Part 1

REACTION TYPES

ALKYLATION

Alkylation is usually used to increase performance of a product and involves the conversion of, for example, an amine to its alkylated homologs as in the reaction of aniline with methyl alcohol in the presence of sulfuric acid catalyst:

$$C_6H_5NH_2 + 2CH_3OH \rightarrow C_6H_5N(CH_3)_2 + 2H_2O$$

Thus, aniline, with a considerable excess of methyl alcohol and a catalytic amount of sulfuric acid, is heated in an autoclave at about 200°C for 5 or 6 hours at a high reaction pressure of 540 psi (3.7 MPa). Vacuum distillation is used for purification.

In the alkylation of aniline to diethylaniline by heating aniline and ethyl alcohol, sulfuric acid cannot be used because it will form ether; consequently, hydrochloric acid is employed, but these conditions are so corrosive that the steel used to resist the pressure must be fitted with replaceable enameled liners.

Alkylation reactions employing alkyl halides are carried out in an acidic medium. For example, hydrobromic acid is formed when methyl bromide is used in the alkylation leading, and for such reactions an autoclave with a replaceable enameled liner and a lead-coated cover is suitable.

In the petroleum refining industry, alkylation is the union of an olefin with an aromatic or paraffinic hydrocarbon:

$$CH_2{=}CH_2 + (CH_3)_3CH \rightarrow (CH_3)_3CCH_2CH_3$$

Alkylation processes are exothermic and are fundamentally similar to refining industry polymerization processes but they differ in that only part of the charging stock need be unsaturated. As a result, the *alkylate* product contains no olefins and has a higher octane rating. These methods are based on the reactivity of the tertiary carbon of the *iso*-butane with olefins, such as propylene, butylenes, and amylenes. The product *alkylate* is a mixture of saturated, stable isoparaffins distilling in the gasoline range, which becomes a most desirable component of many high-octane gasolines.

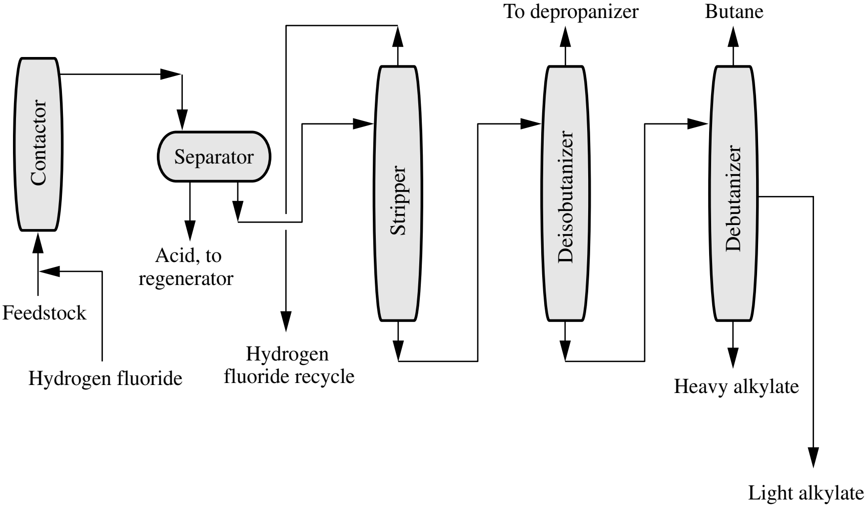

FIGURE 1 Alkylation using hydrogen fluoride.

Alkylation is accomplished by using either of two catalysts: (1) hydrogen fluoride and (2) sulfuric acid. In the alkylation process using liquid hydrogen fluoride (Fig. 1), the acid can be used repeatedly, and there is virtually no acid-disposal problem. The acid/hydrocarbon ratio in the contactor is 2:1 and temperature ranges from 15 to 35°C can be maintained since no refrigeration is necessary. The anhydrous hydrofluoric acid is regenerated by distillation with sufficient pressure to maintain the reactants in the liquid phase.

In many cases, steel is suitable for the construction of alkylating equipment, even in the presence of the strong acid catalysts, as their corrosive effect is greatly lessened by the formation of esters as catalytic intermediate products.

In the petroleum industry, the sulfuric acid and hydrogen fluoride employed as alkylation catalysts must be substantially anhydrous to be effective, and steel equipment is satisfactory. Where conditions are not anhydrous, lead-lined, monel-lined, or enamel-lined equipment is satisfactory. In a few cases, copper or tinned copper is still used, for example, in the manufacture of pharmaceutical and photographic products to lessen contamination with metals.

Distillation is usually the most convenient procedure for product recovery, even in those instances in which the boiling points are rather close together. Frequently such a distillation will furnish a finished material of quality sufficient to meet the demands of the market. If not, other means of purification may be necessary, such as crystallization or separation by means of solvents. The choice of a proper solvent will, in many instances, lead to the crystallization of the alkylated product and to its convenient recovery.

The converse reactions *dealkylation* and *hydrodealkylation* are practiced extensively to convert available feedstocks into other more desirable (marketable), products. Two such processes are: (1) the conversion of toluene or xylene, or the higher-molecular-weight alkyl aromatic compounds, to benzene in the presence of hydrogen and a suitable presence of a dealkylation catalyst and (2) the conversion of toluene in the presence of hydrogen and a fixed bed catalyst to benzene plus mixed xylenes.

AMINATION

Amination is the process of introducing the amino group (–NH_2) into an organic compound as, for example, the production of aniline ($C_6H_5NH_2$) by the reduction of nitrobenzene ($C_6H_5NO_2$) in the liquid phase (Fig. 1) or in the vapor phase in a fluidized bed reactor (Fig. 2). For many decades, the only method of putting an amino group on an aryl nucleus involved adding a nitro (–NO_2) group, then *reduction* to the amino (–NH_2) group.

Without high-pressure vessels and catalysts, reduction had to be done by reagents that would function under atmospheric pressure. The common reducing agents available under these restrictions are:

1. Iron and acid
2. Zinc and alkali
3. Sodium sulfide or polysulfide
4. Sodium hydrosulfite
5. Electrolytic hydrogen
6. Metal hydrides

Now liquid- and gas-phase hydrogenations can be performed on a variety of materials.

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O$$

Where metals are used to produce the reducing hydrogen, several difficult processing problems are created. The expense is so great that it is necessary to find some use for the reacted material. Spent iron can sometimes be used for pigment preparations or to absorb hydrogen sulfide. Stirring a vessel containing much metal is quite difficult.

On a small scale, cracking ammonia can produce hydrogen for reduction. Transport and storage of hydrogen as ammonia is compact, and the cracking procedure involves only a hot pipe packed with catalyst and

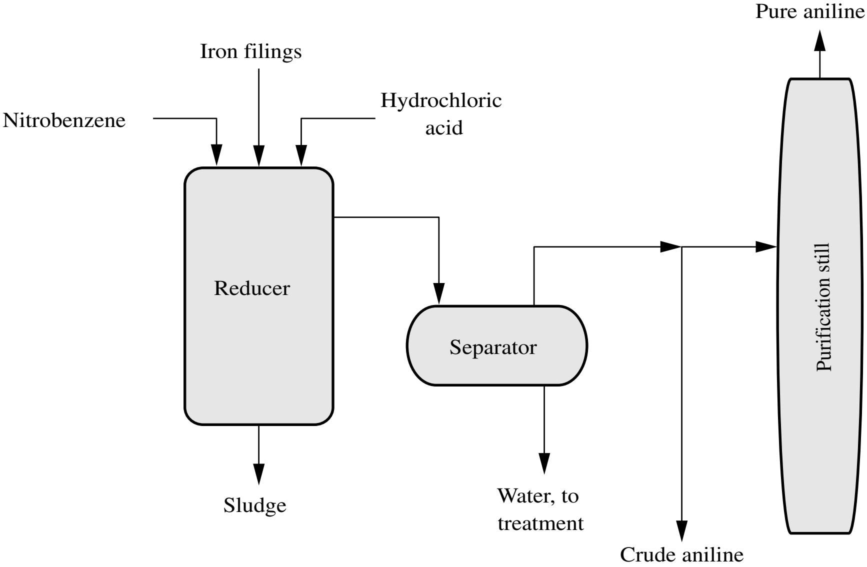

FIGURE 1 Aniline production by the reduction of nitrobenzene.

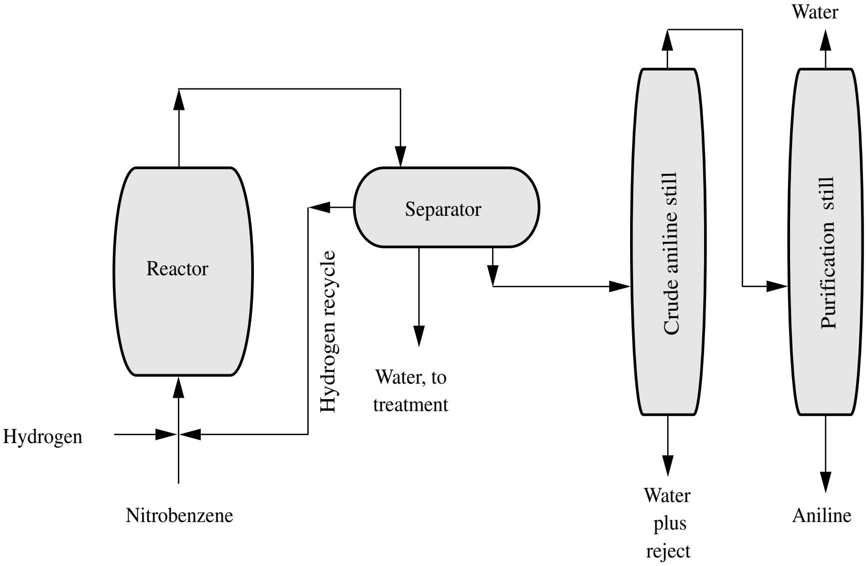

FIGURE 2 Vapor phase reduction of nitrobenzene to aniline.

immersed in a molten salt bath. The nitrogen that accompanies the generated hydrogen is inert.

Amination is also achieved by the use of ammonia (NH_3), in a process referred to as *ammonolysis*. An example is the production of aniline ($C_6H_5NH_2$) from chlorobenzene (C_6H_5Cl) with ammonia (NH_3). The reaction proceeds only under high pressure.

The replacement of a nuclear substituent such as hydroxyl (–OH), chloro, (–Cl), or sulfonic acid ($–SO_3H$) with amino ($–NH_2$) by the use of ammonia (*ammonolysis*) has been practiced for some time with feedstocks that have reaction-inducing groups present thereby making replacement easier. For example, 1,4-dichloro-2-nitrobenzene can be changed readily to 4-chloro-2-nitroaniline by treatment with aqueous ammonia. Other molecules offer more processing difficulty, and pressure vessels are required for the production of aniline from chlorobenzene or from phenol (Fig. 3).

$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

Ammonia is a comparatively low cost reagent, and the process can be balanced to produce the desired amine. The other routes to amines

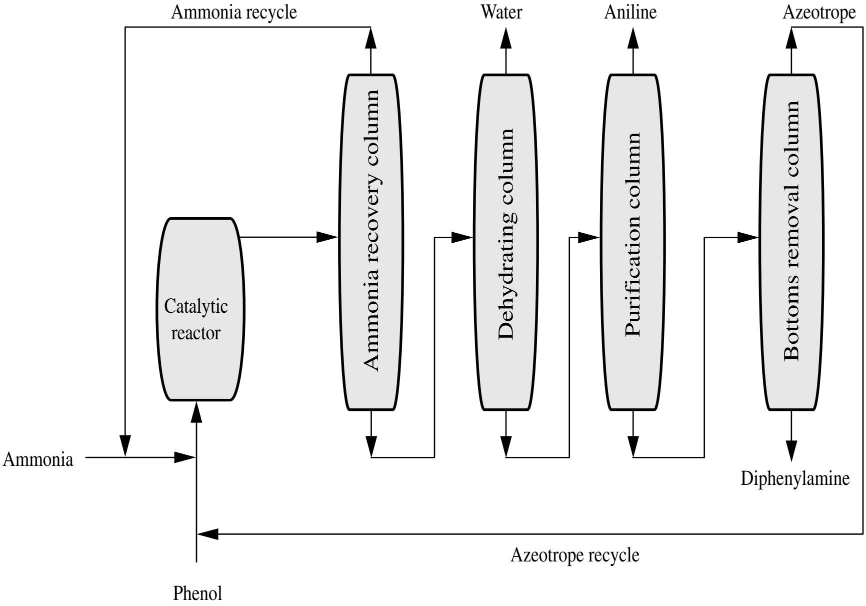

FIGURE 3 Aniline and diphenylamine production from phenol.

through reduction use expensive reagents (iron, Fe, zinc, Zn, or hydrogen, H_2, gas) that make ammonolysis costs quite attractive. Substituted amines can be produced by using substituted ammonia (amines) in place of simple ammonia. The equipment is an agitated iron pressure vessel; stainless steel is also used for vessel construction.

Amination by reduction is usually carried out in cast-iron vessels (1600 gallons capacity, or higher) and alkali reductions in carbon steel vessels of desired sizes. The vessel is usually equipped with a nozzle at the base so that the iron oxide sludge or entire charge may be run out upon completion of the reaction.

In some reducers, a vertical shaft carries a set of cast-iron stirrers to keep the iron particles in suspension in the lower part of the vessel and to maintain all the components of the reaction in intimate contact. In addition, the stirrer assists in the diffusion of the amino compound away from the surface of the metal and thereby makes possible a more extensive contact between nitro body and catalytic surface.

Thus, amination, or reaction with ammonia, is used to form both aliphatic and aromatic amines. Reduction of nitro compounds is the traditional process for producing amines, but ammonia or substituted ammonias (amines) react directly to form amines. The production of aniline by amination now exceeds that produced by reduction (of nitrobenzene).

Oxygen-function compounds also may be subjected to ammonolysis, for example:

1. Methanol plus aluminum phosphate catalyst yields monomethylamine (CH_3NH_2), dimethylamine [$(CH_3)2NH$], and trimethylamine [$(CH_3)3N$]
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Methylamines are produced by reacting gaseous methanol with a catalyst at 350 to 400°C and 290 psi (2.0 MPa), then distilling the reaction mixture. Any ratio of mono-, di-, or trimethylamines is possible by recycling the unwanted products.

An equilibrium mixture of the three ethanolamines is produced when ethylene oxide is bubbled through 28% aqueous ammonia at 30 to 40°C. By recirculating the products of the reaction, altering the temperatures, pressures, and the ratio of ammonia to ethylene oxide, but always having an excess of ammonia, it is possible to make the desired amine predominate. Diluent gas also alters the product ratio.

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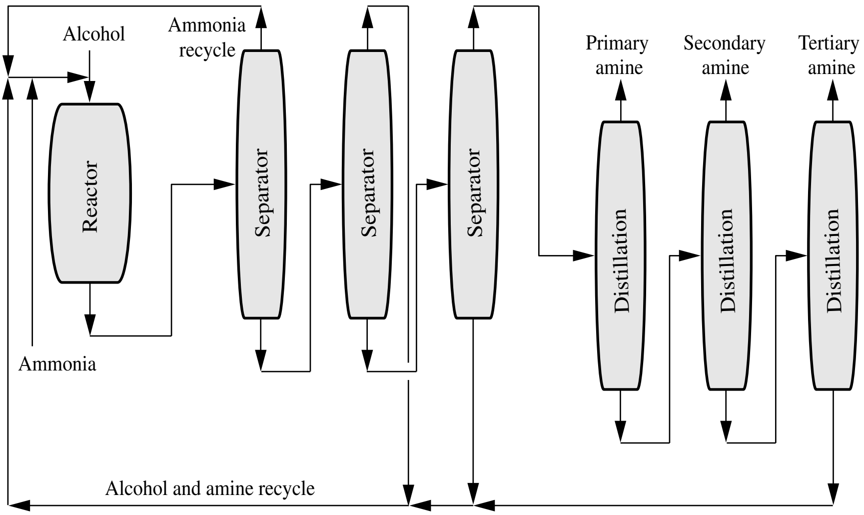

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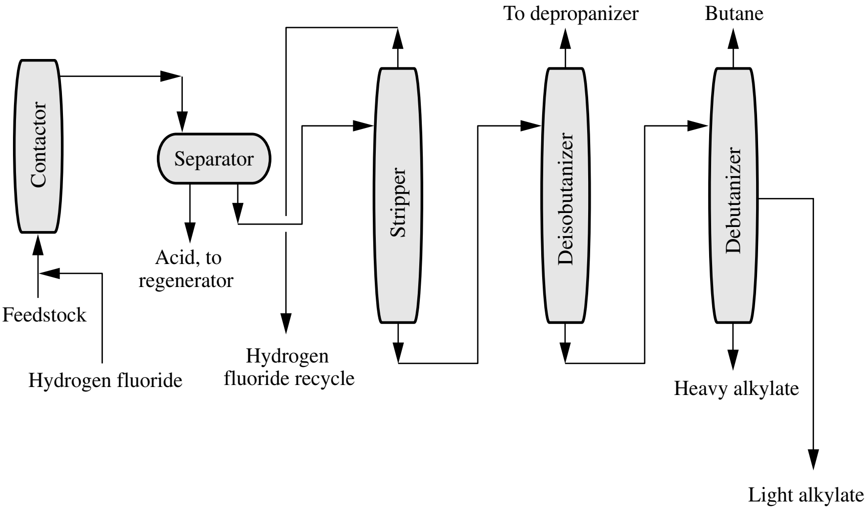

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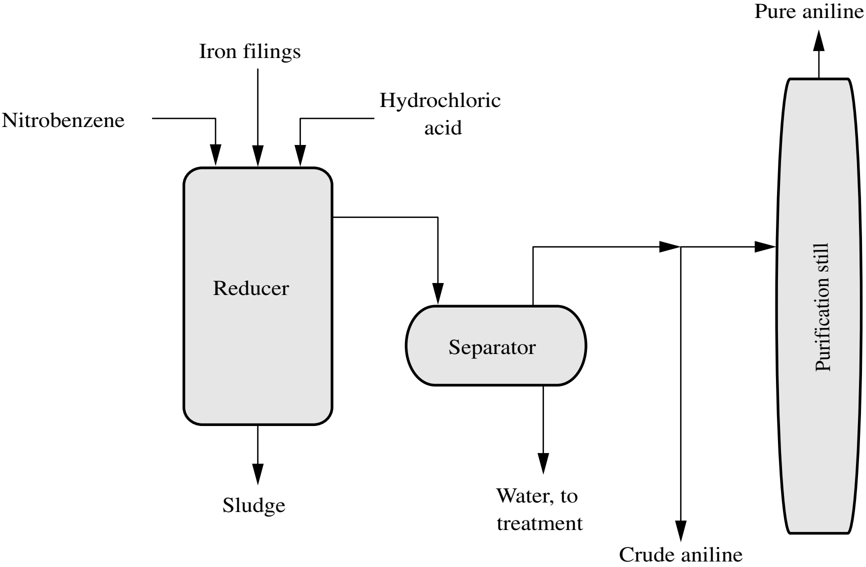

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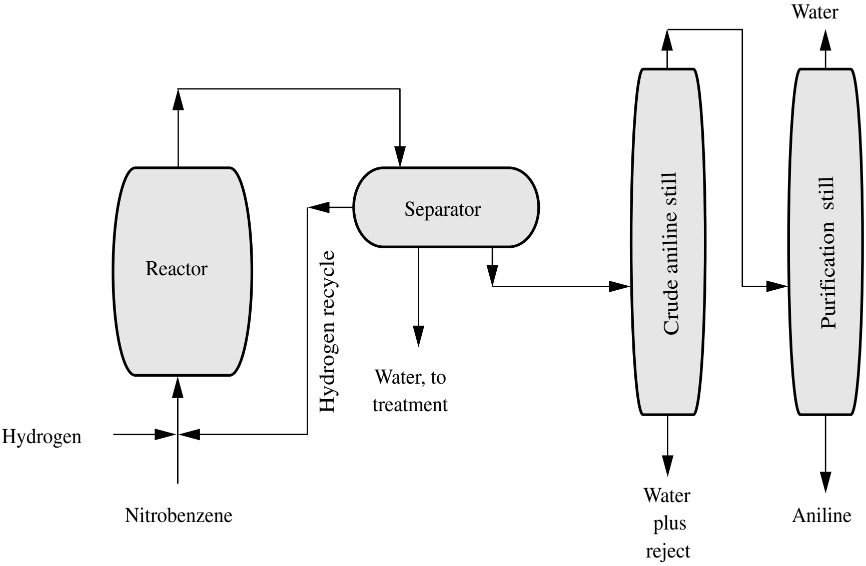

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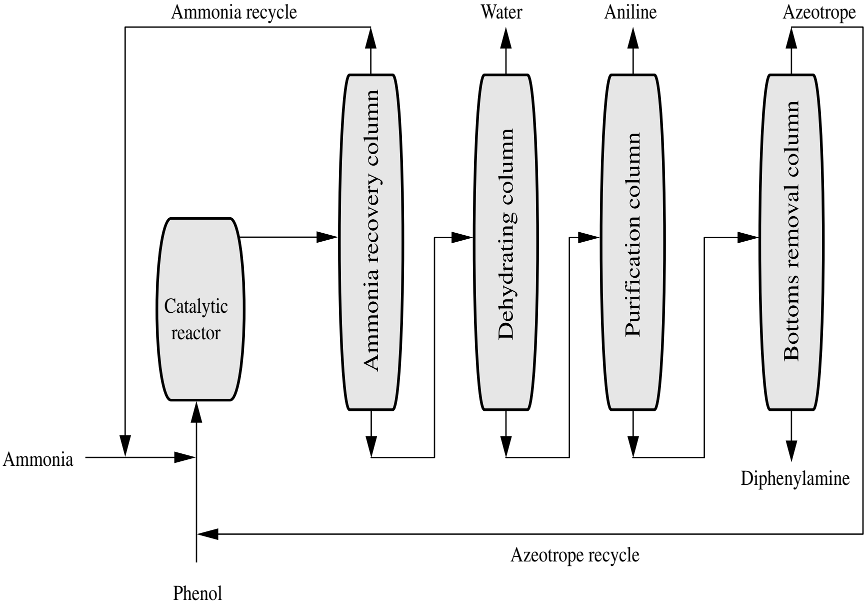

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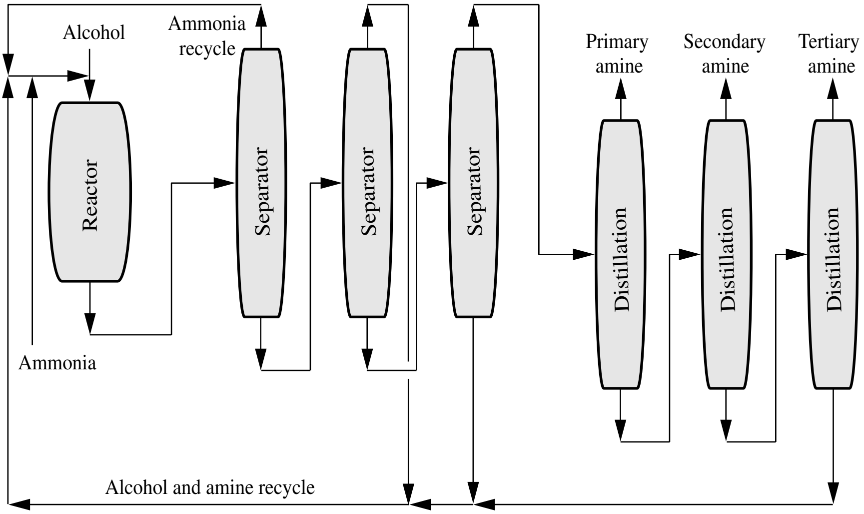

FIGURE 4 Amination process for amine production.

Other alkylamines can be made in similar fashion from the alcohol and ammonia (Fig. 4). Methyl, ethyl, isopropyl, cyclohexyl, and combination amines have comparatively small markets and are usually made by reacting the correct alcohol with anhydrous ammonia in the vapor phase.

CONDENSATION AND ADDITION

There are only a few products manufactured in any considerable tonnage by condensation and addition (Friedel-Crafts) reactions, but those that are find use in several different intermediates and particularly in making high-quality vat dyes.

The agent employed in this reaction is usually an acid chloride or anhydride, catalyzed with aluminum chloride. Phthalic anhydride reacts with chlorobenzene to give *p*-chlorobenzoylbenzoic acid and, in a continuing action, the *p*-chlorobenzoylbenzoic acid forms β-chloroanthraquinone.

Since anthraquinone is a relatively rare and expensive component of coal tar and petroleum, this type of reaction has been the basis for making relatively inexpensive anthraquinone derivatives for use in making many fast dyes for cotton.

Friedel-Crafts reactions are highly corrosive, and the aluminum-containing residues are difficult to dispose.

DEHYDRATION

Dehydration is the removal of water or the elements of water, in the correct proportion, from a substance or system or chemical compound. The elements of water may be removed from a single molecule or from more than one molecule, as in the dehydration of alcohol, which may yield ethylene by loss of the elements of water from one molecule or ethyl ether by loss of the elements of water from two molecules:

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$$

$$2CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O$$

The latter reaction is commonly used in the production of ethers by the dehydration of alcohols.

Vapor-phase dehydration over catalysts such as alumina is also practiced. Hydration of olefins to produce alcohols, usually over an acidic catalyst, produces substantial quantities of ethers as by-products. The reverse reaction, ethers to alcohols, can be accomplished by recycling the ethers over a catalyst.

In food processing, dehydration is the removal of more than 95% of the water by use of thermal energy. However, there is no clearly defined line of demarcation between *drying* and *dehydrating*, the latter sometimes being considered as a supplement of drying.

The term *dehydration* is not generally applied to situations where there is a loss of water as the result of evaporation. The distinction between the terms drying and dehydrating may be somewhat clarified by the fact that most substances can be dried beyond their capability of restoration.

Rehydration or *reconstitution* is the restoration of a dehydrated food product to its original edible condition by the simple addition of water, usually just prior to consumption or further processing.

DEHYDROGENATION

Dehydrogenation is a reaction that results in the removal of hydrogen from an organic compound or compounds, as in the dehydrogenation of ethane to ethylene:

$$CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2$$

This process is brought about in several ways. The most common method is to heat hydrocarbons to high temperature, as in thermal cracking, that causes some dehydrogenation, indicated by the presence of unsaturated compounds and free hydrogen.

In the chemical process industries, nickel, cobalt, platinum, palladium, and mixtures containing potassium, chromium, copper, aluminum, and other metals are used in very large-scale dehydrogenation processes.

Styrene is produced from ethylbenzene by dehydrogenation (Fig. 1). Many lower molecular weight aliphatic *ketones* are made by *dehydration*

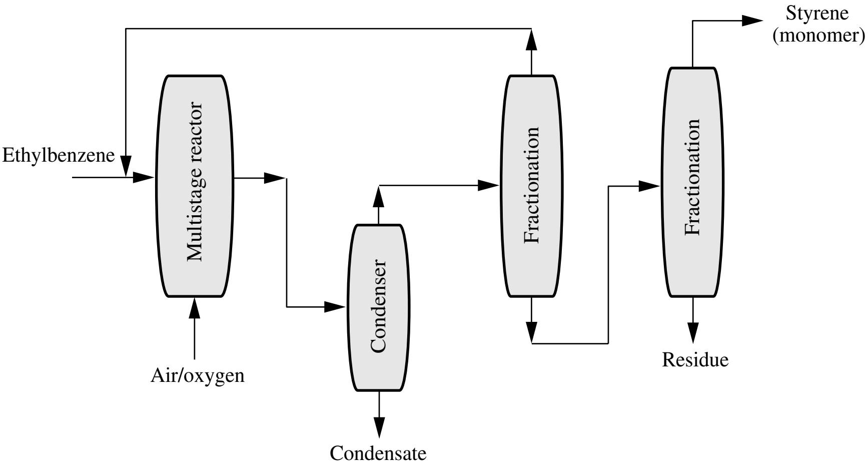

FIGURE 1 Manufacture of styrene from ethylbenzene.

of alcohols. Acetone, methyl ethyl ketone, and cyclohexanone can be made in this fashion.

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

Acetone is the ketone used in largest quantity and is produced as a by-product of the manufacture of phenol via cumene. Manufacture from *iso*-propanol is by the reaction:

$$(CH_3)_2CHOH \rightarrow (CH_3)_2C{=}O$$

This reaction takes place at 350ºC and 200 kPa with copper or zinc acetate as the catalyst; conversion is 85 to 90 percent. Purification by distillation follows.

The dehydrogenation of *n*-paraffins yields detergent alkylates and *n*-olefins. The catalytic use of rhenium for selective dehydrogenation has increased in recent years since dehydrogenation is one of the most commonly practiced of the chemical unit processes.

See ***Hydrogenation.***

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Styrene is produced from ethylbenzene by dehydrogenation (Fig. 1). Many lower molecular weight aliphatic *ketones* are made by *dehydration*

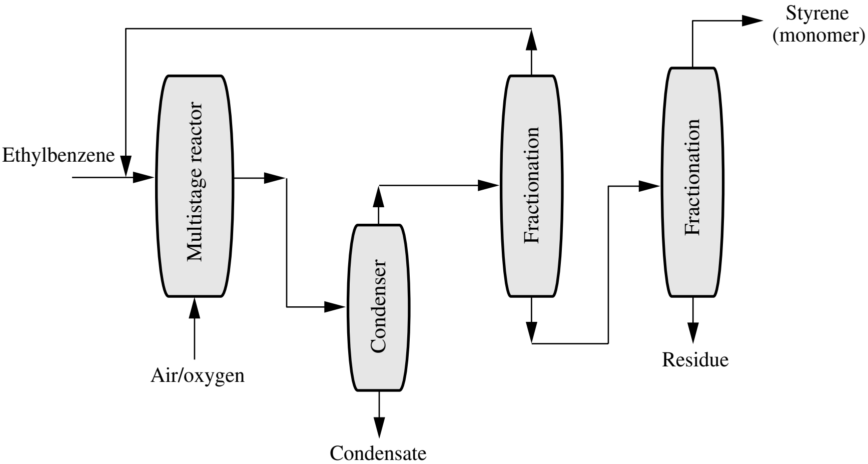

FIGURE 1 Manufacture of styrene from ethylbenzene.

of alcohols. Acetone, methyl ethyl ketone, and cyclohexanone can be made in this fashion.

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

Acetone is the ketone used in largest quantity and is produced as a by-product of the manufacture of phenol via cumene. Manufacture from *iso*-propanol is by the reaction:

$$(CH_3)_2CHOH \rightarrow (CH_3)_2C{=}O$$

This reaction takes place at 350ºC and 200 kPa with copper or zinc acetate as the catalyst; conversion is 85 to 90 percent. Purification by distillation follows.

The dehydrogenation of *n*-paraffins yields detergent alkylates and *n*-olefins. The catalytic use of rhenium for selective dehydrogenation has increased in recent years since dehydrogenation is one of the most commonly practiced of the chemical unit processes.

*See **Hydrogenation.***

CONDENSATION AND ADDITION

There are only a few products manufactured in any considerable tonnage by condensation and addition (Friedel-Crafts) reactions, but those that are find use in several different intermediates and particularly in making high-quality vat dyes.

The agent employed in this reaction is usually an acid chloride or anhydride, catalyzed with aluminum chloride. Phthalic anhydride reacts with chlorobenzene to give *p*-chlorobenzoylbenzoic acid and, in a continuing action, the *p*-chlorobenzoylbenzoic acid forms β-chloroanthraquinone.

Since anthraquinone is a relatively rare and expensive component of coal tar and petroleum, this type of reaction has been the basis for making relatively inexpensive anthraquinone derivatives for use in making many fast dyes for cotton.

Friedel-Crafts reactions are highly corrosive, and the aluminum-containing residues are difficult to dispose.

DEHYDRATION

Dehydration is the removal of water or the elements of water, in the correct proportion, from a substance or system or chemical compound. The elements of water may be removed from a single molecule or from more than one molecule, as in the dehydration of alcohol, which may yield ethylene by loss of the elements of water from one molecule or ethyl ether by loss of the elements of water from two molecules:

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$$

$$2CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O$$

The latter reaction is commonly used in the production of ethers by the dehydration of alcohols.

Vapor-phase dehydration over catalysts such as alumina is also practiced. Hydration of olefins to produce alcohols, usually over an acidic catalyst, produces substantial quantities of ethers as by-products. The reverse reaction, ethers to alcohols, can be accomplished by recycling the ethers over a catalyst.

In food processing, dehydration is the removal of more than 95% of the water by use of thermal energy. However, there is no clearly defined line of demarcation between *drying* and *dehydrating*, the latter sometimes being considered as a supplement of drying.

The term *dehydration* is not generally applied to situations where there is a loss of water as the result of evaporation. The distinction between the terms drying and dehydrating may be somewhat clarified by the fact that most substances can be dried beyond their capability of restoration.

Rehydration or *reconstitution* is the restoration of a dehydrated food product to its original edible condition by the simple addition of water, usually just prior to consumption or further processing.

DEHYDROGENATION

Dehydrogenation is a reaction that results in the removal of hydrogen from an organic compound or compounds, as in the dehydrogenation of ethane to ethylene:

$$CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2$$

This process is brought about in several ways. The most common method is to heat hydrocarbons to high temperature, as in thermal cracking, that causes some dehydrogenation, indicated by the presence of unsaturated compounds and free hydrogen.

In the chemical process industries, nickel, cobalt, platinum, palladium, and mixtures containing potassium, chromium, copper, aluminum, and other metals are used in very large-scale dehydrogenation processes.

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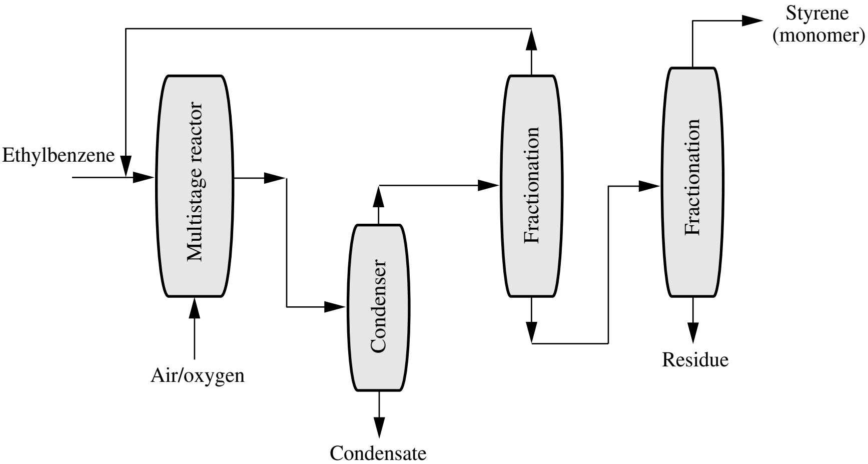

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See ***Hydrogenation.***

ESTERIFICATION

A variety of solvents, monomers, medicines, perfumes, and explosives are made from esters of nitric acid. Ethyl acetate, *n*-butyl acetate, *iso*-butyl acetate, glycerol trinitrate, pentaerythritol tetranitrate (PETN), glycol dinitrate, and cellulose nitrate are examples of such reactions.

Ester manufacture is a relatively simple process in which the alcohol and an acid are heated together in the presence of a sulfuric acid catalyst, and the reaction is driven to completion by removing the products as formed (usually by distillation) and employing an excess of one of the reagents. In the case of ethyl acetate, esterification takes place in a column that takes a ternary azeotrope. Alcohol can be added to the condensed overhead liquid to wash out the alcohol, which is then purified by distillation and returned to the column to react.

Amyl, butyl, and *iso*-propyl acetates are all made from acetic acid and the appropriate alcohols. All are useful lacquer solvents and their slow rate of evaporation (compared to acetone or ethyl acetate) prevents the surface of the drying lacquer from falling below the dew point, which would cause condensation on the film and a mottled surface appearance (*blushing*). Other esters of importance are used in perfumery and in plasticizers and include methyl salicylate, methyl anthranilate, diethyl-phthalate, dibutyl-phthalate, and di-2-ethylhexyl-phthalate.

Unsaturated vinyl esters for use in polymerization reactions are made by the esterification of olefins. The most important ones are vinyl esters: vinyl acetate, vinyl chloride, acrylonitrile, and vinyl fluoride. The addition reaction may be carried out in either the liquid, vapor, or mixed phases, depending on the properties of the acid. Care must be taken to reduce the polymerization of the vinyl ester produced.

Esters of allyl alcohol, e.g., diallyl phthalate, are used as bifunctional polymerization monomers and can be prepared by simple esterification of phthalic anhydride with allyl alcohol. Several acrylic esters, such as ethyl or methyl acrylates, are also widely used and can be made from acrylic acid and the appropriate alcohol. The esters are more volatile than the corresponding acids.

ETHYNYLATION

The *ethynylation* reaction involves the addition of acetylene to carbonyl compounds.

$$HC{\equiv}CH + R^1COR^2 \rightarrow HC{\equiv}CC(OH)R^1R^2$$

Heavy metal acetylides, particularly cuprous acetylide ($CuC{\equiv}CH$), catalyze the addition of acetylene ($HC{\equiv}CH$) to aldehydes ($RCH{=}O$).

FERMENTATION

Fermentation processes produce a wide range of chemicals that complement the various chemicals produced by nonfermentation routes. For example, alcohol, acetone, butyl alcohol, and acetic acid are produced by fermentation as well as by synthetic routes. Almost all the major antibiotics are obtained from fermentation processes.

Fermentation under controlled conditions involves chemical conversions, and some of the more important processes are:

1. O*xidation,* e.g., ethyl alcohol to acetic acid, sucrose to citric acid, and dextrose to gluconic acid
2. *Reduction,* e.g., aldehydes to alcohols (acetaldehyde to ethyl alcohol) and sulfur to hydrogen sulfide
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FRIEDEL-CRAFTS REACTIONS

Several chemicals are manufactured by application of the Friedel-Crafts condensation reaction. Efficient operation of any such process depends on:

1. The preparation and handling of reactants
2. The design and construction of the apparatus
3. The control of the reaction so as to lead practically exclusively to the formation of the specific products desired
4. The storage of the catalyst (aluminum chloride)

Several of the starting reactants, such as acid anhydrides, acid chlorides, and alkyl halides, are susceptible to hydrolysis. The absorption of moisture by these chemicals results in the production of compounds that are less active, require more aluminum chloride for condensation, and generally lead to lower yields of desired product. Furthermore, the ingress of moisture into storage containers for these active components usually results in corrosion problems.

Anhydrous aluminum chloride needs to be stored in iron drums under conditions that ensure the absence of moisture. When, however, moisture contacts the aluminum chloride, hydrogen chloride is formed, the quantity of hydrogen chloride thus formed depends on the amount of water and the degree of agitation of the halide. If sufficient moisture is present, particularly in the free space in the container or reaction vessel or at the point of contact with the outside atmosphere, then hydrochloric acid is formed and leads to corrosion of the storage container.

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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 (–OH) or sulfonic ($–SO_3H$). 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^{o}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.

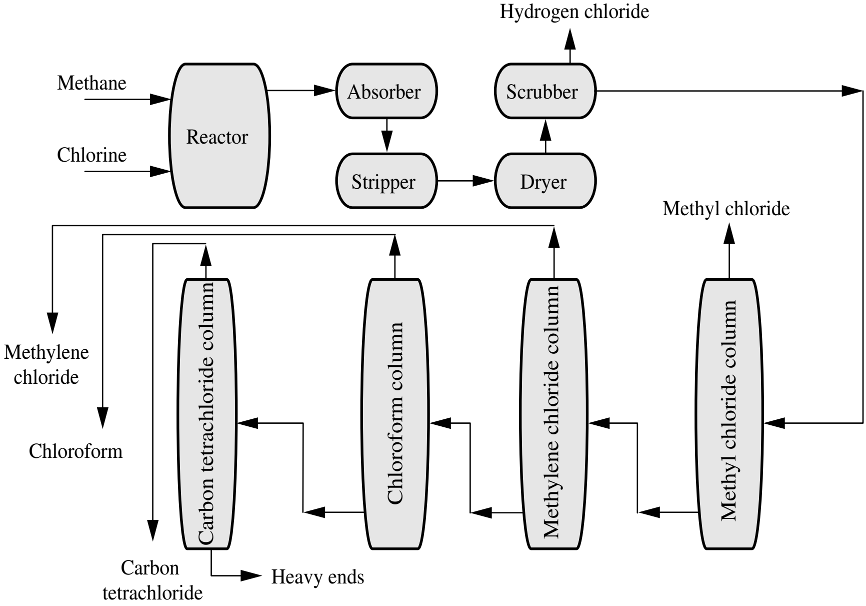

FIGURE 1 Production of chloromethanes by chlorination of methane.

When chlorination has to be carried out at a low temperature, it is often beneficial to circulate cooling water through a lead coil within the chlorinator or circulate the charge through an outside cooling system rather than to make use of an external jacket. When the temperature is to be maintained at 0°C or below, a calcium chloride brine, cooled by a refrigerating machine, is employed.

Most chlorination reactions produce hydrogen chloride as a by-product, and a method was searched for to make this useful for further use:

$$4HCl + O_2 \rightarrow 2H_2O + 2C1_2$$

However, this is not a true equilibrium reaction, with a tendency to favor hydrogen chloride. The reaction can be used and driven to completion by use of the *oxychlorination* procedure that reacts the chlorine with a reactive substance as soon as it is formed, thus driving the reaction to completion as, for example, in the oxychlorination of methane:

$$CH_4 + HCl + O_2 \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + H_2O$$

This chlorination can be accomplished with chlorine but a mole of hydrogen chloride is produced for every chlorine atom introduced into the methane, and this must be disposed of to prevent environmental pollution. Thus, the use

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:

$$C_6H_6 + C1_2 \rightarrow C_6H_5Cl + HCl$$

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.

$$3CH_2{=}CH_2 + 2H_2SO_4 \rightarrow C_2H_5HSO4 + (C_2H_5)_2SO_4$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

$$C_2H_5OH + C_2H_5HSO_4 \rightarrow C_2H_5OC_2H_5$$

The conversion yield of ethylene to ethyl alcohol is 90 percent with a 5 to 10 percent yield of diethyl ether ($C_2H_5OC_2H_5$).

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

$$CH_2{=}CH_2 + H_2O \rightarrow C_2H_5OH$$

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.

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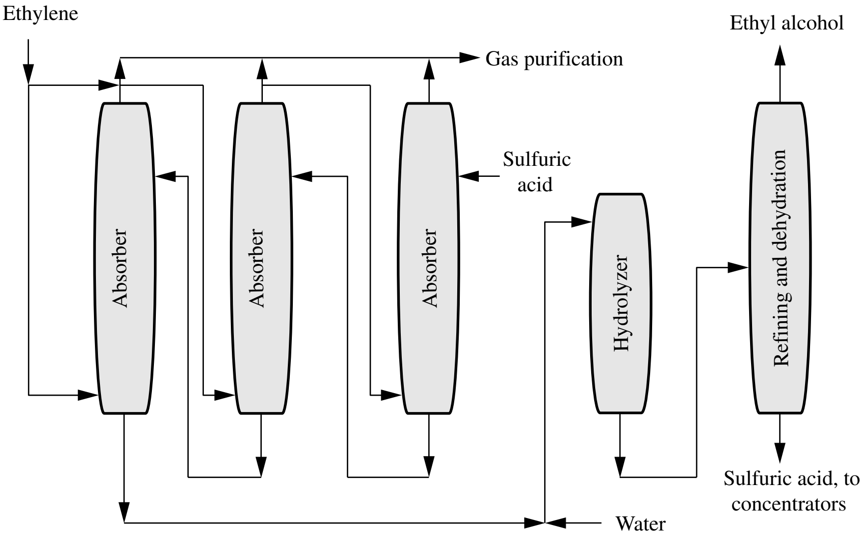

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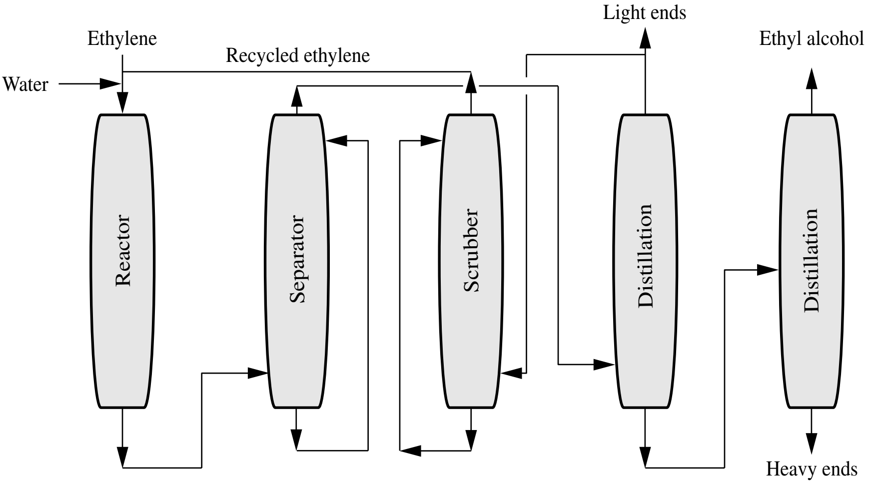

FIGURE 2 Manufacture of ethyl alcohol by direct hydration.

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2. A gas-phase hydration using a fixed-bed-supported phosphoric acid catalyst
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The last three processes (2, 3, and 4) are all essentially direct hydration processes.

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

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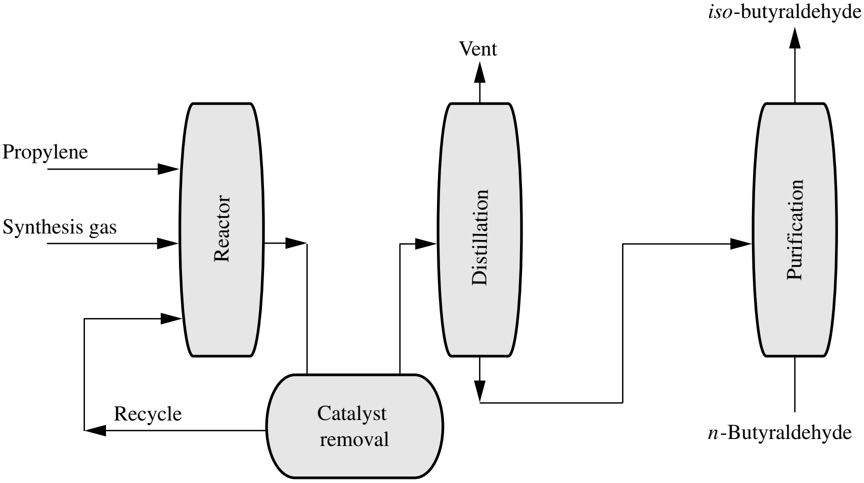

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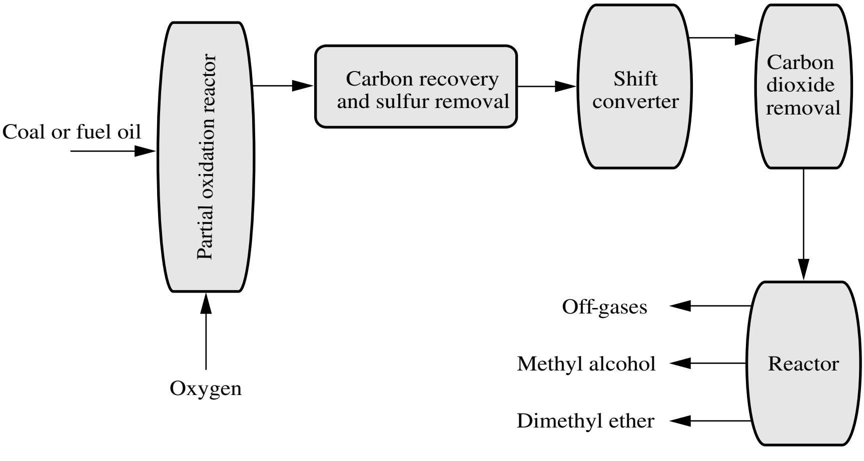

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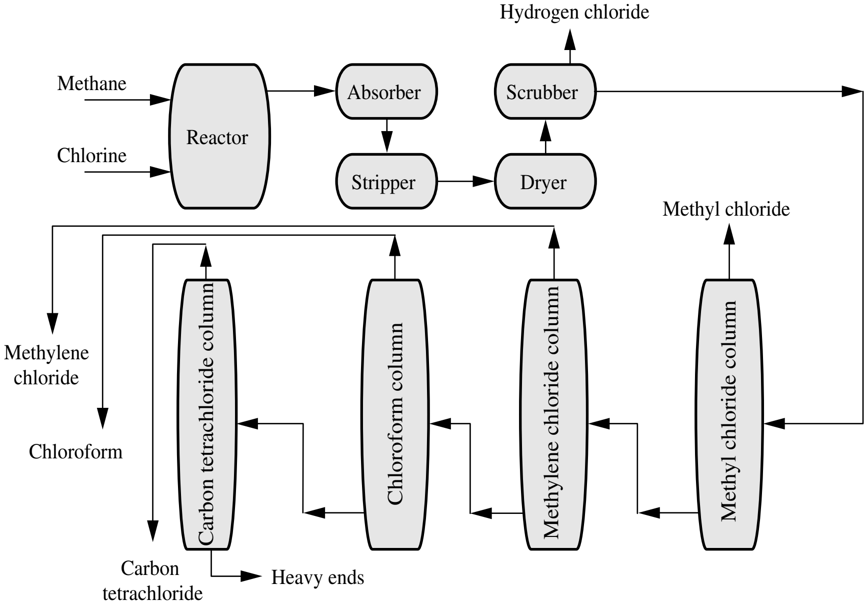

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When chlorination has to be carried out at a low temperature, it is often beneficial to circulate cooling water through a lead coil within the chlorinator or circulate the charge through an outside cooling system rather than to make use of an external jacket. When the temperature is to be maintained at 0°C or below, a calcium chloride brine, cooled by a refrigerating machine, is employed.

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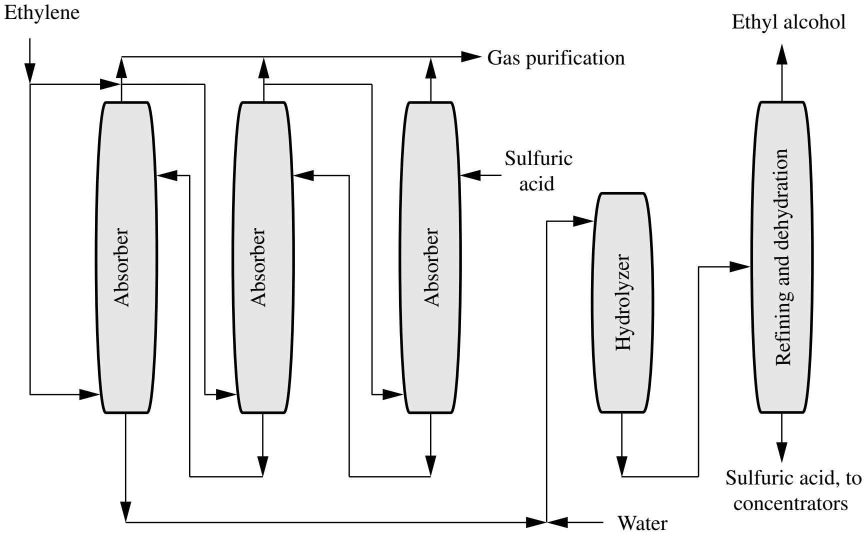

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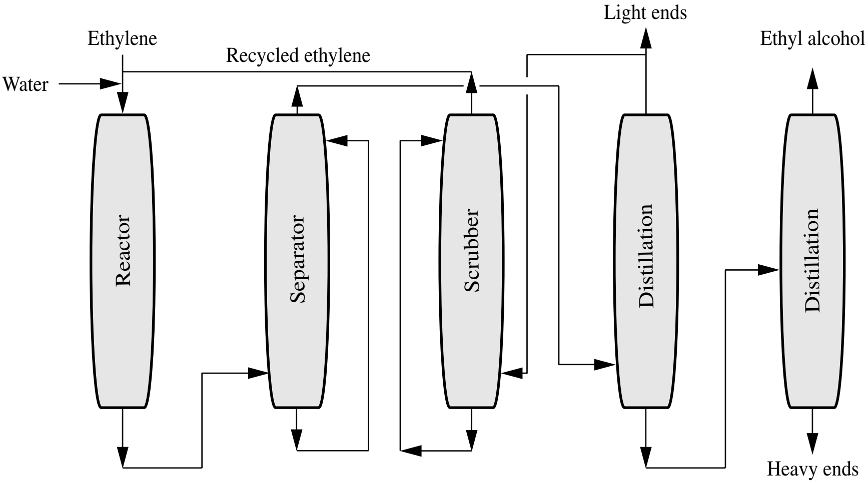

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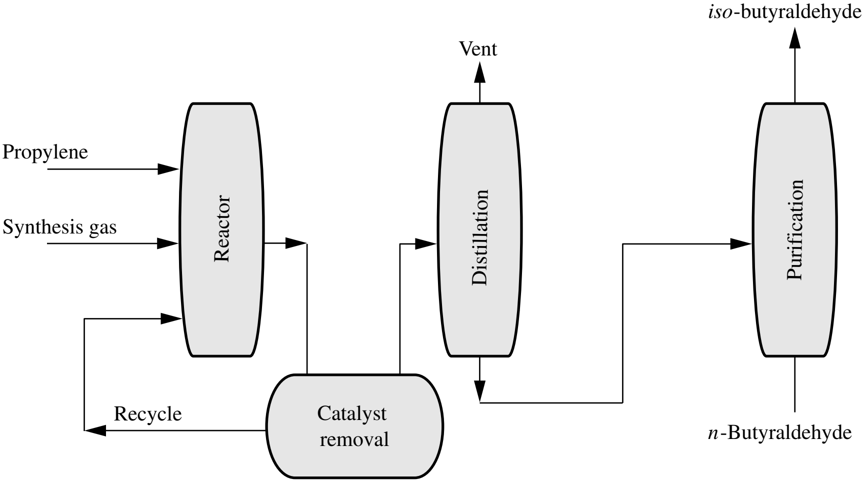

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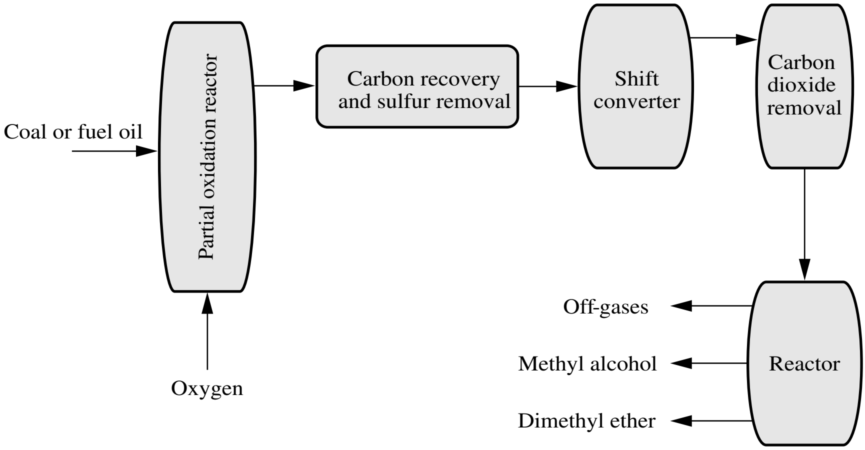

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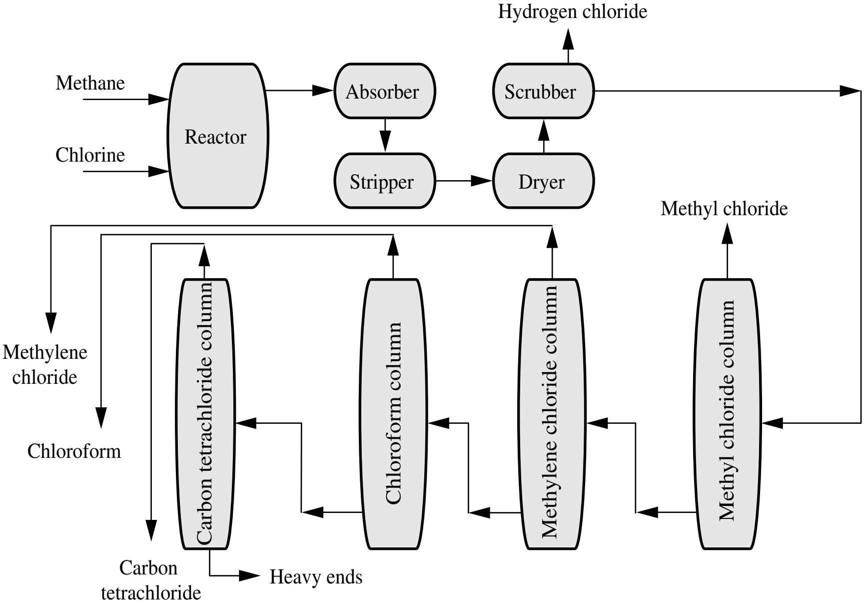

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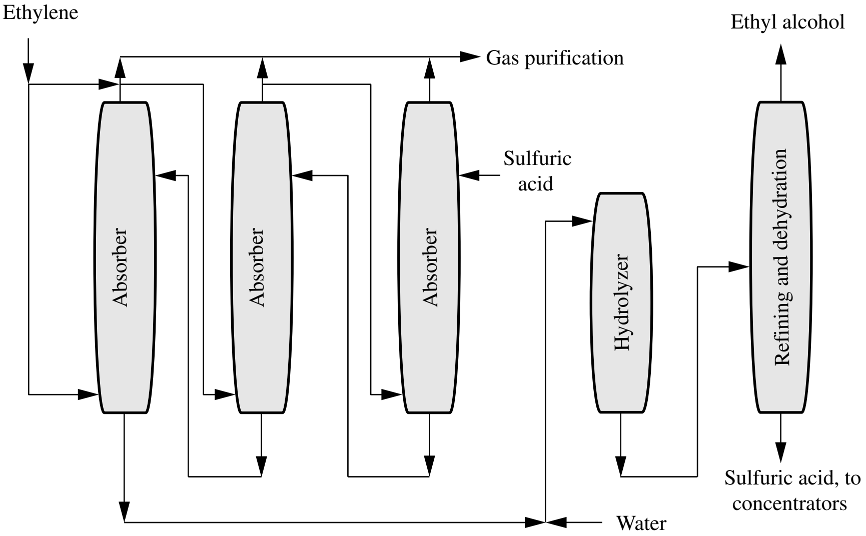

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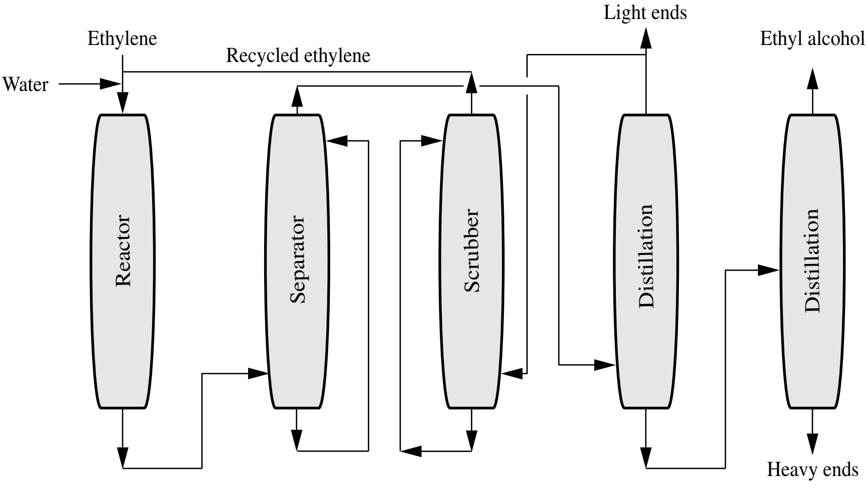

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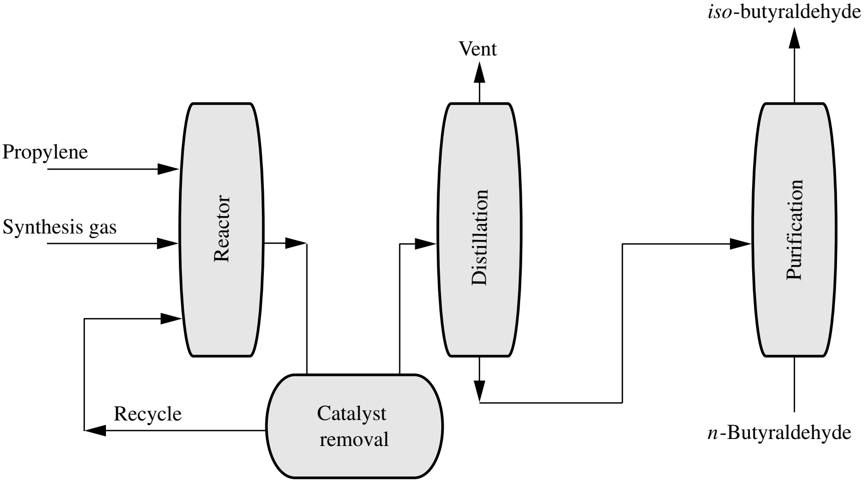

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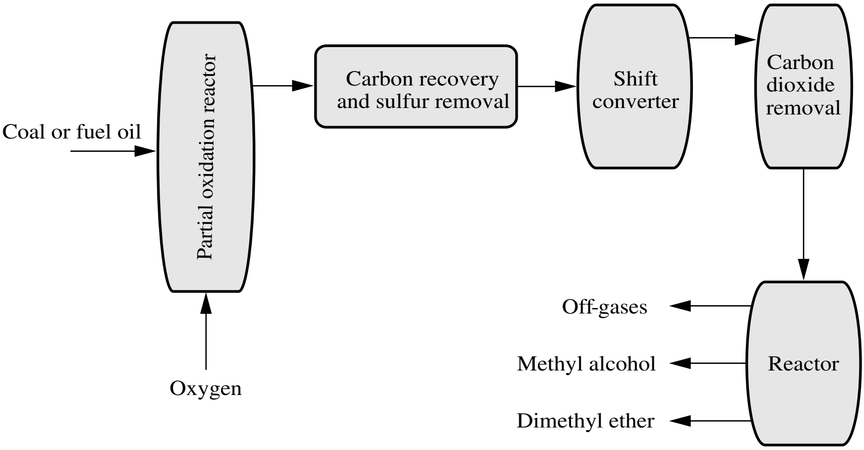

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See ***Dehydrogenation.***

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 (–OH) or sulfonic (–SO_3H). 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.

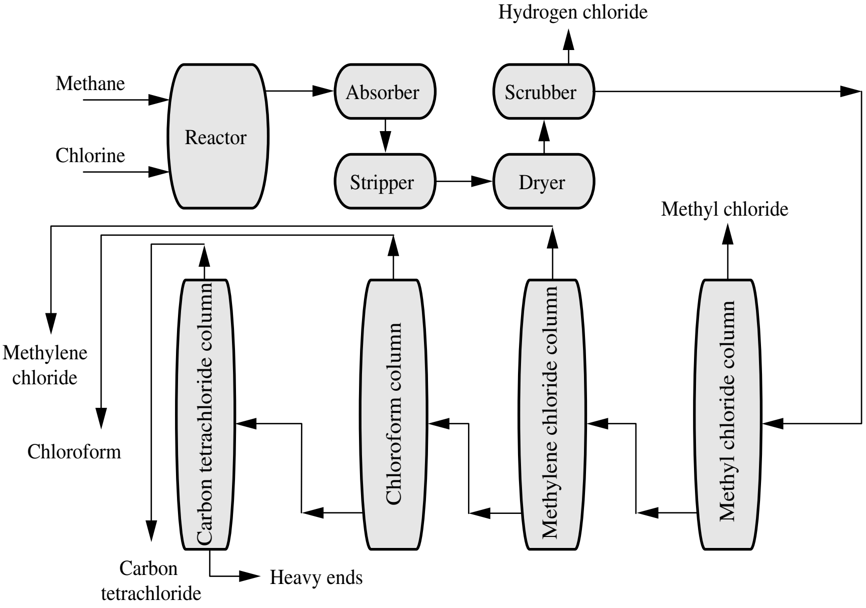

FIGURE 1 Production of chloromethanes by chlorination of methane.

When chlorination has to be carried out at a low temperature, it is often beneficial to circulate cooling water through a lead coil within the chlorinator or circulate the charge through an outside cooling system rather than to make use of an external jacket. When the temperature is to be maintained at 0°C or below, a calcium chloride brine, cooled by a refrigerating machine, is employed.

Most chlorination reactions produce hydrogen chloride as a by-product, and a method was searched for to make this useful for further use:

$$4HCl + O_2 \rightarrow 2H_2O + 2C1_2$$

However, this is not a true equilibrium reaction, with a tendency to favor hydrogen chloride. The reaction can be used and driven to completion by use of the *oxychlorination* procedure that reacts the chlorine with a reactive substance as soon as it is formed, thus driving the reaction to completion as, for example, in the oxychlorination of methane:

$$CH_4 + HCl + O_2 \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + H_2O$$

This chlorination can be accomplished with chlorine but a mole of hydrogen chloride is produced for every chlorine atom introduced into the methane, and this must be disposed of to prevent environmental pollution. Thus, the use

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:

$$C_6H_6 + C1_2 \rightarrow C_6H_5Cl + HCl$$

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.

$$3CH_2{=}CH_2 + 2H_2SO_4 \rightarrow C_2H_5HSO4 + (C_2H_5)_2SO_4$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

$$C_2H_5OH + C_2H_5HSO_4 \rightarrow C_2H_5OC_2H_5$$

The conversion yield of ethylene to ethyl alcohol is 90 percent with a 5 to 10 percent yield of diethyl ether ($C_2H_5OC_2H_5$).

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

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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.

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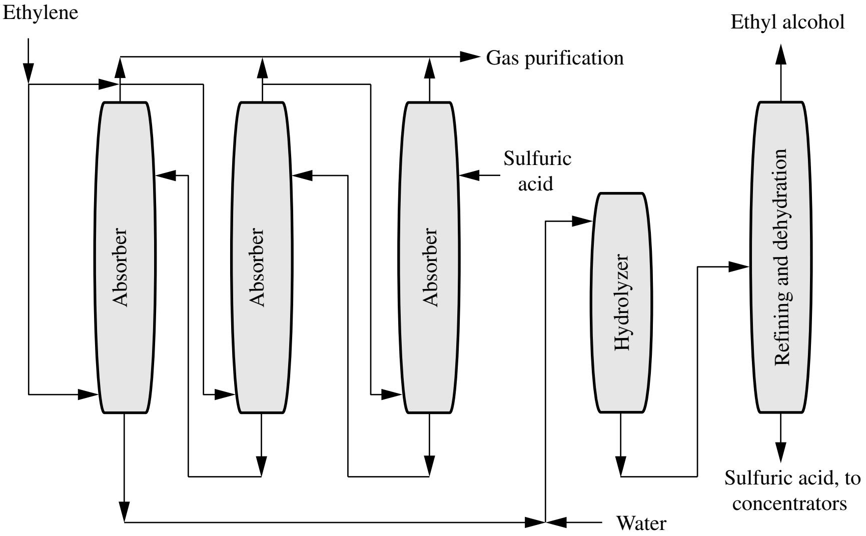

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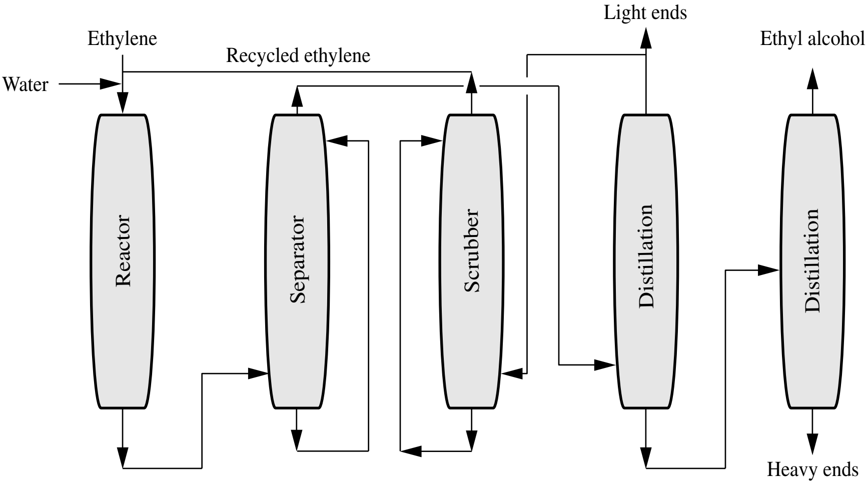

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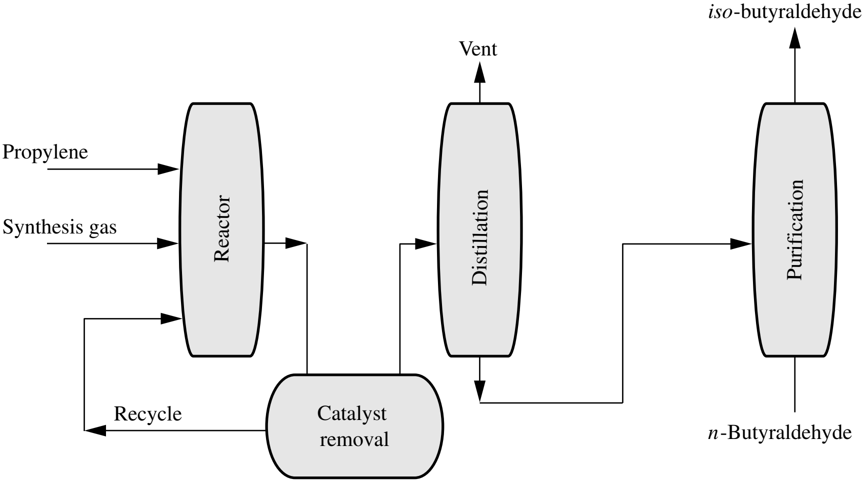

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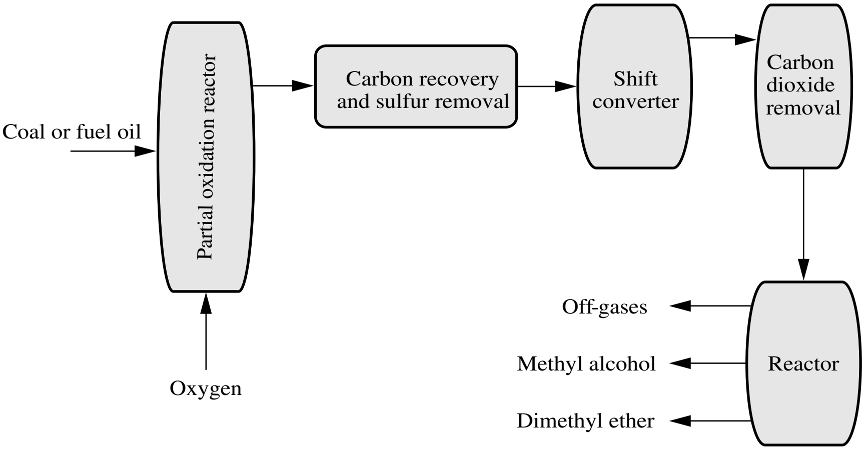

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See ***Dehydrogenation.***

NITRATION

Nitration is the insertion of a nitro group ($-NO_2$) into an organic compound, usually through the agency of the reaction of a hydrocarbon with nitric acid. Concentrated sulfuric acid may be used as a catalyst.

$$ArH + HNO_3 \rightarrow ArNO_2 + H_2O$$

More than one hydrogen atom may be replaced, but replacement of each succeeding hydrogen atom represents a more difficult substitution.

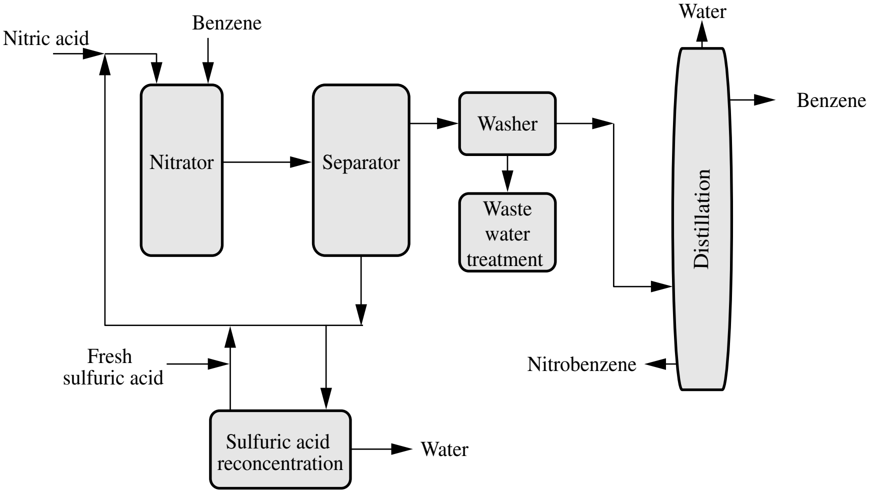
The nitrogen-bearing reactant may be:

1. Strong nitric acid
2. Mixed nitric and sulfuric acid
3. A nitrate plus sulfuric acid
4. Nitrogen pentoxide (N_2O_5)
5. A nitrate plus acetic acid

Both straight chain and ring-type carbon compounds can be nitrated; alkanes yield nitroparaffins.

The process for the production of nitrobenzene from benzene involves the use of mixed acid (Fig. 1), but there are other useful nitrating agents, e.g., inorganic nitrates, oxides of nitrogen, nitric acid plus acetic anhydride, and nitric acid plus phosphoric acid. In fact, the presence of sulfuric acid in quantity is vital to the success of the nitration because it increases the solubility of the hydrocarbon in the reaction mix, thus speeding up the reaction, and promotes the ionization of the nitric acid to give the nitronium ion (NO_2^+), which is the nitrating species. Absorption of water by sulfuric acid favors the nitration reaction and shifts the reaction equilibrium to the product.

Nitration offers a method of making unreactive paraffins into reactive substances without cracking. Because nitric acid and nitrogen oxides are strong oxidizing agents, oxidation always accompanies nitration. Aromatic nitration reactions have been important particularly for the manufacture of explosives. Nitrobenzene is probably the most important nitration product.



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Certain esters of nitric acid (cellulose nitrate, glyceryl trinitrate) are often referred to as nitro compounds (nitrocellulose, nitroglycerin), but this terminology should be avoided.

Vapor-phase nitration of paraffin hydrocarbons, particularly propane, can be brought about by uncatalyzed contact between a large excess of hydrocarbon and nitric acid vapor at around 400°C, followed by quenching. A multiplicity of nitrated and oxidized products results from nitrating propane; nitromethane, nitroethane, nitropropanes, and carbon dioxide all appear, but yields of useful products are fair. Materials of construction must be very oxidation-resistant and are usually of ceramic-lined steel. The nitroparaffins have found limited use as fuels for race cars, submarines, and model airplanes. Their reduction products, the amines, and other hydroxyl compounds resulting from aldol condensations have made a great many new aliphatic syntheses possible because of their ready reactivity.

Nitration reactions are carried out in closed vessels that are provided with an agitating mechanism and means for controlling the reaction temperature. The nitration vessels are usually constructed of cast iron and steel, but often acid-resistant alloys, particularly chrome-nickel steel alloys, are used.

Plants may have large (several hundred gallon capacity) nitration vessels operating in a batch mode or small continuous units. The temperature is held at about 50°C, governed by the rate of feed of benzene. Reaction is rapid in well-stirred and continuous nitration vessels. The reaction products are

decanted from the spent acid and are washed with dilute alkali. The spent acid is sent to some type of recovery system and yields of 98 percent can be anticipated.

Considerable heat evolution accompanies the nitration reaction, oxidation increases it, and the heat of dilution of the sulfuric acid increases it still further. Increased temperature favors dinitration arid oxidation, so the reaction must be cooled to keep it under control. Good heat transfer can be assured by the use of jackets, coils, and good agitation in the nitration vessel. Nitration vessels are usually made of stainless steel, although cast iron stands up well against mixed acid.

When temperature regulation is dependent solely on external jackets, a disproportional increase in nitration vessel capacity as compared with jacket surface occurs when the size of the machine is enlarged. Thus, if the volume is increased from 400 to 800 gallons, the heat-exchange area increases as the square and the volume as the cube of the expanded unit. To overcome this fault, internal cooling coils or tubes are introduced, which have proved satisfactory when installed on the basis of sound calculations that include the several thermal factors entering into this unit process.

A way of providing an efficient agitation inside the nitration vessel is essential if local overheating is to be mitigated. Furthermore, the smoothness of the reaction depends on the dispersion of the reacting material as it comes in contact with the change in the nitration vessel so that a fairly uniform temperature is maintained throughout the vessel.

Nitration vessels are usually equipped with one of three general types of agitating mechanism: (1) single or double impeller, (2) propeller or turbine, with cooling sleeve, and (3) outside tunnel circulation.

The *single-impeller* agitator consists of one vertical shaft containing horizontal arms. The shaft may be placed off center in order to create rapid circulation past, or local turbulence at, the point of contact between the nitrating acid and the organic compound.

The *double-impeller* agitator consists of two vertical shafts rotating in opposite directions, and each shaft has a series of horizontal arms attached. The lower blades have an upward thrust, whereas the upper ones repel the liquid downward. This conformation provides a reaction mix that is essentially homogeneous.

The term *sleeve-and-propeller* agitation is usually applied when the nitration vessel is equipped with a vertical sleeve through which the charge is circulated by the action of a marine propeller or turbine. The sleeve is

usually made of a solid bank of acid-resisting cooling coils through which cold water or brine is circulated at a calculated rate. In order to obtain the maximum efficiency with this type of nitration vessel, it is essential to maintain a rapid circulation of liquid upward or downward in the sleeves and past the coils.

OXIDATION

Oxidation is the addition of oxygen to an organic compound or, conversely, the removal of hydrogen.

Reaction control is the major issue during oxidation reactions. Only partial oxidation is required for conversion of one organic compound into another or complete oxidation to carbon dioxide and water will ensue.

The most common oxidation agent is air, but oxygen is frequently used. Chemical oxidizing agents (nitric acid, dichromates, permanganates, chromic anhydride, chlorates, and hydrogen peroxide) are also often used.

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Several oxidative routes are available to change cyclohexane to cyclohexanone, cyclohexanol, and ultimately to adipic acid or caprolactam. If phenol is hydrogenated, cyclohexanone can be obtained directly; this will react with hydroxylamine to give cyclohexanone oxime that converts to caprolactam on acid rearrangement. Cyclohexane can also be converted to adipic acid, then adiponitrile, which can be converted to hexamethylenediamine. Adipic acid and hexamethylenediamine are used to form nylon 6,6. This route to hexamethylenediamine is competitive with alternative routes through butene.

Acetaldehyde is manufactured by one of several possible processes: (1) the hydration of acetylene, no longer a significant process. (2) the Wacker process, in which ethylene is oxidized directly with air or 99% oxygen (Fig. 1) in the presence of a catalyst such as palladium chloride with a copper chloride promoter. The ethylene gas is bubbled, at atmospheric pressure, through the solution at its boiling point. The heat of reaction is removed by boiling of the water. Unreacted gas is recycled following condensation of the aldehyde and water, which are then separated by distillation, (3) passing ethyl alcohol over a copper or silver gauze catalyst gives a 25 percent conversion to acetaldehyde, with recirculation making a 90 to 95 percent yield possible, and (4) a process in which lower molecular weight paraffin hydrocarbons are oxidized noncatalytically to produce mixed compounds, among them acetaldehyde and acetic acid.

Liquid-phase reactions in which oxidation is secured by the use of oxidizing compounds need no special apparatus in the sense of elaborate means for temperature control and heat removal. There is usually provided a kettle form of apparatus, closed to prevent the loss of volatile materials and fitted with a reflux condenser to return vaporized materials to the reac-

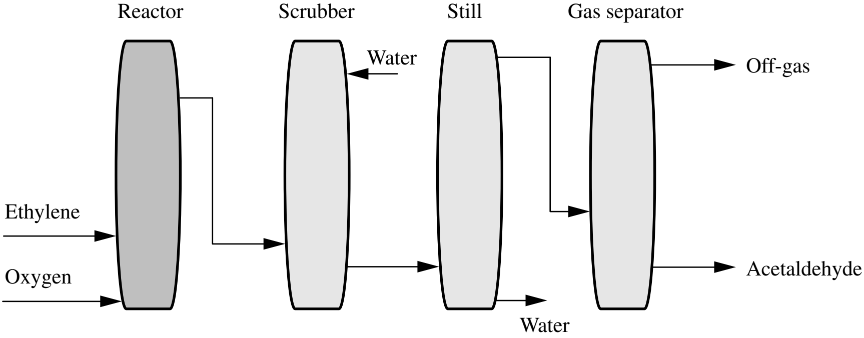

FIGURE 1 Production of acetaldehyde by the oxidation of ethylene.

tion zone, with suitable means for adding reactants rapidly or slowly as may be required and for removing the product, and provided with adequate jackets or coils through which heating or cooling means may be circulated as required.

In the case of liquid-phase reactions in which oxidation is secured by means of atmospheric oxygen—for example, the oxidation of liquid hydrocarbons to fatty acids—special means must be provided to secure adequate mixing and contact of the two immiscible phases of gaseous oxidizing agent and the liquid being oxidized. Although temperature must be controlled and heat removed, the requirements are not severe, since the temperatures are generally low and the rate of heat generation controllable by regulation of the rate of air admission.

Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid and constructed of materials capable of withstanding temperatures that may be considerably higher at these inlet ports than in the main body of the liquid. With materials that are sensitive to overoxidation and under conditions where good contact must be used partly to offset the retarding effect of necessarily low temperatures, thorough mixing may be provided by the use of mechanical stirring or frothing of the liquid.

By their very nature, the vapor-phase oxidation processes result in the concentration of reaction heat in the catalyst zone, from which it must be removed in large quantities at high-temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material, and maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation. With plant-scale operation and with reactions involving deep-seated oxidation, removal of heat constitutes a major problem. With limited oxidation, however, it may become necessary to supply heat even to oxidations conducted on a plant scale.

In the case of vapor-phase oxidation of aliphatic substances such as methanol and the lower molecular weight aliphatic hydrocarbons, the ratio of reacting oxygen is generally lower than in the case of the aromatic hydrocarbons for the formation of the desired products, and for this reason heat removal is simpler. Furthermore, in the case of the hydrocarbons, the proportion of oxygen in the reaction mixture is generally low, resulting in low per-pass conversions and, in some instances, necessitating preliminary heating of the reactants to reaction temperature.

Equipment for the oxidation of the aromatic hydrocarbons requires that the reactor design permit the maintenance of elevated temperatures, allow the removal of large quantities of heat at these elevated temperatures, and provide adequate catalyst surface to promote the reactions.

OXO REACTION

The *oxo reaction* is the general or generic name for a process in which an unsaturated hydrocarbon is reacted with carbon monoxide and hydrogen to form oxygen function compounds, such as aldehydes and alcohols.

In a typical process for the production of oxo alcohols, the feedstock comprises an olefin stream, carbon monoxide, and hydrogen. In a first step, the olefin reacts with CO and H2 in the presence of a catalyst (often cobalt) to produce an aldehyde that has one more carbon atom than the originating olefin:

$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CH{=}O$$

This step is exothermic and requires an ancillary cooling operation.

The raw aldehyde exiting from the oxo reactor then is subjected to a higher temperature to convert the catalyst to a form for easy separation from the reaction products. The subsequent treatment also decomposes unwanted by-products. The raw aldehyde then is hydrogenated in the presence of a catalyst (usually nickel) to form the desired alcohol:

$$RCH_2CH_2CH{=}O + H_2 \rightarrow RCH_2CH_2CH_2OH$$

The raw alcohol then is purified in a fractionating column. In addition to the purified alcohol, by-products include a light hydrocarbon stream and a heavy oil. The hydrogenation step takes place at about 150°C under a pressure of about 1470 psi (10.13 MPa). The olefin conversion usually is about 95 percent.

Among important products manufactured in this manner are substituted propionaldehyde from corresponding substituted ethylene, normal and *iso*-butyraldehyde from propylene, *iso*-octyl alcohol from heptene, and trimethylhexyl alcohol from di-*iso*butylene.

See ***Hydroformylation***.

NITRATION

Nitration is the insertion of a nitro group (–NO_2) into an organic compound, usually through the agency of the reaction of a hydrocarbon with nitric acid. Concentrated sulfuric acid may be used as a catalyst.

$$ArH + HNO_3 \rightarrow ArNO_2 + H_2O$$

More than one hydrogen atom may be replaced, but replacement of each succeeding hydrogen atom represents a more difficult substitution.

The nitrogen-bearing reactant may be:

1. Strong nitric acid
2. Mixed nitric and sulfuric acid
3. A nitrate plus sulfuric acid
4. Nitrogen pentoxide (N_2O_5)
5. A nitrate plus acetic acid

Both straight chain and ring-type carbon compounds can be nitrated; alkanes yield nitroparaffins.

The process for the production of nitrobenzene from benzene involves the use of mixed acid (Fig. 1), but there are other useful nitrating agents, e.g., inorganic nitrates, oxides of nitrogen, nitric acid plus acetic anhydride, and nitric acid plus phosphoric acid. In fact, the presence of sulfuric acid in quantity is vital to the success of the nitration because it increases the solubility of the hydrocarbon in the reaction mix, thus speeding up the reaction, and promotes the ionization of the nitric acid to give the nitronium ion (NO_2^+), which is the nitrating species. Absorption of water by sulfuric acid favors the nitration reaction and shifts the reaction equilibrium to the product.

Nitration offers a method of making unreactive paraffins into reactive substances without cracking. Because nitric acid and nitrogen oxides are strong oxidizing agents, oxidation always accompanies nitration. Aromatic nitration reactions have been important particularly for the manufacture of explosives. Nitrobenzene is probably the most important nitration product.

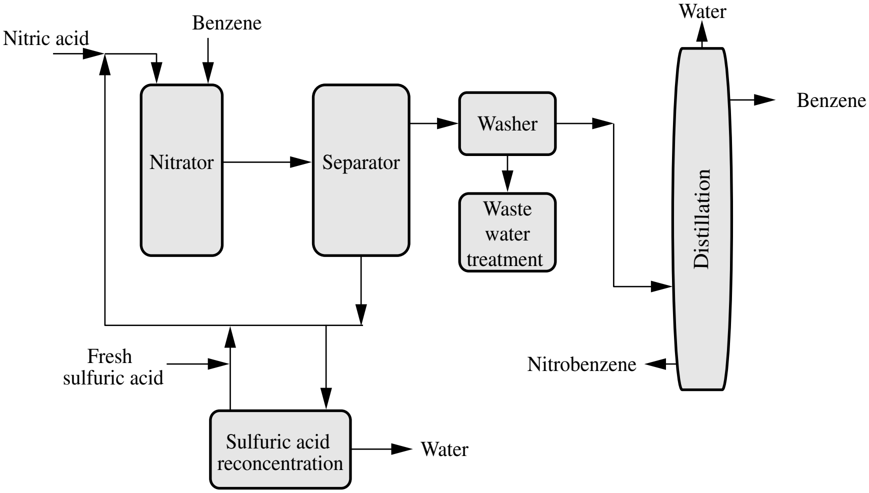

FIGURE 1 Production of nitrobenzene from benzene.

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Vapor-phase nitration of paraffin hydrocarbons, particularly propane, can be brought about by uncatalyzed contact between a large excess of hydrocarbon and nitric acid vapor at around 400°C, followed by quenching. A multiplicity of nitrated and oxidized products results from nitrating propane; nitromethane, nitroethane, nitropropanes, and carbon dioxide all appear, but yields of useful products are fair. Materials of construction must be very oxidation-resistant and are usually of ceramic-lined steel. The nitroparaffins have found limited use as fuels for race cars, submarines, and model airplanes. Their reduction products, the amines, and other hydroxyl compounds resulting from aldol condensations have made a great many new aliphatic syntheses possible because of their ready reactivity.

Nitration reactions are carried out in closed vessels that are provided with an agitating mechanism and means for controlling the reaction temperature. The nitration vessels are usually constructed of cast iron and steel, but often acid-resistant alloys, particularly chrome-nickel steel alloys, are used.

Plants may have large (several hundred gallon capacity) nitration vessels operating in a batch mode or small continuous units. The temperature is held at about 50°C, governed by the rate of feed of benzene. Reaction is rapid in well-stirred and continuous nitration vessels. The reaction products are

decanted from the spent acid and are washed with dilute alkali. The spent acid is sent to some type of recovery system and yields of 98 percent can be anticipated.

Considerable heat evolution accompanies the nitration reaction, oxidation increases it, and the heat of dilution of the sulfuric acid increases it still further. Increased temperature favors dinitration arid oxidation, so the reaction must be cooled to keep it under control. Good heat transfer can be assured by the use of jackets, coils, and good agitation in the nitration vessel. Nitration vessels are usually made of stainless steel, although cast iron stands up well against mixed acid.

When temperature regulation is dependent solely on external jackets, a disproportional increase in nitration vessel capacity as compared with jacket surface occurs when the size of the machine is enlarged. Thus, if the volume is increased from 400 to 800 gallons, the heat-exchange area increases as the square and the volume as the cube of the expanded unit. To overcome this fault, internal cooling coils or tubes are introduced, which have proved satisfactory when installed on the basis of sound calculations that include the several thermal factors entering into this unit process.

A way of providing an efficient agitation inside the nitration vessel is essential if local overheating is to be mitigated. Furthermore, the smoothness of the reaction depends on the dispersion of the reacting material as it comes in contact with the change in the nitration vessel so that a fairly uniform temperature is maintained throughout the vessel.

Nitration vessels are usually equipped with one of three general types of agitating mechanism: (1) single or double impeller, (2) propeller or turbine, with cooling sleeve, and (3) outside tunnel circulation.

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The term *sleeve-and-propeller* agitation is usually applied when the nitration vessel is equipped with a vertical sleeve through which the charge is circulated by the action of a marine propeller or turbine. The sleeve is

usually made of a solid bank of acid-resisting cooling coils through which cold water or brine is circulated at a calculated rate. In order to obtain the maximum efficiency with this type of nitration vessel, it is essential to maintain a rapid circulation of liquid upward or downward in the sleeves and past the coils.

OXIDATION

Oxidation is the addition of oxygen to an organic compound or, conversely, the removal of hydrogen.

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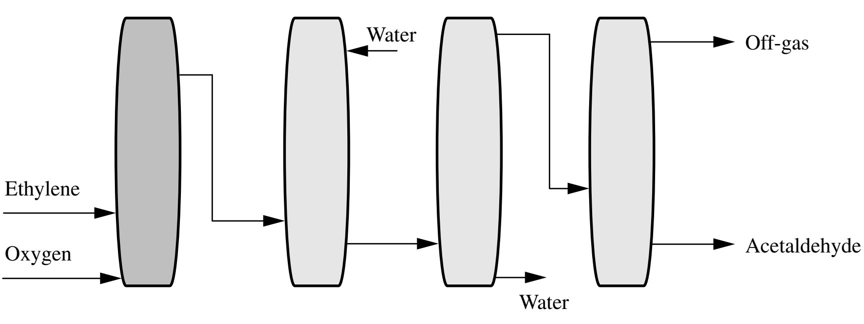

FIGURE 1 Production of acetaldehyde by the oxidation of ethylene.

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This step is exothermic and requires an ancillary cooling operation.

The raw aldehyde exiting from the oxo reactor then is subjected to a higher temperature to convert the catalyst to a form for easy separation from the reaction products. The subsequent treatment also decomposes unwanted by-products. The raw aldehyde then is hydrogenated in the presence of a catalyst (usually nickel) to form the desired alcohol:

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The raw alcohol then is purified in a fractionating column. In addition to the purified alcohol, by-products include a light hydrocarbon stream and a heavy oil. The hydrogenation step takes place at about 150°C under a pressure of about 1470 psi (10.13 MPa). The olefin conversion usually is about 95 percent.

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Nitration is the insertion of a nitro group ($–NO_2$) into an organic compound, usually through the agency of the reaction of a hydrocarbon with nitric acid. Concentrated sulfuric acid may be used as a catalyst.

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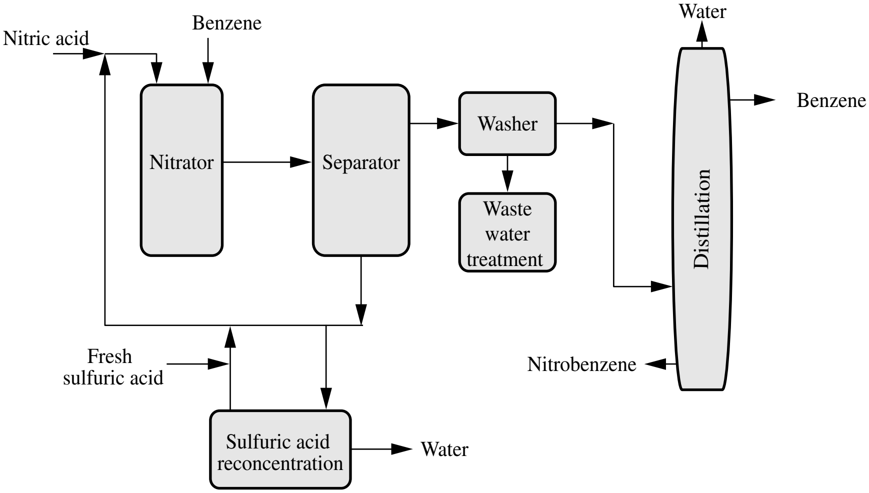

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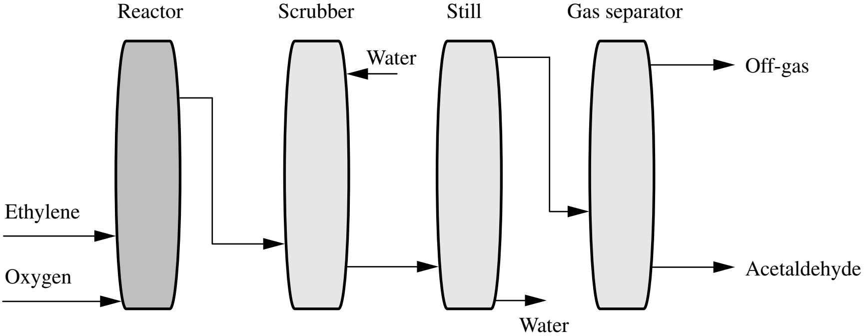

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Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid and constructed of materials capable of withstanding temperatures that may be considerably higher at these inlet ports than in the main body of the liquid. With materials that are sensitive to overoxidation and under conditions where good contact must be used partly to offset the retarding effect of necessarily low temperatures, thorough mixing may be provided by the use of mechanical stirring or frothing of the liquid.

By their very nature, the vapor-phase oxidation processes result in the concentration of reaction heat in the catalyst zone, from which it must be removed in large quantities at high-temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material, and maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation. With plant-scale operation and with reactions involving deep-seated oxidation, removal of heat constitutes a major problem. With limited oxidation, however, it may become necessary to supply heat even to oxidations conducted on a plant scale.

In the case of vapor-phase oxidation of aliphatic substances such as methanol and the lower molecular weight aliphatic hydrocarbons, the ratio of reacting oxygen is generally lower than in the case of the aromatic hydrocarbons for the formation of the desired products, and for this reason heat removal is simpler. Furthermore, in the case of the hydrocarbons, the proportion of oxygen in the reaction mixture is generally low, resulting in low per-pass conversions and, in some instances, necessitating preliminary heating of the reactants to reaction temperature.

Equipment for the oxidation of the aromatic hydrocarbons requires that the reactor design permit the maintenance of elevated temperatures, allow the removal of large quantities of heat at these elevated temperatures, and provide adequate catalyst surface to promote the reactions.

OXO REACTION

The *oxo reaction* is the general or generic name for a process in which an unsaturated hydrocarbon is reacted with carbon monoxide and hydrogen to form oxygen function compounds, such as aldehydes and alcohols.

In a typical process for the production of oxo alcohols, the feedstock comprises an olefin stream, carbon monoxide, and hydrogen. In a first step, the olefin reacts with CO and H2 in the presence of a catalyst (often cobalt) to produce an aldehyde that has one more carbon atom than the originating olefin:

$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CH{=}O$$

This step is exothermic and requires an ancillary cooling operation.

The raw aldehyde exiting from the oxo reactor then is subjected to a higher temperature to convert the catalyst to a form for easy separation from the reaction products. The subsequent treatment also decomposes unwanted by-products. The raw aldehyde then is hydrogenated in the presence of a catalyst (usually nickel) to form the desired alcohol:

$$RCH_2CH_2CH{=}O + H_2 \rightarrow RCH_2CH_2CH_2OH$$

The raw alcohol then is purified in a fractionating column. In addition to the purified alcohol, by-products include a light hydrocarbon stream and a heavy oil. The hydrogenation step takes place at about 150°C under a pressure of about 1470 psi (10.13 MPa). The olefin conversion usually is about 95 percent.

Among important products manufactured in this manner are substituted propionaldehyde from corresponding substituted ethylene, normal and *iso*-butyraldehyde from propylene, *iso*-octyl alcohol from heptene, and trimethylhexyl alcohol from di-*iso*butylene.

See ***Hydroformylation***.

POLYMERIZATION

Polymerization is a process in which similar molecules (usually olefins) are linked to form a high-molecular-weight product; such as the formation of polyethylene from ethylene

$$n\mathrm{CH_2CH_2} \rightarrow \mathrm{H{-}(\ CH_2CH_2)_{\mathit{n}}{-}H}$$

The molecular weight of the polyethylene can range from a few thousand to several hundred thousand.

Polymerization of the monomer in bulk may be carried out in the liquid or vapor state. The monomers and activator are mixed in a reactor and heated or cooled as needed. As most polymerization reactions are exothermic, provision must be made to remove the excess heat. In some cases, the polymers are soluble in their liquid monomers, causing the viscosity of the solution to increase greatly. In other cases, the polymer is not soluble in the monomer and it precipitates out after a small amount of polymerization occurs.

In the petroleum industry, the term *polymerization* takes on a different meaning since the polymerization processes convert by-product hydrocarbon gases produced in cracking into liquid hydrocarbons suitable (of limited or specific molecular weight) for use as high-octane motor and aviation fuels and for petrochemicals.

To combine olefinic gases by polymerization to form heavier fractions, the combining fractions must be unsaturated. Hydrocarbon gases, particularly olefins, from cracking reactors are the major feedstock of polymerization.

$$\mathrm{(CH_3)_2C{=}CH_2} \rightarrow \mathrm{(CH_3)_3CH_2C(CH_3){=}CH_2}$$
$$\mathrm{(CH_3)_3CH_2C(CH_3){=}CH_2} \rightarrow \mathrm{C_{12}H_{24}}$$

Vapor-phase cracking produces considerable quantities of unsaturated gases suitable as feedstocks for polymerization units.

Catalytic polymerization is practical on both large and small scales and is adaptable to combination with reforming to increase the quality of the gasoline. Gasoline produced by polymerization contains a smog-producing olefinic bond. Polymer oligomers are widely used to make detergents.

SULFONATION

Sulfonation is the introduction of a sulfonic acid group ($-SO_3H$) into an organic compound as, for example, in the production of an aromatic sulfonic acid from the corresponding aromatic hydrocarbon.

$$\mathrm{ArH + H_2SO_4 \rightarrow ArSO_3H + H_2O}$$

The usual sulfonating agent is concentrated sulfuric acid, but sulfur trioxide, chlorosulfonic acid, metallic sulfates, and sulfamic acid are also occasionally used. However, because of the nature and properties of sulfuric acid, it is desirable to use it for nucleophilic substitution wherever possible.

For each substance being sulfonated, there is a critical concentration of acid below which sulfonation ceases. The removal of the water formed in the reaction is therefore essential. The use of a very large excess of acid, while expensive, can maintain an essentially constant concentration as the reaction progresses. It is not easy to volatilize water from concentrated solutions of sulfuric acid, but azeotropic distillation can sometimes help.

The sulfonation reaction is exothermic, but not highly corrosive, so sulfonation can be conducted in steel, stainless-steel, or cast-iron sulfonators. A jacket heated with hot oil or steam can serve to heat the contents sufficiently to get the reaction started, then carry away the heat of reaction. A good agitator, a condenser, and a fume control system are usually also provided.

1- and 2-naphthalenesulfonic acids are formed simultaneously when naphthalene is sulfonated with concentrated sulfuric acid. The isomers must be separated if pure α- or β-naphthol are to be prepared from the product mix. Variations in time, temperature, sulfuric acid concentration, and acid/hydrocarbon ratio alter the yields to favor one particular isomer, but a pure single substance is never formed. Using similar acid/hydrocarbon ratios, sulfonation at 40ºC yields 96% alpha isomer, 4% beta, while at 160^0C the proportions are 15% α-naphthol, 8.5% β-naphthol.

The α-sulfonic acid can be hydrolyzed to naphthalene by passing steam at 160°C into the sulfonation mass. The naphthalene so formed passes out with the steam and can be recovered. The pure β-sulfonic acid left behind can be hydrolyzed by caustic fusion to yield relatively pure β-naphthol.

In general, separations are based on some of the following consideration:

1. Variations in the *rate* of hydrolysis of two isomers
2. Variations in the solubility of various salts in water
3. Differences in solubility in solvents other than water
4. Differences in solubility accentuated by common-ion effect (salt additions)
5. Differences in properties of derivatives
6. Differences based on molecular size, such as using molecular sieves or absorption.

Sulfonation reactions may be carried out in batch reactors or in continuous reactors. Continuous sulfonation reactions are feasible only when the organic compounds possess certain chemical and physical properties, and are practical in only a relatively few industrial processes. Most commercial sulfonation reactions are batch operations.

Continuous operations are feasible and practical (1) where the organic compound (benzene or naphthalene) can be volatilized, (2) when reaction rates are high (as in the chlorosulfonation of paraffins and the sulfonation of alcohols), and (3) where production is large (as in the manufacture of detergents, such as alkylaryl sulfonates).

Water of reaction forms during most sulfonation reactions, and unless a method is devised to prevent excessive dilution because of water formed during the reaction, the rate of sulfonation will be reduced. In the interests of economy in sulfuric acid consumption, it is advantageous to remove or chemically combine this water of reaction. For example, the use of reduced pressure for removing the water of reaction has some technical advantages in the sulfonation of phenol and of benzene.

The use of the partial-pressure distillation is predicated upon the ability of the diluent, or an excess of volatile reactant, to remove the water of reaction as it is formed and, hence, to maintain a high concentration of sulfuric acid. If this concentration is maintained, the necessity for using excess sulfuric acid is eliminated, since its only function is to maintain the acid concentration above the desired value. Azeotropic removal of the water of reaction in the sulfonation of benzene can be achieved by using an excess of vaporized benzene.

The use of oleum ($H_2SO_4{\cdot}SO_3$) for maintaining the necessary sulfur trioxide concentration of a sulfonation mixture is a practical procedure. Preferably the oleum and organic compound should be added gradually and concurrently to a large volume of cycle acid so as to take up the water as rapidly as it is formed by the reaction. Sulfur trioxide may be added intermittently to the sulfonation reactor to maintain the sulfur trioxide concentration above the value for the desired degree of sulfonation.

VINYLATION

Unlike ethynylation, in which acetylene adds across a carbonyl group and the triple bond is retained, in vinylation a labile hydrogen compound adds to acetylene, forming a double bond.

$$XH + HC{\equiv}CH \rightarrow CH_2{=}CHX$$

Catalytic vinylation has been applied to the manufacture of a wide range of alcohols, phenols, thiols, carboxylic acids, and certain amines and amides. Vinyl acetate is no longer prepared this way in many countries, although some minor vinyl esters such as vinyl stearate may still be manufactured by this route. However, the manufacture of vinyl-pyrrolidinone and vinyl ethers still depends on acetylene as the starting material.

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