

Natubhai V. Patel College of Pure & Applied Sciences
B.Sc. Semester VI
Industrial chemistry (Vocational)
US06CICV02: Heavy and fine organic chemicals
UNIT – 2

SYLLABUS

Raw materials, flow chart, effluent management, kinetics and uses of triphenyl phosphine, alkyl phosphates, Glycerol, sorbitol, melamine, formaldehyde, formic acid

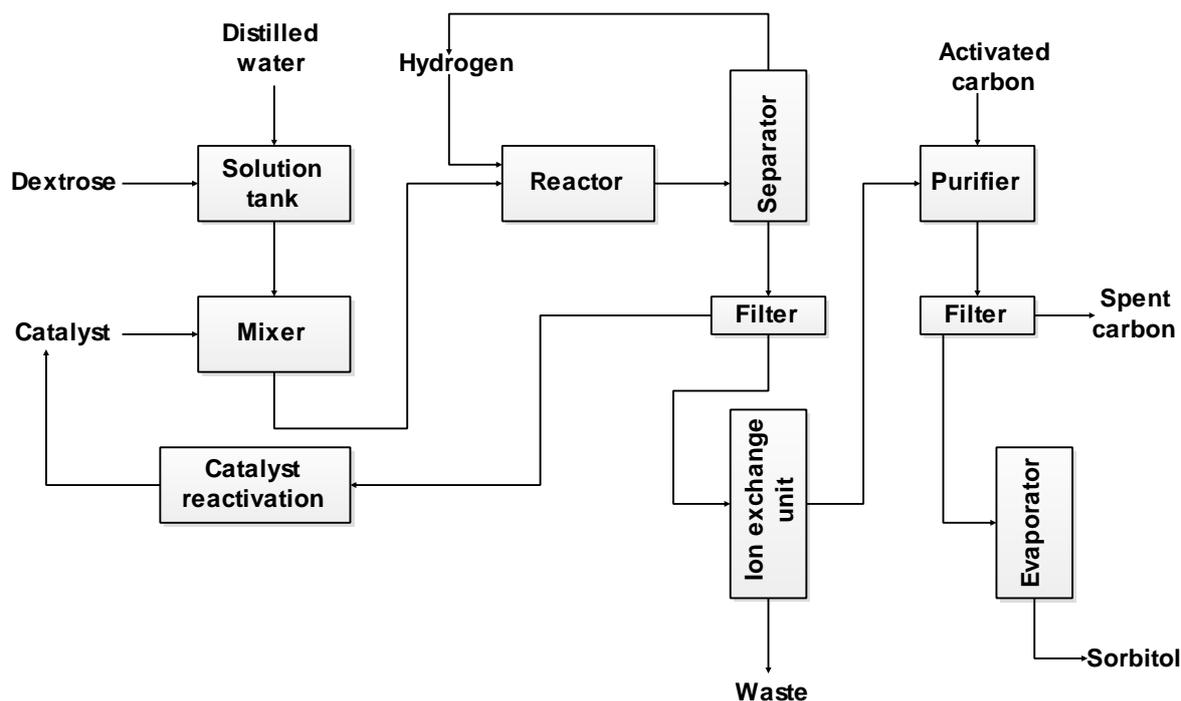
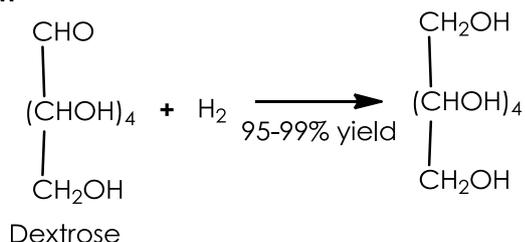
2.0 SORBITOL**2.0.1 From dextrose by Catalytic hydrogenation**

Figure: Production of Sorbitol from dextrose by catalytic hydrogenation

2.0.1.1 Raw Materials

Basis - 1 ton Sorbitol (85%)	
Dextrose	1900 lb
Hydrogen (STP)	5000 cu ft
Catalyst loss (nickel)	2 to 3 lb
Activated carbon	20 to 30 lb
Acid and alkali for ion-exchange Resin regeneration	variable

2.0.1.2 Reaction**2.0.1.3 Manufacture**

The catalytic hydrogenation of dextrose yields Sorbitol. Dextrose dissolved in warm distilled water so that a 50 % solution results. From the dissolver the solution is fed into a weigh-tank mixer, where finely powdered nickel (1 part), supported on clay or diatomaceous earth

(4 parts), is added as the catalyst. The ratio of solution to catalyst is such that the slurry contains 2 percent nickel based on glucose. This slurry is fed into a continuous reactor at pressure of 100 to 125 atm. Hydrogen, compressed to about 175 atm., is bubbled into the vertical-tube reactor with the slurry. Reaction temperature may vary from 280 to 400°F. The reactants pass through the reactor in a matter of minutes and are discharged into a tank, where the excess hydrogen is removed for recompression and recycling.

The Sorbitol-spent catalyst slurry is filtered in a pressure leaf filter; the separated catalyst is reprocessed and reused. The clear crude sorbitol solution is passed through a two-stage ion-exchange unit containing organic ion-exchange resins. Metallic cations are removed in the first stage, and anions are absorbed in the second. All process equipment prior to this step is constructed of ordinary steel. The demineralizer itself is rubber-lined, and subsequent equipment is either stainless steel or stainless-clad steel to insure freedom from impurities.

The treated solution is then purified and decolorized by activated carbon which is subsequently removed by filtration. The purified dilute (about 50 per cent) sorbitol solution is fed into a single-effect continuous evaporator, where at about 200°F and 27.5 in. Hg vacuum the solution is concentrated. Sorbitol to 70 per cent concentration results, which is then ready for shipment. Commercial 85 percent and crystalline sorbitol may be prepared from the 70 percent solution.

2.0.2 Uses

	Per Cent
Ascorbic acid	25
Food	15
Pharmaceuticals	13
Surfactants	15
Cosmetics and dentifrices	20
Adhesives, resins and miscellaneous	<u>12</u>
	100

About 60% of sorbitol production is captive. Accordingly most producers have use for a good portion of their production, either in the manufacture of ascorbic acid (Vitamin C) or for the production of surfactants. Merchant sorbitol goes chiefly into the food, pharmaceutical, and cosmetic fields. A promising use that has not developed as rapidly as had been hoped initially by manufacturers is in the manufacture of sorbitol polyethers for rigid polyurethane foam production.

2.1 FORMALDEHYDE

2.1.1 From Methanol

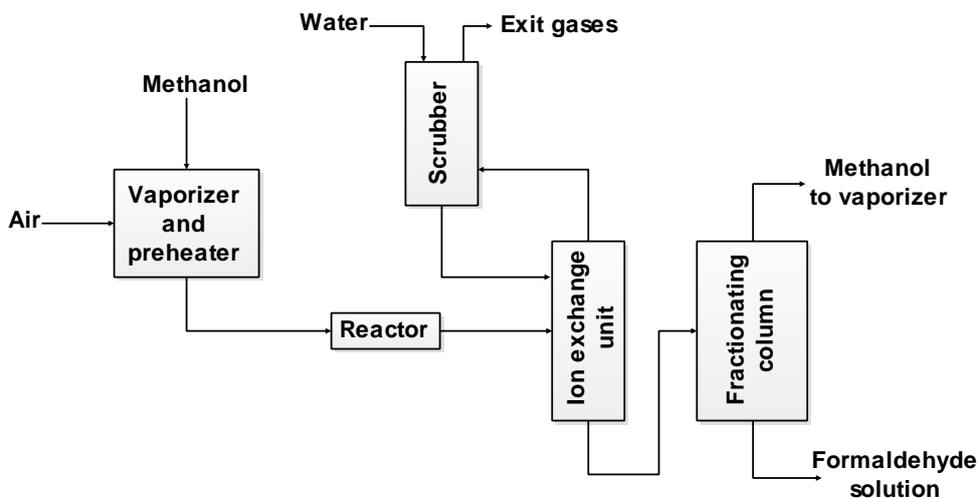
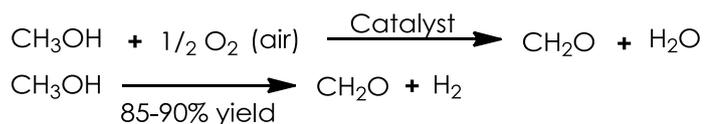


Figure: Production of Formaldehyde from methanol

2.1.1.1 Raw materials

Basis-1 ton Formaldehyde (37%)	
Methanol	930 lb
Air	25000 cu ft at 32°F

2.1.1.2 Reaction**2.1.1.3 Manufacture**

Formaldehyde may be made either by catalytic vapour-phase oxidation of methanol or by a combination oxidation-dehydrogenation process. In either case the formaldehyde and any unreacted product gases are absorbed in water and separated by distillation.

Air and methanol are mixed in such a ratio that the gas mixture contains 30 to 50 percent methanol volume. This is generally accomplished by mechanical mixing or by maintaining the methanol at a constant level and temperature in the vaporizer, through which air is either drawn or forced by vacuum compression. The alcohol-air mixture passes through a preheater (100 to 300°C), in order to remove any residual alcohol spray and to eliminate the possibility of partial condensation, and then to a reactor.

The catalyst chamber (reactor) contains a metal or metal oxide catalyst. Silver and copper are the most satisfactory metal catalysts and are generally used in the form of multilayer gauze or screens. The reaction over these catalysts is essentially a combination of dehydrogenation and oxidation, the former being responsible for high yields, whereas the latter supplies heat and aids in keeping the catalyst active. Therefore, an optimum balance between the two reactions is maintained by using sufficient amount of air to make the net reaction thermally self-supporting once it has been initiated. The catalyst temperature approximates 450 to 600°C, and the contact time is about 0.01 sec.

The most satisfactory metal oxide catalyst consists of a mixture of the oxide of molybdenum, iron, or vanadium. The reaction over this type of catalyst is mainly one of oxidation and requires a large excess of air (5 to 10 times that required by the metallic catalyst). A very high conversion is obtained by this process, so that very little methanol remains to be removed in subsequent operations.

The hot reaction gases from the converter containing the metal catalyst are delivered directly to a column, where an preliminary separation of formaldehyde and unchanged methanol takes place. This is accomplished by multi tubular coolers which are so fixed that alternate scrubbing and cooling is conducted; the gases then pass to a final scrubber fed with cold water and are finally vented to dry atmosphere. This exit gases contains 19-22% hydrogen and 74-75% nitrogen. The hydrogen content is a good indication of the catalyst efficiency and an analysis of the exit gases for hydrogen may be used for process control. The gases also contain between 4-5% carbon dioxide, together with traces of carbon di oxide, oxygen and methane which represent direct loss of methanol by over oxidation.

The combine condensate and scrubber liquor from the main column (containing formaldehyde, water and 15% unreacted methanol) are fed at suitable points into a fractionating column where 37% formaldehyde plus the desired amount of methanol stabilizer is removed from the bottom and excess methanol is removed from the top and returned to vaporize. Overall yields are 85-90% by wt based on the methanol charge.

When the iron-molybdenum oxide catalyst is used the reactor effluent gases are sent to a heat exchanger (to give up heat to reactor feed) and then directly to an absorption tower. Demineralized water is fed to the top of the tower. Nitrogen, oxygen and carbon dioxide go overhead, and a formaldehyde-methanol solution passes out the bottom yield is said to approach 98%

2.1.2 From natural gas

Formaldehyde also manufactured directly from natural gas, methane and other aliphatic hydrocarbons. This process yields a mixture of products varying with the nature of starting material. The formaldehyde is generally obtained in the form of dilute solutions from which it must be concentrated. Difficulties are also encountered in the separation of formaldehyde and other aldehydes and by-products formed in the reaction. One such process, which utilizes butane as a starting material is described under acetaldehyde a comparable process using natural gas as a raw material, operates the temperature of 430-480°C and 7 to 20 atm. Mixed catalysts of aluminum phosphate and metal oxides may be employed. The liquid reaction product contains approximately 34 to 36 percent methanol,

20 to 23 per cent formaldehyde, and 5 to 6 percent acetaldehyde, plus varying amounts of higher aldehydes, ketones, alcohols and water. After preliminary separation, the formaldehyde solution is freed of formic acid by ion-exchange refining.

2.1.3 Uses

	Per cent
Resin	60
Pentaerythritol	09
Ethylene glycol	12
Hexamethylene tetramine	05
Miscellaneous	<u>14</u>
	100

Synthetic resins continue to require the largest quantities of formaldehyde. Accordingly, formaldehyde production increases will reflect increased demand for phenol-, urea-, and melamine-formaldehyde resins. Greatest potential however, is in the manufacture of polyacetal resins, which may well turn out to be the largest use for formaldehyde. Expansion of minor formaldehyde uses will also be factor in the expected increased demand for formaldehyde.

2.2 FORMIC ACID

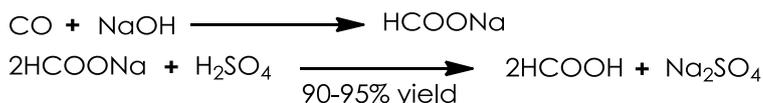
2.2.1 From sodium formate

2.2.1.1 Raw material

Basis - 1 ton Formic acid (90%)

Sodium Hydroxide	1950 lb
Carbon monoxide	1450 lb
Sulphuric acid	2300 lb

2.2.2.2 Reaction



2.2.1.3 Manufacture

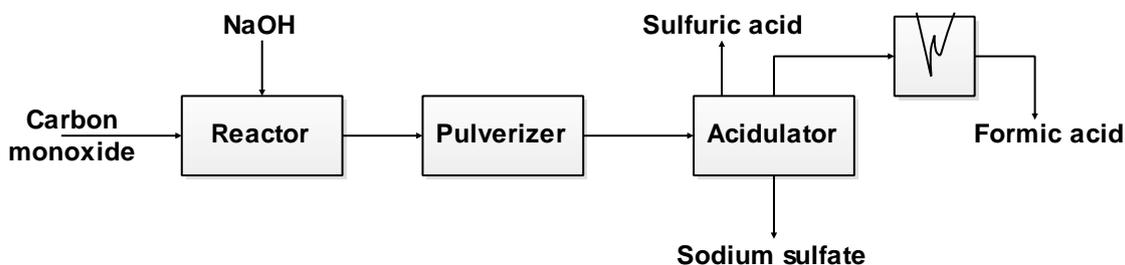


Figure: By pyrolysis of ethylene dichloride

Sodium hydroxide (97 to 98 percent) is charged into a jacketed, agitated, autoclave (reactor), or into a packed tower. Carbon monoxide, usually obtained by the incomplete combustion of coke followed by the removal of carbon dioxide, is reacted with the caustic soda at 150 to 200°C under a pressure of 100 to 150 psi. The resulting reaction product is essentially crude sodium formate.

This reaction product, or sodium formate obtained as a by-product in other processes, may be acidified with dilute sulfuric acid and the resulting formic acid distilled off. However, only dilute formic acid (below 75%) can be obtained by distillation because of the proximity of the formic acid and water boiling points. The addition of concentrated sulphuric acid to dry sodium formate results in quite extensive with formation of carbon monoxide.

This decomposition is minimized by adding concentrated sulphuric acid to a slurry of powdered sodium formate in a sufficient quantity of performed formic acid (85 to 90 per cent). The liberated formic acid to 85 to 90 per cent strength is separated from the sodium sulfate by any convenient method such as distillation. The yield based on sodium hydroxide charged is 90 to 95 percent.

As an alternate procedure, producer gas (carbon monoxide and hydrogen) and a dilute sodium hydroxide solution (25 to 30 per cent NaOH) may be reacted under essentially

the same conditions. The effluent liquor may be dried to yield sodium formate.

2.2.2 From Methyl formate

Formic acid may also be produced by the acid hydrolysis of methyl formate. Methanol and carbon monoxide are reacted at about 200°C under a pressure of 20 to 25 atm to give methyl formate. The formate is converted to dilute formic acid and methanol by action of water and catalytic amounts of sulfuric acid. Essentially anhydrous or concentrated formic acid may be obtained by subjecting methyl formate to reaction with glutaric or oxalic acid while admixed with an admixed esterification catalyst such as sulphuric acid. Formic acid is liberated, and the formed methyl esters of the dibasic acid are hydrolyzed with water to liberate methanol. The regenerated dibasic acid is recovered.

2.2.3 From by-products

Formic acid is obtained as a by-product in the manufacture of acetaldehyde and formaldehyde by the catalytic oxidation of paraffin hydrocarbons, one company also recovers formic acid from wood pulp cooking waste.

2.2.4 Uses

	Per cent
Textile dyeing and finishing	55
Chemicals	15
Leather tanning	10
Miscellaneous	<u>20</u>
	100

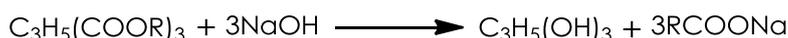
2.3 GLYCERINE

2.3.1 By Product from soap manufacture

2.3.1.1 Raw material

Basis – 1 ton Glycerine (plus 2.2 ton salt)	
Spent lye (5% glycerine)	22 tons
Sodium hydroxide	200lb
Ferric chloride	110lb
Alluminium sulfate	22lb
Activated carbon	5-10lb
Steam	8000lb
Electricity	10Kwhr

2.3.1.2 Reaction



75% Yield (hydrolysis or saponification and recovery)

90% recovery (from spent soap lye)

2.3.1.3 Manufacture

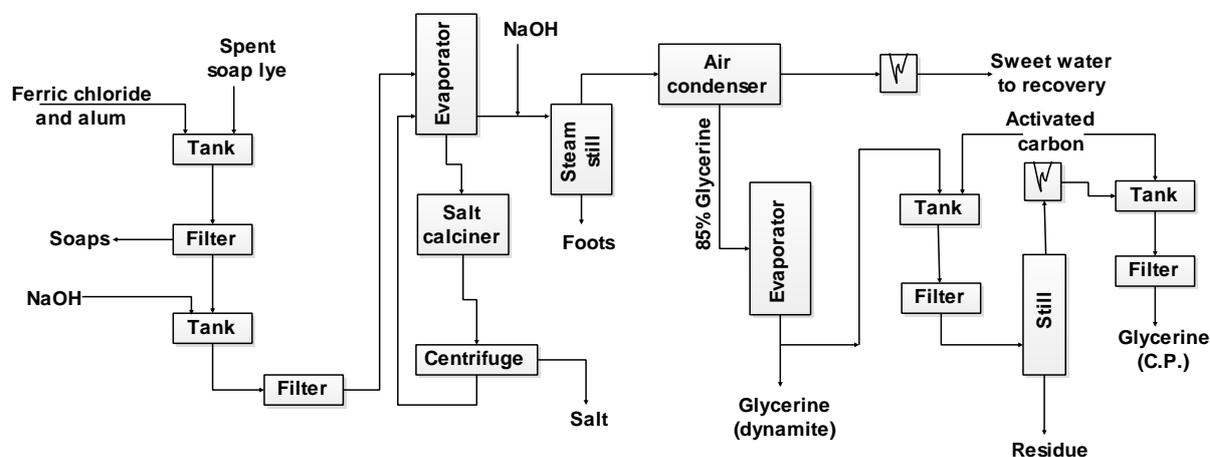


Figure: Production of glycerol from soap manufacturing

The hydrolysis or saponification of fats and oils in the manufacture of free fatty acids

and soap yields glycerine as by-product.

In the hydrolysis process, the mixed glycerides of various fatty acids (the main constituents of fats and oil) are split to give free fatty acids and glycerine. This may be accomplished by several process: for example, the hydrolysis by water at ordinary pressures with the aid of a catalyst (Twitchell Process), the high-temperature-high-pressure hydrolysis with or without a catalyst (autoclave process), and the continuously countercurrent hydrolysis at high temperature and pressures with or without the aid of a catalyst (Ittner process).

The saponification method generally utilizes sodium hydroxide as the alkali and is operated batch by batch or continuously to give soap and glycerine. In the older, more common batch processes, the saponified product is separated into a soap and mixture called spent soap lyes by graining with sodium chloride. The continuous process is operated at high temperatures and pressures to give a reaction mixture, which may be separated by mechanical means (passage through muslin line spraying chambers) into powdered soap and vapours of aqueous glycerine.

The hydrolysis and continuous saponification process yields aqueous salt free solutions containing 15% generally this solutions requires very little chemical treatment (mere neutralization with lime or barium hydrate) and are concentrated by evaporation to give crude glycerine known as "88% saponification crude". In the batch spent soap lyes are intense 3-8% glycerine 5-15% sodium chloride water and small quantities of alkali, soap fatty acids and other organic impurities after chemical treatment the spent lyes are concentrated to yield a crude glycerine is known as "80% soap lye crude" since the recovery of glycerine from spent soap lye is a major source of supply and entails a more involved procedure, it is described in detail (see flowsheet).

Spent lye, which has been allowed to cool and settle to remove much of the, is pumped in to an open steel tank fitted with an agitator. Ferric chloride in solutions is added in the required amount to form insoluble precipitates with the soap and carbonated alkali impurities. Approximately 5 lb ferric chloride per ton of lye is needed; an additional pound of aluminium sulfate (per ton of lye) is customarily used for low grade lye to obtain a more complete removal of impurities. Just enough of hydrochloric acid is added to cause precipitation of the metallic soaps the slightly acid lyes are filtered and run into a second tank where enough aqueous sodium hydroxide is added to bring them over to the alkaline side after filtration the lye contains 4-10% glycerine and 10-18% salt. This material is concentrated in a double effect evaporator which is provided with salt catchers. Much of the salt crystallizes during evaporation and is periodically dropped from the evaporator cone into the salt chambers, from here the salt is removed, centrifuged (or filtered on a nutsch filter), washed and returned to the soap plant for reuse. The evaporation is stopped when the glycerine content of liquor is reached 80%. This crude product, 80% soap lye crude, contains 43% salt, about 0.1% soap and smaller amount of organic impurities.

The crude soap-lye glycerine or crude saponification glycerine (from the hydrolysis plants) is refined by steam distillation under vacuum. The crude material is first made strongly alkaline to hold back fatty acid impurities and is then charged into a direct-steam still. The vapors are condensed by passage through a series of air condensers and finally through a water-cooled condenser. Most of the glycerine is removed by the air-cooled condensers as 85 percent refined glycerine; the water containing about 1 to 2 % glycerine is collected in the water-cooled condenser. This material, known as Sweet water, is separately by evaporation to remove the glycerine.

The 85 per cent refined glycerine is concentrated to give the 99 percent dynamite grade, By decolorizing with activated carbon, a pale-yellow high gravity or industrial grade may be obtained, USP to C.P. Glycerine is produced by passing the dynamite grade of glycerine through activated carbon, redistilling and then recolorising with activated carbon. This water-white product contains 95 to 98 per cent glycerine; the rest is water. The recovery yield of C.P. glycerine from spent soap lye is approximately 90 per cent.

In many modern plants, various sweet waters, and sometimes crude glycerine stocks, are purified by ion-exchange treatment. This process not only removes dissolved salts but also odor and color bodies. The purified glycerine solution is then concentrated by conventional vacuum distillation.

2.3.2 From Propylene via Allyl chloride

2.3.2.1 Raw material

Basis-1 ton glycerine (99%)	
Propylene	1250 lb
Sodium hydroxide	900 lb
Chlorine	4000 lb
Hydrated lime	900 lb

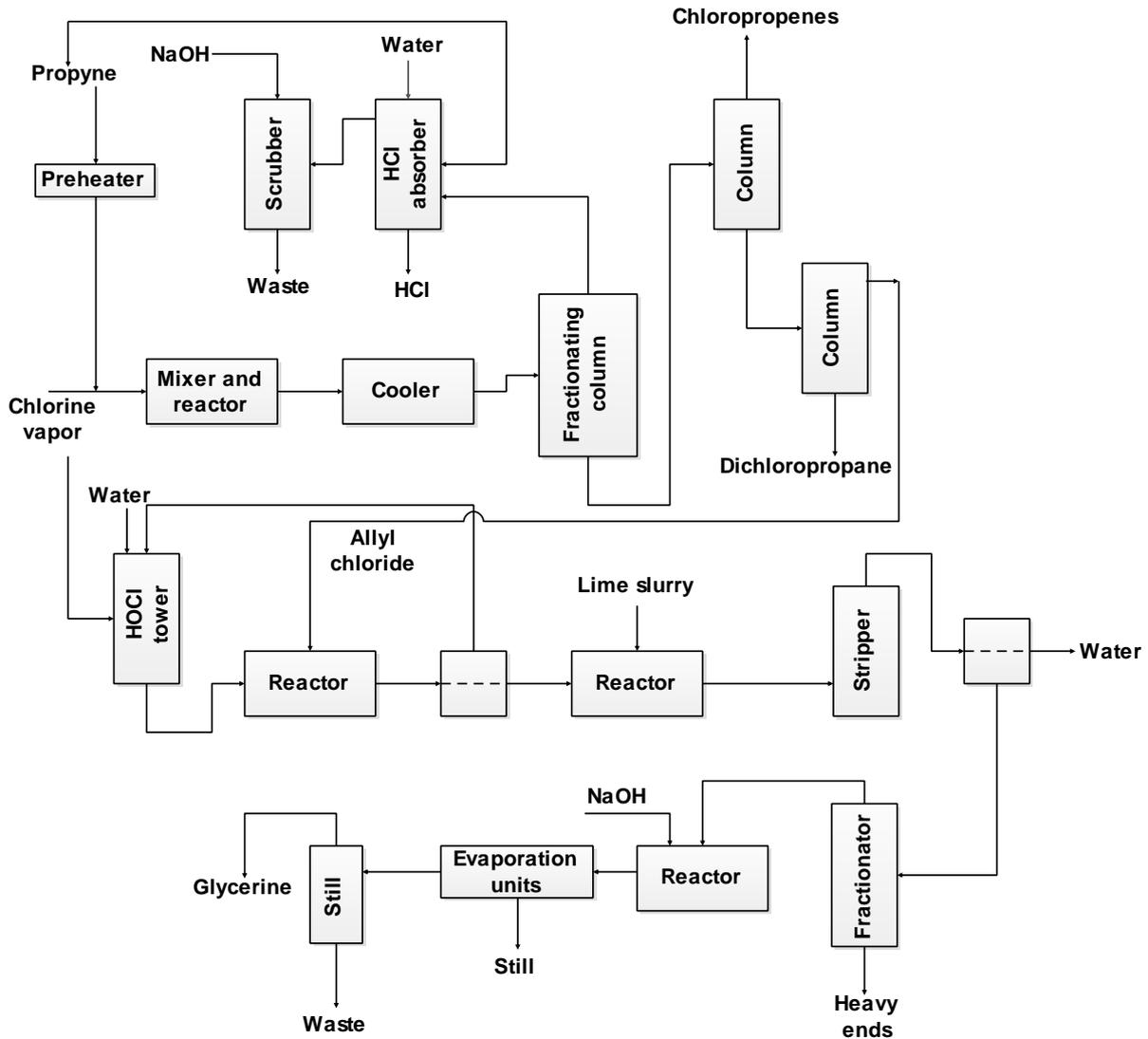
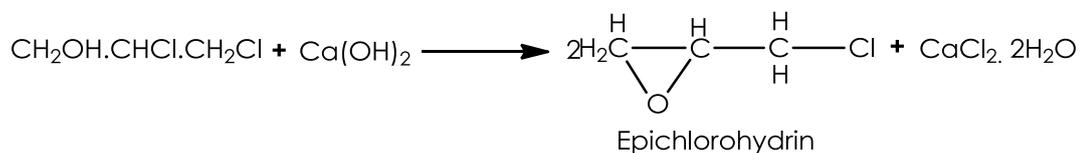
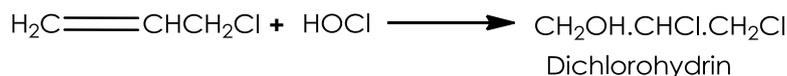
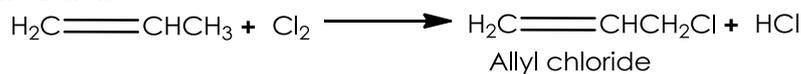
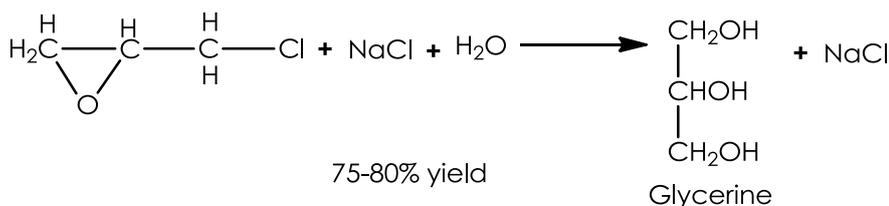


Figure: Production of glycerol from propylene via allyl chloride

2.3.2.2 Reaction





2.3.2.3 Manufacture

The high temperature continuous chlorination of propylene (obtained by petroleum-cracking processes) yields allyl chloride, which is converted to dichlorohydrins by reaction with hypochlorous acid. Reaction of the dichlorohydrins with milk of lime yields epichlorohydrin which may be converted to glycerine by hydrolysis with aqueous sodium hydroxide.

Dry propylene gas is passed through a preheater maintained at about 400°C and is mixed with chlorine in ratio of 4 moles of propylene to 1 mole of chlorine. The chlorine is previously vaporized by passing the liquid through hot-water heaters. The vaporized chlorine reaches the mixing jet at 60 psi and 20°C. The mixed gases pass from the jet into a steel tube reactor that is insulated for temperature. The exothermic nature of the reaction increases the temperature of the reaction mixture from 400 to 500°C. The time of residence of the gases in the reaction zone is not too critical and is probably in the range of 2 to 3 sec. The reactor is maintained at a pressure of about 15 psig. Utilization of chlorine in the reactor is over 99 percent. Two reactors are run alternately to allow cleanout of carbon, which is done a once every 2 weeks. Based on the moles of chlorine fed to the reactor, approximately 80 percent, allyl chloride, plus varying amounts of chloropropenes, mixed dichlorided, trichlorides, and heavier residues are obtained. Of these by-products, the cis-and trans-1, 3-dichloropropenes and 1,2-dichloropropane occur in largest quantities (ca, 15 percent). One mole of hydrogen chloride is formed with each mole of allyl chloride.

The reaction products are recovered continuously by being passed through a cooler into a fractionating column where the excess propylene and hydrogen chloride are separated from the organic chlorides. Liquid propylene (from storage) is used as reflux, and the top of the fractionator are passed is cooled to about 40°C by self-refrigeration of propylene in a flash drum. The heads from the fractionator are passed into an absorber, where hydrogen chloride is recovered as hydrochloric acid of commercial concentration (32 per cent by weight HCl). Liquid propylene is injected into the absorber to remove the heat of absorption, and the propylene leaving the top is scrubbed with aqueous sodium hydroxide. The propylene then compressed and returned to storage for reuse.

The crude allyl chloride from the bottom of the fractionating column is distilled in two columns. Light ends (mostly 2-chloropropene) and traces of propylene are taken as vapors from the first column, and refined allyl chloride is taken overhead from the second. The yield based on propylene is about 85 per cent of theoretical. The bottoms, containing mostly dichloropropenes, are sent to storage.

Allyl chloride is fed to a stirred tank where it is reacted with hypochlorous acid (formed in a tower by contacting gaseous chlorine and water) to form a mixture of dichlorohydrins. The reaction takes place in the aqueous phase so the concentration of allyl chloride in the tank is held to a minimum to avoid side reaction in the nonaqueous phase. Reaction temperature is held between 85 and 100°F. By steam distillation of the product, epichlorohydrin (and a small amount of dichlorohydrins) is removed as the water azeotrope. It is then purified (to 98% purity) by distillation.

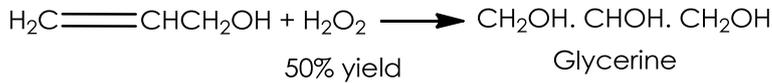
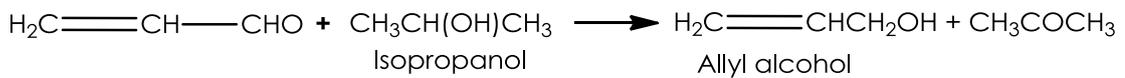
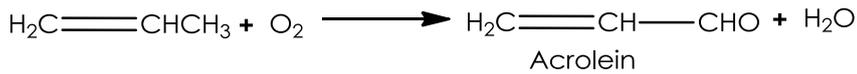
Glycerine is produced from epichlorohydrin by hydrolysis with a 10 percent caustic soda solution in a stirred reactor. Conversion is almost complete in 30 min at 150°C. The product, a dilute glycerine solution containing sodium chloride, is purified and concentrated by evaporation and distillation in the conventional manner.

2.3.3 From Propylene via Acrolein

2.3.3.1 Raw material

Basis -1 ton glycerine (99%) (plus 1,980 lb acetone)	
Propylene	1850 lb
Oxygen	460 lb
Isopropanol	2200 lb
Hydrogen peroxide (100%)	970 lb

2.3.3.2 Reaction



2.3.3.3 Manufacture

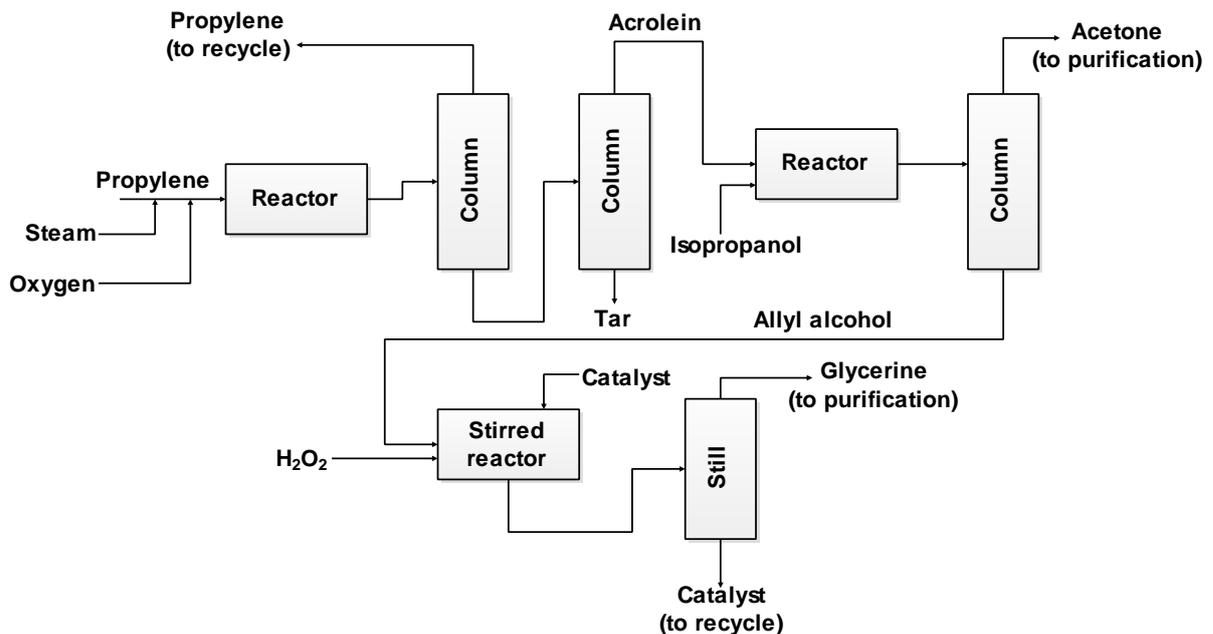


Figure: Production of glycerine from propylene via acrolein

Glycerine is also produced by catalytic vapour phase oxidation of propylene to acrolein, followed by reaction of the acrolein with isopropanol to yield allyl alcohol and acetone. The allyl alcohol is then oxidized to glycerine with hydrogen peroxide.

Propylene and steam in about equal amounts (slight excess of steam) are mixed with oxygen (25 percent based on weight of propylene) and sent to a reactor. In the presence of a supported copper oxide catalyst, about 20 per cent of the propylene is oxidized to acrolein. Typical reaction conditions are 350°C, 2 atmospheres pressure and 0.8 sec residence time. The reaction mixture is cooled and distilled to separate acrolein from unreacted propylene and tarry by-products. Acrolein yield is 85 percent.

The purified acrolein (1 mole) is then reacted with isopropanol (2 to 6 moles) in the vapour phase in the presence of a catalyst containing uncalcined magnesia and zinc oxide. The reaction which takes place at 400°C yields a mixture of allyl alcohol and acetone. Yield of allyl alcohol is 77 percent based on acrolein charged. The allyl alcohol and acetone are separated by distillation.

Purified allyl alcohol is reacted with 2 molar water solution of hydrogen peroxide containing 0.2 per cent tungstic oxide. After 2 hours reaction time at 60 to 70°C, the resulting glycerine-water solution is sent to a still where high-purity glycerine is produced. The recovered catalyst solution is recycled. Yield of glycerine based on allyl alcohol is 80 to 90 percent. The overall yield of glycerine based on propylene charged to the oxidation unit is about 50 per cent.

It is interesting to note that propylene and oxygen are the only raw materials needed in this process. The intermediates, isopropanol and hydrogen peroxide are both made from propylene. Acetone, a by-product of both hydrogen peroxide and allyl alcohol production is formed in fairly large quantities.

2.3.4 Uses

	Per Cent
Alkyd resins and ester gums	22
Cellophane	19
Drugs and cosmetics	19
Tobacco	15
Food and beverages	10
Explosives	06
Miscellaneous and export	<u>09</u>
	100

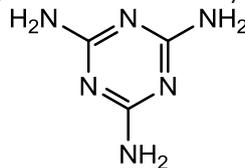
Glycerine enjoys very wide use in industry because of both its chemical and its properties. Its greatest use as a chemical is in the manufacture of alkyd resins, whereas its chief uses because of physical properties greater upon its moistening, lubricating, and softening characteristics. In all fields it must compete with other polyhydride alcohols such as ethylene glycol, pentaerythritol, and sorbitol. The competition of these other polyols for various uses formerly served entirely by glycerine cannot be underestimated. For instance, glycerine has been entirely supplanted in the "permanent" antifreeze field by ethylene glycol; pentaerythritol is making serious inroads in the alkyd resin field; sorbitol has become major competition as a humectant.

Further, alkyd resins are gradually losing out to epoxies, latexes, and acrylics; and cellophane, the second largest user of glycerine, is meeting increased competition from other films. Consequently, demand is not expected to increase, unless some unforeseen new use develops.

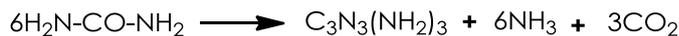
The size and cost of glycerine-recovery units in soap factories varies widely, the former being dependent on the amount of soap produced and the amount of glycerine left in the soap, and the latter on the type of recovery equipment used.

2.4 MELAMINE

Melamine is 2,4,6-triamino-1,3,5-triazine. It mainly exists in amino form.

**2.4.1 Manufacture**

Melamine can be synthesized from urea at 390 to 410°C.



The overall reaction is endothermic, requiring 649KJ per mole of melamine starting with molten urea at 135°C.

The processes themselves may be subdivided into two categories.

1. Noncatalytic, high pressure (≥ 8 MPa) processes
2. Catalytic, low pressure processes (1 MPa)

Each type includes three stages:

- a. Synthesis
- b. Melamine recovery and purification
- c. Off-gas treatment

2.4.1.1 Low pressure processes

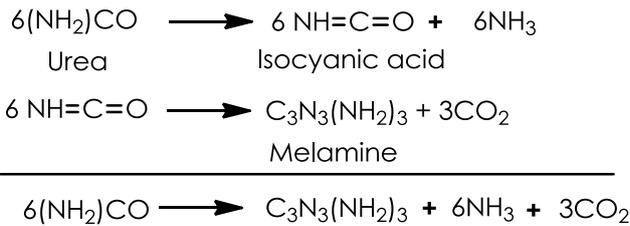
Temperature : 390 to 410°C

Pressure : From atmospheric to 1 MPa

Catalyst : Fluidised bed catalyst

The fluidizing gas is either pure ammonia or the ammonia-carbon dioxide mixture formed during the course of reaction. Catalyst includes alumina and materials of silicaalumina type.

➤ **Reaction**



➤ **Recovery**

Melamine leaves the reactor in gaseous form together with the fluidizing gas; it is separated from ammonia and carbon dioxide by quenching the gas stream either by water (followed by crystallization) or with cold reaction gas (desublimation). Yield is approx 90-95% based on area.

Worldwide three low-pressure processes are in commercial operation.

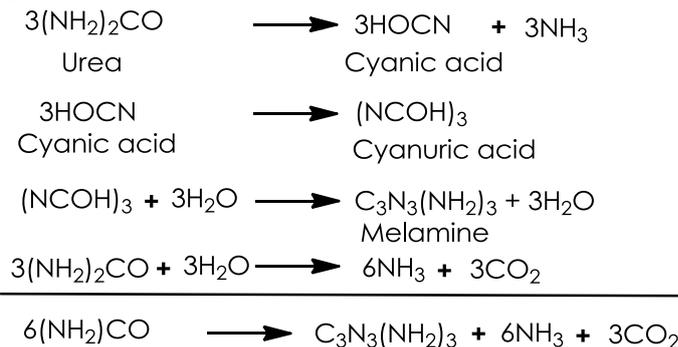
- The BASF Process
- The chemie Linz process
- The stamicarbon process

2.4.1.2 High pressure processes

Temperature : > 370°C
 Pressure : > 7 MPa
 Catalyst : No Catalyst.

It differs from low-pressure processes by producing Melamine in the liquid instead of the vapour phase.

➤ **Reaction**



In general molten area is injected at high pressure into a molten melamine-area mixture in the reactor, where it undergoes conversion to melamine. Sufficient residence time is provided in the reactor to ensure complete reaction; leading to melamine with a purity >94%. Heat is supplied to the reactor either by electric heater elements or by a molten salt-heat-transfer system.

➤ **Recovery**

Melamine is recovered from melamine-ammonia-carbon dioxide gas mixture by cooling followed by crystallization.

There are three high-pressure processes in commercial operation.

- Melamine Chemicals Process
- Montedison (Ausind) Proccss
- Nissan Process.

Advantages

- High-pressure processes have the advantage of providing high-pressure off-gas suitable for use in the area synthesis facility.
- Liquid phase operation also lends itself to smaller reaction vessels.

Disadvantages

Highly corrosive nature of the system dictates use of expensive, corrosion - resistant material such as titanium.

2.4.2 Effluent management

➤ **Low-pressure processes**

Exhaust gas containing carbon dioxide & ammonia is fed to an absorber at high pressure where carbon dioxide is removed. The ammonia is then compressed & recycled as fluidizing & area-atomisation gas for the reactor.

➤ **High-pressure processes**

The off-gas stream represents high pressure (>10MPa) ammonia and carbon dioxide, which can be used directly as feed to the area facility. Alternatively this gas stream can be treated in a monoethanolamine scrubber recover ammonia & remove carbon dioxide.

2.4.3 Quality specifications

Melamine is manufactured and sold as fine white, powdered crystals. The particle size is the most important factor which is generally reported by producers. The reason is the rate of dissolution of melamine in formaldehyde solutions depends on particle size.

Particle sizes ranging from 15 to 100 μm are available for various applications. Some additional criteria are content of inorganic ash, moisture, pH, resin reaction time and resin colour. Generally the purity is 99.9%.

Application	Consumption pattern		
	Europe	United states	Japan
Laminates	47	35	06
Glue, adhesives	25	04	62
Molding compounds	09	09	16
Coatings	08	39	12
Paper, textiles	11	05	03
Other	-	08	01
Total	100	100	100

2.5 TRIPHENYL PHOSPHINE

Phosphine is compounds in which phosphorus has a coordination number of 3 and an oxidation state of 3. They are derived from phosphine (PH_3). Successive formal substitution of 1, 2, or 3 hydrogen atoms of PH_3 , by alkyl or aryl groups gives primary, secondary, and tertiary phosphines.

Under normal conditions, PH_3 , methylphosphine CH_3PH_2 , trifluoromethylphosphine CF_3PH_2 and bis(trifluoromethyl) phosphine $(\text{CF}_3)_2\text{PH}$, are gases. Most of the known phosphines are colorless liquids at 0.1 MPa and 20°C , usually immiscible with water, and have a density of 0.8-0.85 g/cm^3 , tert-alkylphosphines with a chain length > C12 tend to crystallize at room temperature. Phosphines that contain a rigid organic group, e.g. 9H-9 phosphabicyclononane are crystalline.

Phosphines have an intense and penetrating odor, often described as resembling garlic, even in the ppb range. For phosphine itself, the odour threshold is extremely dependent on the purity of the gas. High purity PH_3 (5N), as used in the semiconductor industry, is detectable by smell only when the concentration is at a dangerously toxic level (>1000 ppm), but when PH_3 is produced by the hydrolysis of AIP or Mg_3P_2 (see also Phosphorus Compounds. Inorganic), it can be detected even at ca. 20 ppb. The MAK value for PH_3 is 0.1 ppm and the TLV value, 0.3 ppm. There are no MAK or TLV limits for any other phosphines, with the exception of phenylphosphine.

Phosphine, PH_3 like some other low molecular mass phosphines (e.g., phenylphosphine, methylphosphine, dimethylphosphine and trimethylphosphine), is very toxic. The LC50 and Lf350 values show that the acute toxicity decreases with increasing molecular mass.

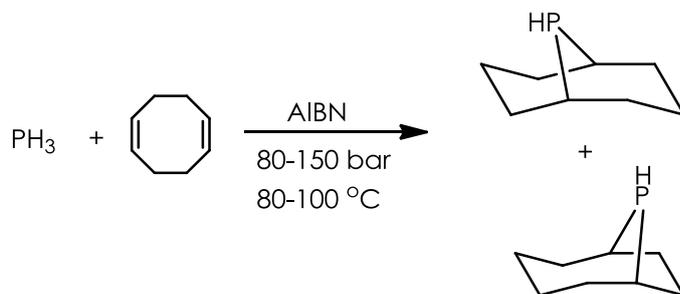
The presence of an electron lone pair gives rise to the three principal properties of the phosphines.

- Oxidizability
- Ability to function as a ligand in complexes
- Nucleophilicity

2.5.1 Manufacture

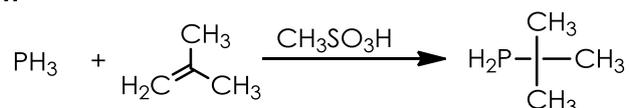
2.5.1.1 Primary and secondary phosphines

The radical-induced addition of alkenes to PH_3 , produces primary and secondary phosphines good selectivity provided that linear (α -alkenes are not used. Commercially, 9H-9-phosphabicyclononane (American cyanamide) and disobutylphosphine (American Cyanamid) are produced by this method. Azobisisobutyronitrile (AIBN) is used as the initiator.



Primary phosphines are produced selectively, though only in moderate yield, by the acid-catalyzed reaction, this reaction yields Makownikoff products, *tert*-butylphosphine can be obtained from PH_3 and isobutene in this way. This substance has been proposed as a substitute for high-purity PH_3 , for use in the semiconductor industry.

2.5.1.2 Reaction



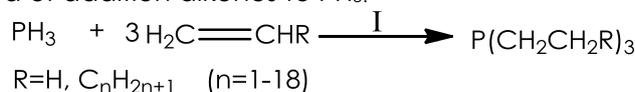
Reaction of PCl_3 with organometallic compounds. The Grignard reaction with phosphorous trichlorides offers an industrial route to tertiary phosphines.



Triphenyl phosphine, which is important as a catalyst ligand and as an intermediate in the synthesis of Wittig reagents, is also produced by BASF in a reaction analogous to the Wurtz reaction.



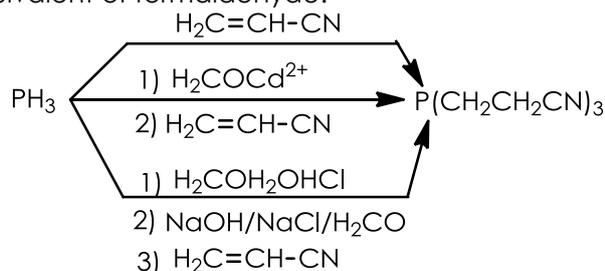
Addition of unsaturated compounds to PH_3 trialkyl phosphines are obtained by the radical-induced addition of alkenes to PH_3 .



I = Initiator (E.g. azobisisobutyronitrile)

Both the Grignard process and the PH_3 route has advantages and disadvantages. For example, trimethylphosphine and trialkyl phosphines cannot be obtained by the PH_3 process. Only linear α -alkenes react smoothly to give tertiary phosphines, and phosphines with sterically hindered groups are generally not obtainable in this way. On the other hand, the Grignard process has a potential pollution problem due to the by-product magnesium salts.

Tris (2-cyanoethyl) phosphine, which is of interest as an intermediate, can be obtained either directly by radical-base-catalyzed reaction of PH_3 with acrylonitrile, or by reacting tris(hydroxymethyl) phosphine with acrylonitrile. Tris(hydroxymethyl)phosphine can be obtained by reacting PH_3 with formaldehyde in the presence of metal catalysts (e.g. Cd^{2+}), but is more conveniently produced from commercially more readily available tetrakis(hydroxymethyl) phosphonium chloride or sulfate by reaction with aqueous NaOH with loss of one equivalent of formaldehyde.



The industrial production of tertiary phosphines with differing groups on the phosphorous atom is carried out by a number of methods.

2.5.2 Uses

Primary and secondary phosphines are intermediates, not usually isolated, in the production of tertiary phosphines and their derivatives. Also, phosphinic and dithiophosphinic

acids, obtained by oxidation of secondary phosphine, have been used to a limited extent for solvent extraction and flotation processes. High-purity tri-*n*-butylphosphine can partially replace the more toxic PH_3 in the production and doping of semiconductors in the electronics industry.

Triphenyl phosphine (TPP) has the greatest industrial importance of all the tertiary phosphines as a ligand in homogeneous catalysis (hydroformylation, hydrogenation and oligomerization), and as a starting material in the preparation of Wittig reagents, especially for the synthesis of vitamin A and in the production of β -carotene can be sulfonated by a process developed by Rhone-Poulenc Hoechst. The rhodium complexes of sulfonated TPP used in hydroformylation are water soluble and can therefore easily be separated from the organic phase.

The phosphinoethanesulfonate salt is also water-soluble. It is used as an antioxidant and complexing agent for silver in the production of positive transparencies.

The tertiary bicyclic phosphines enable long chain α -alkenes to be hydroformylated and hydrogenated, in high yield to give alcohols for detergents.

2.6 ALKYL PHOSPHATES

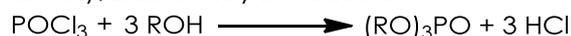
Triethylphosphate is used as a catalyst in the production of acetic anhydride by the ketene process, as a desensitizing agent for peroxides, and as a solvent and plasticizer for cellulose acetate. Tributyl phosphate is used for solvent extraction in hydrometallurgy. Tris (2-ethylhexyl) phosphate is used as a solvent in the production of hydrogen peroxide and is also used as a plasticizer with flameproofing properties.

Tris (chloroalkyl) phosphates are used as fire retardants for polyurethane foams, polyesters, and other plastics. In addition a large-number of other halogen-containing, sometimes oligomeric trialkyl phosphates with mixed ester groups are marketed as flameproofing agents.

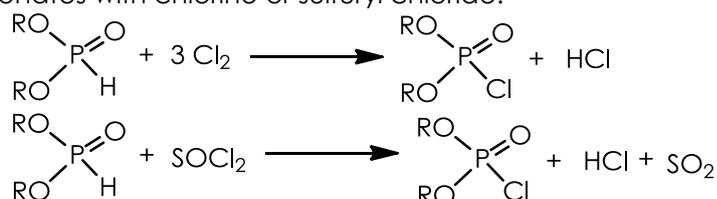
2.6.1 Manufacture

Important raw materials for the production of esters of phosphoric acid are phosphoryl chloride, phosphorus pentoxide, polyphosphoric acid and trialkyl phosphites.

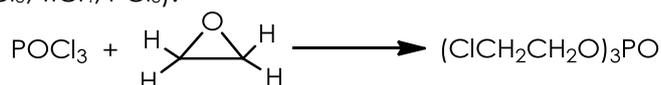
Phosphorus oxychloride reacts with phenols to form triaryl phosphates. With aliphatic alcohols, the hydrogen chloride formed must be removed by vacuum or by purging with an inert gas. Alternatively, bases may be added.



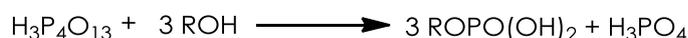
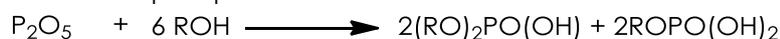
If a substoichiometric amount of alcohol is used, ester chlorides of phosphoric acid are formed. However, diester chlorides of phosphoric acid are better obtained by reacting dialkyl phosphonates with chlorine or sulfuryl chloride.



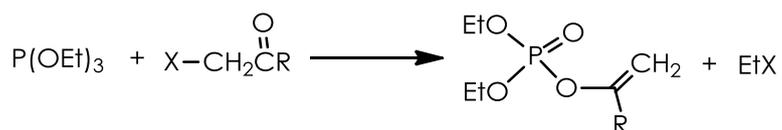
The reaction of ethylene oxide or propylene oxide to POCl_3 at 40-100°C affords tris (2-chloroethyl) or tris (2-chloropropyl) phosphate. To ensure complete reaction, catalysts must be added (AlCl_3 , TiCl_4 , PCl_3).



The mixture of mono- and diesters is formed when alcohols or phenols are reacted with phosphorus pentoxide, while the reaction with polyphosphoric acid yields monoesters of phosphoric acid and free phosphoric acid.



An important method for the production of insecticidal vinyl phosphates is the reaction between trialkylphosphites and α -halocarbonyl compounds (Perkow Reaction).



2.6.1.1 Mono-and dialkyl phosphates

Only a small number of public compounds in this class are of industrial importance. Bis (2-ethylhexyl) DEHPA, is used in Hydrometallurgy as an extraction solvent for a large number of metals. It is produced by chlorinating bis (2-ethylhexyl) phosphonate to give the phosphate diester chloride, followed by hydrolysis, or by saponification of tris is (2-ethylhexyl) phosphate. Products with a high with monoester content, obtained from ethoxylated alcohols, are used as defoamers in washing powders (Sokalan S, BASF).

Esters of thiophosphoric acid are used in plant protection (Insect Control; Fungicides) and as flotation agents in ore preparation, lubricant additives, for solvent extraction of metals, and in rubber production.

Mixtures of mono-and diesters of phosphoric acid are of major industrial importance. Their properties can be varied over a wide range by choice of the alcohol or phenol. Ethoxylated alcohols are most commonly used. The wide range of applications includes emulsifiers in plant protection, cleaning agents, cosmetics and in the paper and textile industries. Mixtures of mono-and diesters are also used as acid hardeners for resins. Manufacturers (trade names) include.

Mixtures of monoesters of phosphoric acid with free phosphoric acid are also marketed. These are mainly used as components of detergents.