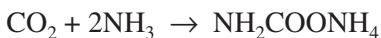


UREA

Urea (H_2NCONH_2 , carbamide; melting point: 135°C , density: 1.3230) is a colorless crystalline solid, somewhat hygroscopic, that sublimes unchanged under vacuum at its melting point and decomposes above the melting point at atmospheric pressure, producing ammonia (NH_3), isocyanic acid (HNCO), cyanuric acid [$(\text{HNCO})_3$], biuret ($\text{H}_2\text{NHCONHCONH}_2$), and several other minor products. Urea is very soluble in water (being a component of urine), soluble in alcohol, and slightly soluble in ether.

There are several approaches to the manufacture of urea, but the principal method is that of combining carbon dioxide with ammonia to form ammonium carbamate (Figs. 1 and 2):



This exothermic reaction is followed by an endothermic decomposition of the ammonium carbamate:



Both are equilibrium reactions. The formation reaction goes to virtual completion under usual reaction conditions, but the decomposition reaction is less complete. Unconverted carbon dioxide and ammonia, along with undecomposed carbamate, must be recovered and reused.

In the process, a 2:1 molar ratio of ammonia and carbon dioxide (excess ammonia) are heated in the reactor for 2 hours at 190°C and 1500 to 3000 psi (10.3 to 20.6 MPa) to form ammonium carbamate, with most of the heat of reaction carried away as useful process steam. The carbamate decomposition reaction is both slow and endothermic. The mix of unreacted reagents and carbamate flows to the reactor-decomposer. The reactor must be heated to force the reaction to proceed. For all the unreacted gases and undecomposed carbamate to be removed from the product, the urea must be heated at lower pressure (400 kPa). The reagents are reacted and

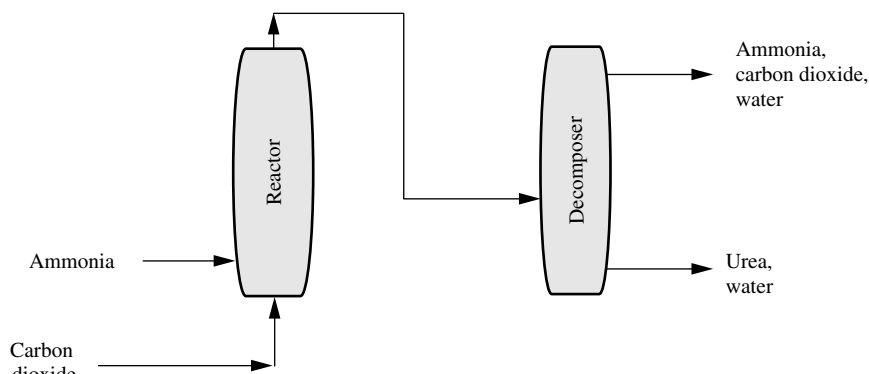


FIGURE 1 Once-through process for urea manufacture.

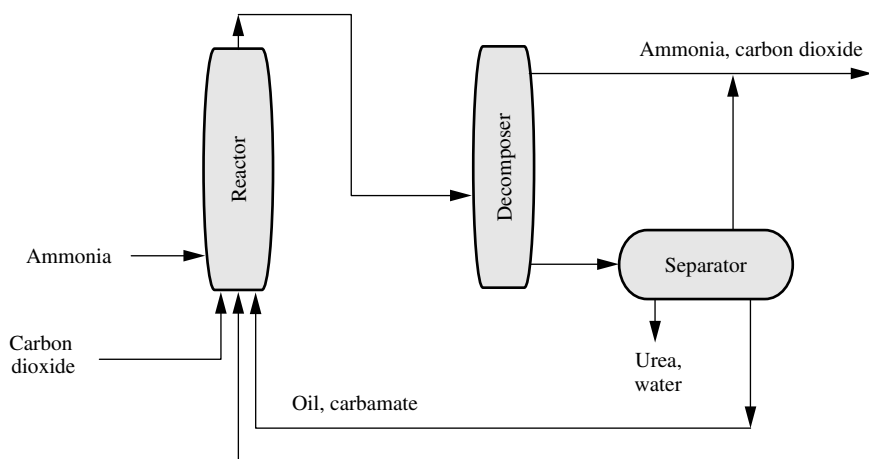


FIGURE 2 Recycle process for urea manufacture.

pumped back into the system. Evaporation and prilling or granulating produce the final product.

The mixture formed is approximately 35% urea, 8% ammonium carbamate, 10% water, and 47% ammonia. It is cooled to 150°C and the ammonia is distilled at 60°C. The residue from the ammonia still enters the crystallizer vessel at 15°C. More ammonia is removed by vacuum. The resulting slurry is centrifuged. All excess nitrogenous materials are combined and processed into liquid fertilizer, which contains a mixture of all these materials.

The corrosive nature of the reactants usually requires the reaction vessels to be lined with lead, titanium, zirconium, silver, or stainless steel. In the second step of the process, only about one-half of the ammonium car-

bamate is dehydrated in the first pass. Thus, the excess carbamate, after separation from the urea, must be recycled to the urea reactor or used for other products, such as the production of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$.

Urea is used as a solid fertilizer, a liquid fertilizer and miscellaneous applications such as animal feed, urea, formaldehyde resins, melamine, and adhesives. Presently, the most popular nitrogen fertilizer is a urea-ammonium nitrate solution. Urea-formaldehyde resins have large use as a plywood adhesive. Melamine-formaldehyde resins are used as dinnerware and for extra-hard surfaces (Formica®). The melamine is synthesized by condensation of urea molecules.

As a fertilizer, urea is a convenient form for fixed nitrogen and has the highest nitrogen content (46% by weight) available in a solid fertilizer. It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard. It dissolves readily in water and leaves no salt residue after use on crops and can often be used for foliar feeding.

Urea is also used as a protein food supplement for ruminants, in melamine production, and as an ingredient in the manufacture of pharmaceuticals (e.g., barbiturates), synthetic resins, plastics (urethanes), adhesives, coatings, textile antishrink agents, and ion exchange resins. It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid, and phthalocyanines.

UREA RESINS

Urea resins (urea formaldehyde polymers) are formed by the reaction of urea with formaldehyde (Fig. 1). Monomethylolurea ($\text{HOH}_2\text{CNHCONH}_2$) and dimethylolurea ($(\text{HOH}_2\text{CNHCONHCH}_2\text{OH})$) are formed first under alkaline conditions. Continued reaction under acidic conditions gives a fairly linear, low-molecular-weight intermediate polymer.

A catalyst and controlled temperature are also needed and, since the amine may not be readily soluble in water or formalin at room temperature, it is necessary to heat it to about 80°C to obtain the methylol compounds for many amine-formaldehyde resins.

Heating for an extended period of time under acidic conditions will give a complex thermoset polymer of poorly defined structure including ring formation.

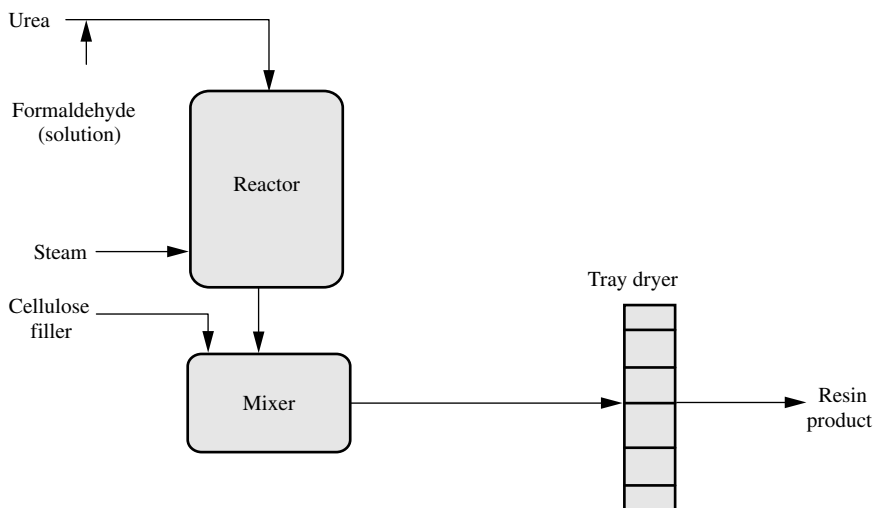


FIGURE 1 Manufacture of urea-formaldehyde resins.

VALIUM

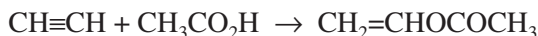
Valium (diazepam) is a substituted benzodiazepine made by a series of reactions, one of which involves cyclization.

It is prepared by treating *p*-chloromethylaniline with benzoyl chloride and hydroxylamine to produce the benzophenone oxime. Reaction of the oxime with chloroacetyl chloride in the presence of sodium hydroxide, and subsequent reduction, yields diazepam.

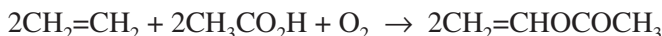
See Benzodiazepines.

VINYL ACETATE

The older process for the production of vinyl acetate (melting point: -93.2°C , boiling point: 72.3°C , density: 0.9317) involved the reaction of acetylene with acetic acid in the liquid phase with zinc amalgam as the catalyst.



A newer method is based on the reaction of acetic acid with ethylene and has replaced the older acetylene chemistry.



A Wacker catalyst is used in this process, similar to that for the manufacture of acetic acid. Since the acetic acid can also be made from ethylene, the basic raw material is solely ethylene. A liquid-phase process has been replaced by a vapor-phase reaction run at 70 to 140 psi and 175 to 200°C . Catalysts may be (1) carbon–palladium chloride–cupric chloride ($\text{C-PdCl}_2\text{-CuCl}_2$), (2) palladium chloride–alumina ($\text{PdCl}_2\text{-Al}_2\text{O}_3$), or (3) palladium–carbon–potassium acetate (Pd-C-KOAc). The product is distilled into water, acetaldehyde that can be recycled to acetic acid, and the pure colorless liquid, which is collected at 72°C . The yield is 95percent.

The reaction is conducted in a fixed-bed tubular reactor and is highly exothermic. With proper conditions, the only significant by-product is carbon dioxide. Enough heat is recovered as steam to perform the recovery distillation. Reaction is at 175 to 200°C under a pressure of 475 to 1000 kPa. To prevent polymerization, an inhibitor such as diphenylamine or hydroquinone is added.

Vinyl acetate is used for the manufacture of poly(vinyl acetate) resins (Fig. 1), poly(vinyl alcohol), and poly(vinyl butyral). Poly(vinyl acetate) is used primarily in adhesives, coatings, and paints. Copolymers of poly(vinyl acetate) with poly(vinyl chloride) are used in flooring, phonograph

records, and PVC pipe. Poly(vinyl alcohol) is used in textile sizing, adhesives, emulsifiers, and paper coatings. Poly(vinyl butyral) is the plastic inner liner of most safety glass.

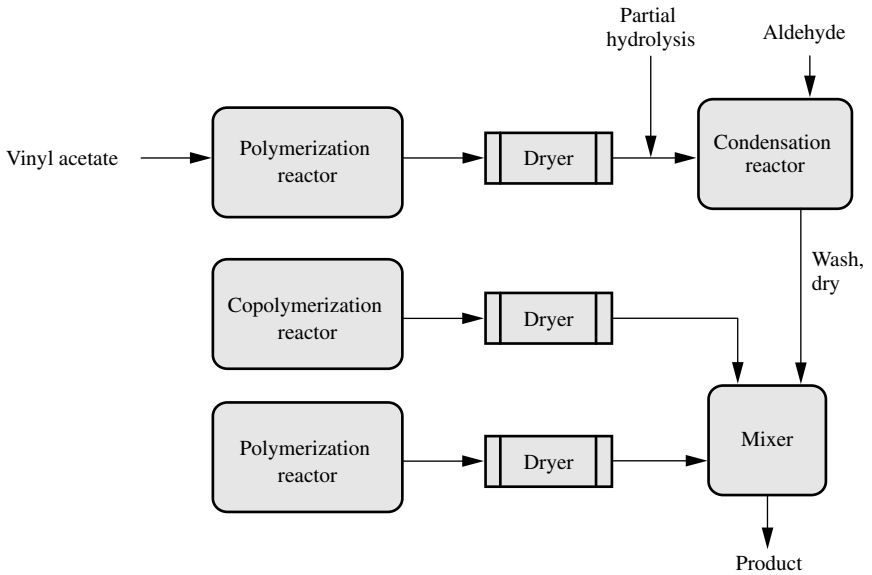
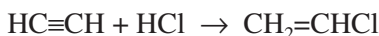


FIGURE 1 Manufacture of polyvinyl acetate resins.

VINYL CHLORIDE

Vinyl chloride (1-chloroethylene; boiling point -31.6°C , density: 1.2137, flash point: -16°C) is manufactured by the addition of hydrogen chloride to acetylene in the presence of mercuric (Hg^{2+}) salts.



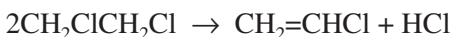
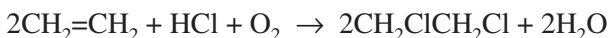
The process is combined with the process in which hydrogen chloride is produced by thermal dehydrochlorination of ethylene dichloride.

Thus, vinyl chloride is manufactured by the thermal dehydrochlorination of ethylene dichloride at 95 percent yield at temperatures of 480 to 510°C under a pressure of 50 psi with a charcoal catalyst.



Vinyl chloride is separated from ethylene dichloride by fractional distillation. Although the conversion is low, 50 to 60 percent, recycling the ethylene dichloride allows an overall 99 percent yield.

More modern processes use the oxychlorination concept (Fig. 1) in which the vinyl chloride is produced from ethylene, chlorine, and oxygen.



Vinyl chloride readily polymerizes, so it is stabilized with inhibitors to polymerization during storage.

The single use of vinyl chloride is in the manufacture of poly(vinyl chloride) plastic, which finds diverse applications in the building and construction industry as well as in the electrical, apparel, and packaging industries. Poly(vinyl chloride) does degrade relatively fast for a polymer, but various heat, ozone, and ultraviolet stabilizers make it a useful polymer. A wide variety of desirable properties can be obtained by using various

amounts of plasticizers, such that both rigid and plasticized poly(vinyl chloride) have large markets. A lesser amount of the produced vinyl chloride is used for production of chlorinated solvents.

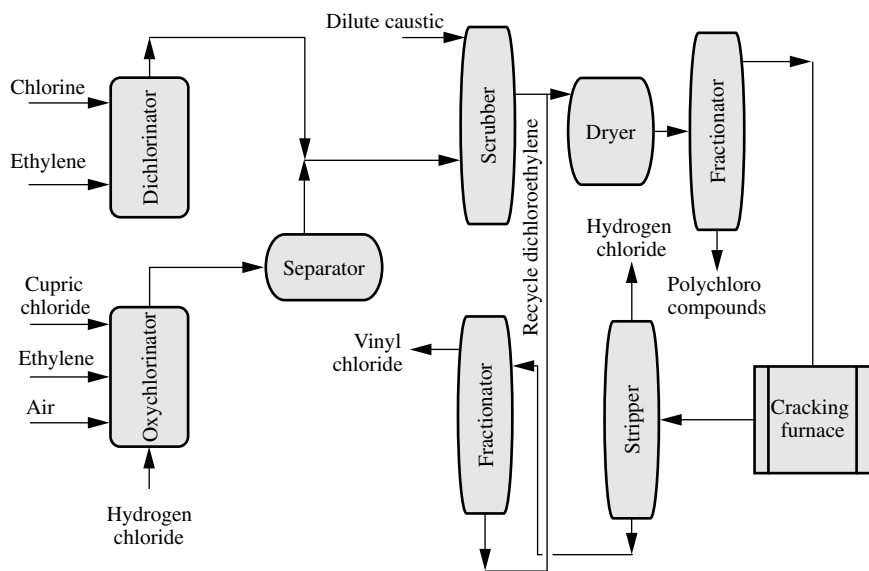
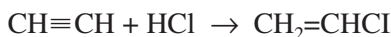
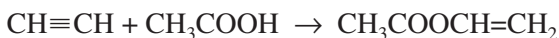


FIGURE 1 Manufacture of vinyl chloride by the oxychlorination process.

VINYL ESTERS

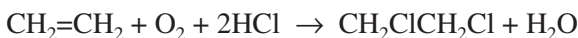
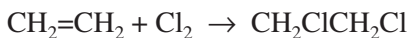
The addition of acids to acetylene furnishes the respective esters by addition across the double bond.



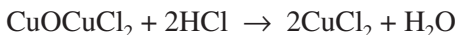
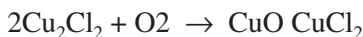
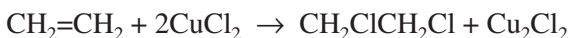
If two molecules of acid react, a compound such as 1,1-ethane diacetate is formed:



Vinyl chloride is usually prepared by the oxychlorination (dehydrochlorination) of ethylene.



The cupric chloride (CuCl_2) catalyst (on an inert fixed carrier) may react as follows:



Exposure to vinyl chloride vapors, even in very small concentrations, causes some workers to develop liver cancer. The government requires that worker exposure to vinyl chloride monomer be no more than 1 ppm over an 8-hour period, and no more than 5 ppm for any 15-minute period. To achieve this requires extensive and expensive pollution-abatement systems.

Vinyl acetate is also made from ethylene in a vapor-phase process. The feed mixture is ethylene, acetic acid, and oxygen, and is circulated through a fixed-bed tubular reactor. The catalyst is a noble metal, probably palladium, and has a life of several years.

See also Vinyl Acetate, Vinyl Chloride, Vinyl Ethers, and Vinyl Fluoride.

VINYL ETHERS

The principal commercial vinyl ethers are methyl vinyl ether (methoxyethene, boiling point: 5.5°C, density: 0.7311, flash point -56°C); ethyl vinyl ether (ethoxyethene, boiling point: 35.7°C, density: 0.7541, flash point: -18°C); and butyl vinyl ether (1-ethenyloxybutane, boiling point: 93.5°C, density: 0.7792, flash point: -1°C). Others such as the *iso*-propyl, *iso*-butyl, hydroxybutyl, decyl, hexadecyl, and octadecyl ethers, as well as the divinyl ethers of butanediol vinyl ethers are miscible with nearly all organic solvents.

The principal methods of manufacture of vinyl ethers utilize vinylation of alcohols or cracking of acetals.

Vinyl ethers undergo all of the expected reactions of olefinic compounds plus a number of other reactions. For example, vinyl ethers react with alcohols give acetals. The acetals are stable under neutral or alkaline conditions and are easily hydrolyzed with dilute acid after other desired reactions have occurred. Reaction of a vinyl ether with water gives acetaldehyde and the corresponding alcohol and reaction of vinyl ethers with carboxylic acids gives 1-alkoxyethyl esters and with thiols gives thioacetals.

Hydrogen halides react vigorously with vinyl ethers to give 1-haloethyl ethers, which are reactive intermediates for further synthesis. Conditions must be carefully selected to avoid polymerization of the vinyl ether, Hydrogen cyanide adds at high temperature to give a 2-alkoxypropionitrile.

Chlorine and bromine add vigorously, giving, with proper control, high yields of 1,2-dihaloethyl ethers. In the presence of an alcohol, halogens add as hypohalites, which give 2-haloacetals. With methanol and iodine, this is used as a method of quantitative analysis by titrating unconsumed iodine with standard thiosulfate solution.

Vinyl ethers serve as a source of vinyl groups for transvinylation of such compounds as 2-pyrrolidinone or caprolactam.

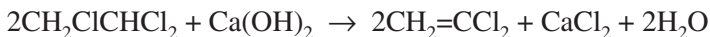
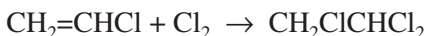
VINYL FLUORIDE

Vinyl fluoride ($\text{CH}_2=\text{CHF}$; melting point: -160.5°C , boiling point: -72.2°C), the monomer for poly(vinyl fluoride), is manufactured by addition of hydrogen fluoride to acetylene:



VINYLENIDE CHLORIDE

Vinylidene chloride can be prepared by the reaction of 1,1,2-trichloroethane (prepared by the chlorination of vinyl chloride) with aqueous alkali.



Other methods are based on bromochloroethane, trichloroethyl acetate, tetrachloroethane, and catalytic cracking of trichloroethane. Catalytic processes produce hydrogen chloride as a by-product.

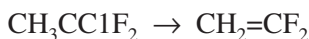
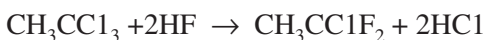
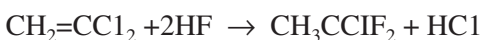
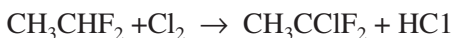
The most common commercial process for the manufacture of vinylidene chloride is the dehydrochlorination of 1,1,2-trichloroethane with lime or caustic in slight excess (2 to 10%). A continuous liquid-phase reaction at 98 to 99°C gives a 90 percent yield of vinylidene.

Washing with water, drying, and fractional distillation purifies vinylidene chloride. It forms an azeotrope with 6% by weight of methyl alcohol, and purification can be achieved by distillation of the azeotrope, followed by extraction of the methanol with water; an inhibitor is usually added at this point.

Commercial grades of vinylidene fluoride may contain an inhibitor such as the monomethyl ether of hydroquinone (MEHQ). This inhibitor can be removed by distillation or by washing with 25% by weight aqueous caustic under an inert atmosphere at low temperatures.

VINYLENIDE FLUORIDE

Vinylidene fluoride is manufactured by the thermal elimination of hydrogen chloride from 1-chloro-1,1-difluoroethane. The starting material (1-chloro-1,1-difluoroethane) is manufactured by any of several different routes.



Dehydrohalogenation of 1-bromo-1,1-difluoroethane or 1,1,1-trifluoroethane, or dehalogenation of 1,2-dichloro-1,1-difluoroethane are alternative routes.

1-chloro-1,1-difluoroethane can also be continuously prepared by the pyrolysis of trifluoromethane (CHF_3) in the presence of a catalyst and either methane or ethylene.