

HALOGENATION

Halogenation is almost always chlorination, for the difference in cost between chlorine and the other halogens, particularly on a molar basis, is quite substantial. In some cases, the presence of bromine (Br), iodine (I), or fluorine (F) confers additional properties to warrant manufacture.

Chlorination proceeds (1) by addition to an unsaturated bond, (2) by substitution for hydrogen, or (3) by replacement of another group such as hydroxyl ($-\text{OH}$) or sulfonic ($-\text{SO}_3\text{H}$). Light catalyzes some chlorination reactions, temperature has a profound effect, and polychlorination almost always occurs to some degree. All halogenation reactions are strongly exothermic.

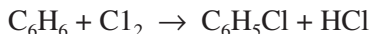
In the chlorination process (Fig.1), chlorine and methane (fresh and recycled) are charged in the ratio 0.6/1.0 to a reactor in which the temperature is maintained at 340 to 370°C. The reaction product contains chlorinated hydrocarbons with unreacted methane, hydrogen chloride, chlorine, and heavier chlorinated products. Secondary chlorination reactions take place at ambient temperature in a light-catalyzed reactor that converts methylene chloride to chloroform, and in a reactor that converts chloroform to carbon tetrachloride. By changing reagent ratios, temperatures, and recycling ratio, it is possible to vary the product mix somewhat to satisfy market demands. Ignition is avoided by using narrow channels and high velocities in the reactor. The chlorine conversion is total, and the methane conversion around 65 percent.

Equipment for the commercial chlorination reactions is more difficult to select, since the combination of halogen, oxygen, halogen acid, water, and heat is particularly corrosive. Alloys such as Hastelloy and Durichlor resist well and are often used, and glass, glass-enameled steel, and tantalum are totally resistant but not always available. Anhydrous conditions permit operation with steel or nickel alloys. With nonaqueous media, apparatus constructed of iron and lined with plastics and/or lead and glazed tile is the most suitable, though chemical stoneware, fused quartz, glass, or glass-lined equipment can be used for either the whole plant or specific apparatus.

of by-product hydrogen chloride from other processes is frequently available and the use of cuprous chloride (CuCl) and cupric chloride (CuCl_2), along with some potassium chloride (KCl) as a molten salt catalyst, enhances the reaction progress.

Ethane can be chlorinated under conditions very similar to those for methane to yield mixed chlorinated ethanes.

Chlorobenzene is used as a solvent and for the manufacture of nitrochlorobenzenes. It is manufactured by passing dry chlorine through benzene, using ferric chloride (FeCl_3) as a catalyst:



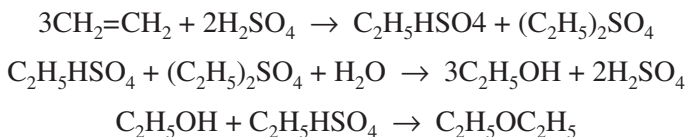
The reaction rates favor production of chlorobenzene over dichlorobenzene by 8.5:1, provided that the temperature is maintained below 60°C . The hydrogen chloride generated is washed free of chlorine with benzene, then absorbed in water. Distillation separates the chlorobenzene, leaving mixed isomers of dichlorobenzene.

In aqueous media, when hydrochloric acid is present in either the liquid or vapor phase and particularly when under pressure, tantalum is undoubtedly the most resistant material of construction. Reactors and catalytic tubes lined with this metal give satisfactory service for prolonged periods.

HYDRATION AND HYDROLYSIS

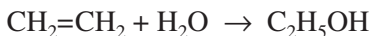
Ethyl alcohol is a product of fermentation of sugars and cellulose but the alcohol is manufactured mostly by the hydration of ethylene.

An indirect process for the manufacture of ethyl alcohol involves the dissolution of ethylene in sulfuric acid to form ethyl sulfate, which is hydrolyzed to form ethyl alcohol (Fig. 1). There is always some by-product diethyl ether that can be either sold or recirculated.



The conversion yield of ethylene to ethyl alcohol is 90 percent with a 5 to 10 percent yield of diethyl ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$).

A direct hydration method using phosphoric acid as a catalyst at 300°C is also available (Fig. 2):



and produces ethyl alcohol in yields in excess of 92 percent. The conversion per pass is 4 to 25 percent, depending on the activity of the catalyst used.

In this process, ethylene and water are combined with a recycle stream in the ratio ethylene/water 1/0.6 (mole ratio), a furnace heats the mixture to 300°C, and the gases react over the catalyst of phosphoric acid absorbed on diatomaceous earth. Unreacted reagents are separated and recirculated. By-product acetaldehyde (CH_3CHO) is hydrogenated over a catalyst to form more ethyl alcohol.

Iso-propyl alcohol is a widely used and easily made alcohol. It is used in making acetone, cosmetics, chemical derivatives, and as a process solvent. There are four processes that are available for the manufacture of *iso*-propyl alcohol:

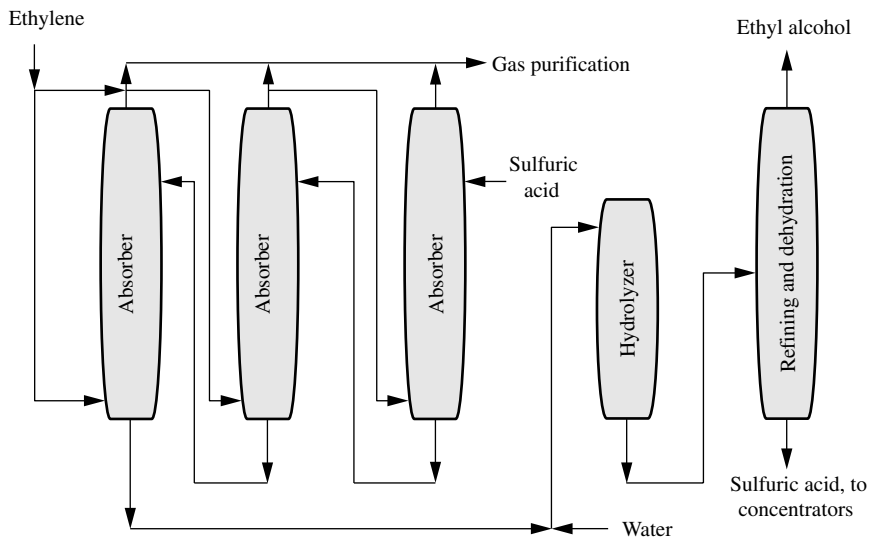


FIGURE 1 Manufacture of ethyl alcohol from ethylene and sulfuric acid.

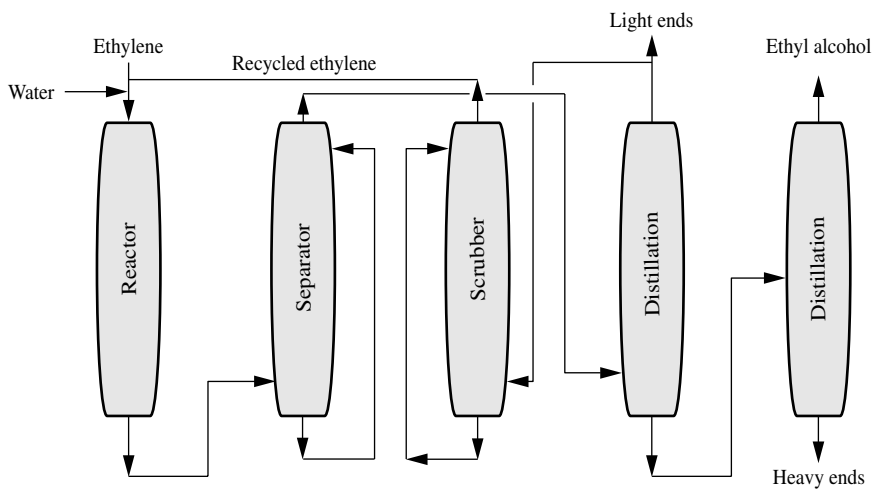


FIGURE 2 Manufacture of ethyl alcohol by direct hydration.

1. A sulfuric acid process similar to the one described for ethanol hydration
2. A gas-phase hydration using a fixed-bed-supported phosphoric acid catalyst
3. A mixed-phase reaction using a cation exchange resin catalyst
4. A liquid-phase hydration in the presence of a dissolved tungsten catalyst

The last three processes (2, 3, and 4) are all essentially direct hydration processes.



Per-pass conversions vary from a low of 5 to a high of 70 percent for the gas-phase reaction.

Secondary butanol ($\text{CH}_3\text{CH}_2\text{CHOHCH}_3$) is manufactured by processes similar to those described for ethylene and propylene.

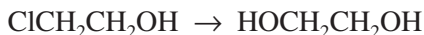
Hydrolysis usually refers to the replacement of a sulfonic group ($-\text{SO}_3\text{H}$) or a chloro group ($-\text{Cl}$) with an hydroxyl group ($-\text{OH}$) and is usually accomplished by fusion with alkali. Hydrolysis uses a far wider range of reagents and operating conditions than most chemical conversion processes.

Polysubstituted molecules may be hydrolyzed with less drastic conditions. Enzymes, acids, or sometimes water can also bring about hydrolysis alone.



Acidification will give the hydroxyl compound (ArOH). Most hydrolysis reactions are modestly exothermic.

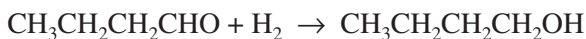
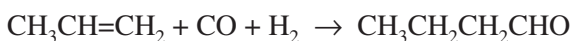
The more efficient route via cumene has superceded the fusion of benzene sulfonic acid with caustic soda for the manufacture of phenol, and the hydrolysis of chlorobenzene to phenol requires far more drastic conditions and is no longer competitive. Ethylene chlorohydrin can be hydrolyzed to glycol with aqueous sodium carbonate.



Cast-iron or steel open fusion pots heated to the high temperatures required (200 to 325°C) with oil, electricity, or directly with gas, are standard equipment.

HYDROFORMYLATION

The hydroformylation (oxo) reactions offer ways of converting α -olefins to aldehydes and/or alcohols containing an additional carbon atom.



In the process (Fig. 1), the olefin in a liquid state is reacted at 27 to 30 MPa and 150 to 170°C in the presence of a soluble cobalt catalyst. The aldehyde and a lesser amount of the alcohol are formed and flashed off along with steam, and the catalyst is recycled. Conversions of over 97 percent are obtained, and the reaction is strongly exothermic. The carbon monoxide and hydrogen are usually in the form of *synthesis gas*.

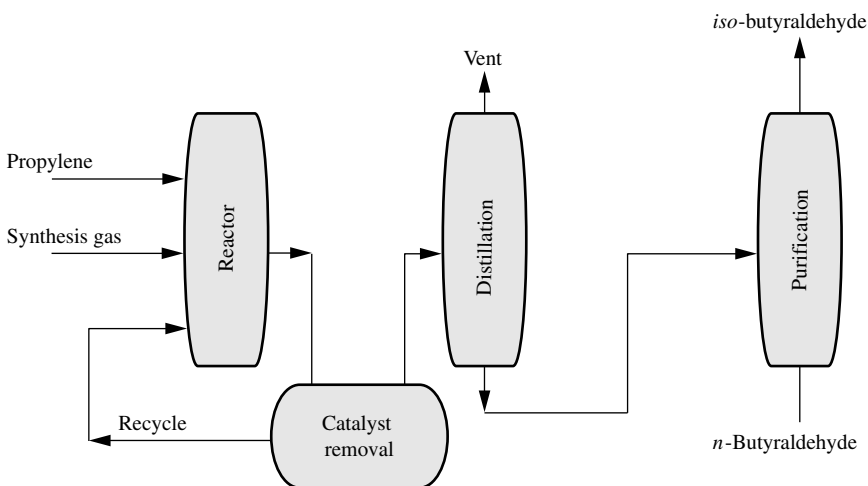


FIGURE 1 Manufacture of butyraldehyde by the hydroformylation (oxo) reaction.

When propylene is used as the hydrocarbon, *n*- and *iso*-butyraldehyde are formed. This reaction is most frequently run with the C₃ and C₇ to C₁₂ olefins. When C₇ olefins are used, a series of dimethyl- and ethylhexanols and methyl heptanols are formed that are used as octyl alcohols to make plasticizers and esters.

See Oxo Reaction.

HYDROGENATION

In its simplest interpretation, hydrogenation is the addition of hydrogen to a chemical compound. Generally, the process involves elevated temperature and relatively high pressure in the presence of a catalyst.

Hydrogenation yields many useful chemicals, and its use has increased phenomenally, particularly in the petroleum refining industry. Besides saturating double bonds, hydrogenation can be used to eliminate other elements from a molecule. These elements include oxygen, nitrogen, halogens, and particularly sulfur. Cracking (thermal decomposition) in the presence of hydrogen is particularly effective in desulfurizing high-boiling petroleum fractions, thereby producing lower-boiling and higher-quality products.

Although occasionally hydrogen for a reaction is provided by donor solvents and a few older reactions use hydrogen generated by acid or alkali acting upon a metal, gaseous hydrogen is the usual hydrogenating agent.

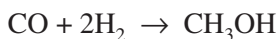
Hydrogenation is generally carried out in the presence of a catalyst and under elevated temperature and pressure. Noble metals, nickel, copper, and various metal oxide combinations are the common catalysts.

Nickel, prepared in finely divided form by reduction of nickel oxide in a stream of hydrogen gas at about 300°C, was introduced by 1897 as a catalyst for the reaction of hydrogen with unsaturated organic substances to be conducted at about 175°C. Nickel proved to be one of the most successful catalysts for such reactions. The unsaturated organic substances that are hydrogenated are usually those containing a double bond, but those containing a triple bond also may be hydrogenated. Platinum black, palladium black, copper metal, copper oxide, nickel oxide, aluminum, and other materials have subsequently been developed as hydrogenation catalysts. Temperatures and pressures have been increased in many instances to improve yields of desired product. The hydrogenation of methyl ester to fatty alcohol and methanol, for example, occurs at about 290 to 315°C and 3000 psi (20.7 MPa). In the hydrotreating of liquid hydrocarbon fuels to improve quality, the reaction may take place in fixed-bed reactors at pressures ranging from 100 to 3000 psi (690 kPa to 20.7 MPa).

Many hydrogenation processes are of a proprietary nature, with numerous combinations of catalysts, temperature, and pressure possible.

Lower pressures and higher temperatures favor dehydrogenation, but the catalysts used are the same as for hydrogenation.

Methyl alcohol (methanol) is manufactured from a mixture of carbon monoxide and hydrogen (synthesis gas), using a copper-based catalyst.



In the process (Fig. 1), the reactor temperature is 250 to 260°C at a pressure of 725 to 1150 psi (5 to 8 MPa). High- and low-boiling impurities are removed in two columns and the unreacted gas is recirculated.

New catalysts have helped increase the conversion and yields. The older, high-pressure processes used zinc-chromium catalysts, but the low-pressure units use highly active copper catalysts. Liquid-entrained micrometer-sized catalysts have been developed that can convert as much as 25 percent per pass. Contact of the synthesis gases with hot iron catalyzes competing reactions and also forms volatile iron carbonyl that fouls the copper catalyst. Some reactors are lined with copper.

Because the catalyst is sensitive to sulfur, the gases are purified by one of several sulfur-removing processes, then are fed through heat exchangers into one of two types of reactors. With bed-in-place reactors, steam at around 4.5 kPa, in quantity sufficient to drive the gas compressors, can be generated. A tray-type reactor with gases introduced just above every bed

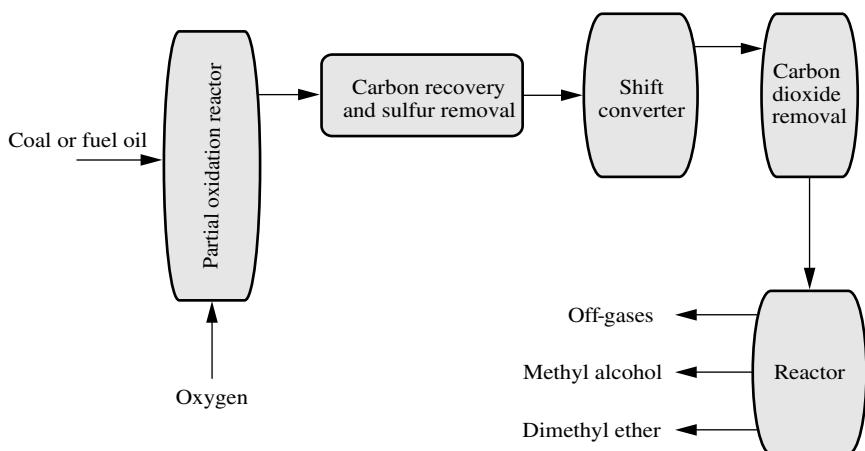


FIGURE 1 Manufacture of methyl alcohol from synthesis gas.

for cooling offers more nearly isothermal operation but does not give convenient heat recovery.

Reaction vessels are usually of two types: one in which the contents are agitated or stirred in some way and the other in which the reactor and contents are stationary. The first is used with materials such as solids or liquids that need to be brought into intimate contact with the catalyst and the hydrogen. The second type is used where the substance may have sufficient vapor pressure at the temperature of operation so that a gas-phase as well as a liquid-phase reaction is possible. It is also most frequently used in continuous operation where larger quantities of material need to be processed than can be done conveniently with batch methods.

In hydrogenation processes, heating of the ingoing materials is best accomplished by heat exchange with the outgoing materials and adding additional heat by means of high-pressure pipe coils. A pipe coil is the only convenient and efficient method of heating, for the reactor is usually so large that heating it is very difficult. It is usually better practice to add all the heat needed to the materials before they enter the reactor and then simply have the reactor properly insulated thermally. Hydrogenation reactions are usually exothermic, so that once the process is started, the problem may be one of heat removal. This is accomplished by allowing the heat of reaction to flow into the ingoing materials by heat exchange in the reactor, or, if it is still in excess, by recycling and cooling in heat exchangers the proper portion of the material to maintain the desired temperature.

See Dehydrogenation.