

Natubhai V. Patel College of Pure & Applied Sciences
B.Sc. Semester VI
Industrial chemistry (Vocational)
US06CICV02: Heavy and fine organic chemicals
UNIT – 3

SYLLABUS

Chlorination of methane: Methyl chloride, dichloromethane, chloroform, carbon tetrachloride. Ethanolamine, mono, di, and tri-ethanolamines, dialkylaminoethanols (dimethyl, diethyl)

3.0 METHYL CHLORIDE AND DICHLORO METHANE**3.0.1 From methane by chlorination****3.0.1.1 Raw materials**

Basis - 1 ton methyl chloride
 Chlorine
 Methane (STP)

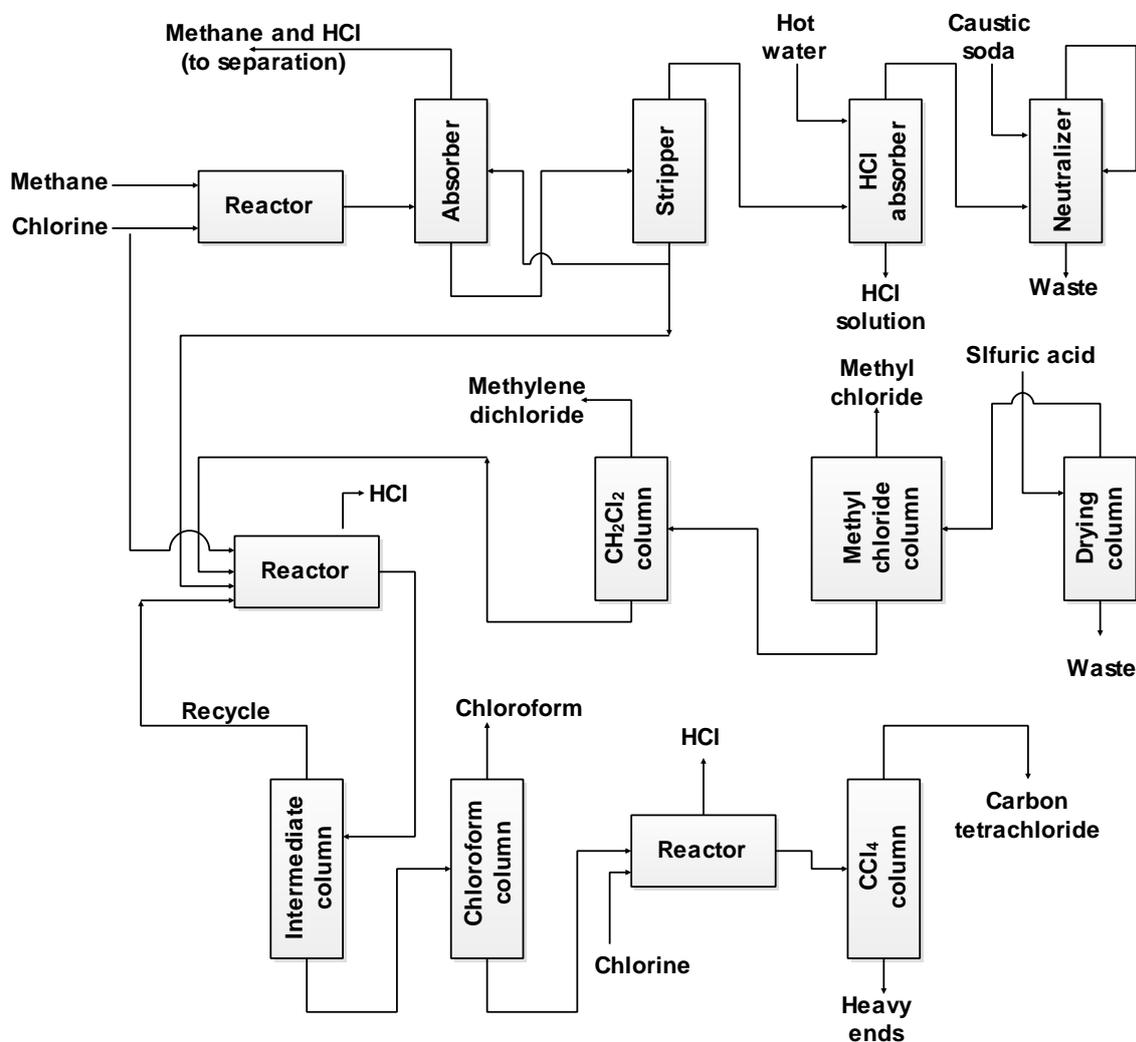
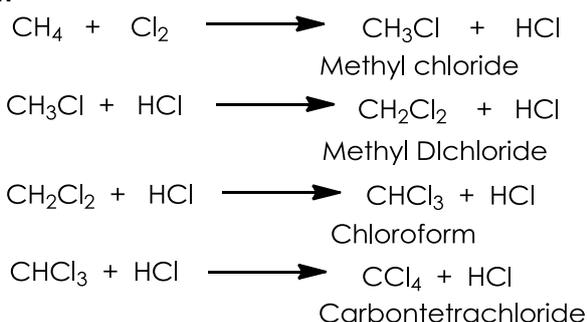


Figure: Production of Methyl chloride from methane by chlorination

3.0.1.2 Reaction

Yield (chlorinated methane) - 99-100% (based on chlorine)

85-99% (based on methane)

3.0.1.3 Manufacture

The reaction between chlorine and methane in the presence of light or a catalyst may be controlled so as to yield predominantly methyl chloride, with the formation of smaller amounts of methylene dichloride, chloroform and carbon tetrachloride, if methylene dichloride is desired in largest amount, the methylene dichloride may be recycled to chlorinator. In normal practice, however, the desired chlorinated compound is carbon tetrachloride, so most of the other chloromethanes are recycled.

One commercial process in which all four chloromethane are produced is shown in the flow sheet. Methane (99% pure) is mixed with chlorine in a mole ratio of 1.7 to 1. The reactants are preheated and fed to a reactor fitted with mercury arc lamps to promote the reaction. At 350 to 370°C and only slightly above atmospheric pressure, and with residence times controlled so that the temperature desired may be held, completely used up, and about 65% of the methane is reacted. A typical range of products leaving the reactor is as follows: methyl chloride - 58.5 per cent; methylene dichloride - 29.3 per cent; chloroform - 9.7 per cent; and carbon tetrachloride - 2.3 per cent. The effluent gases from the reactor also contain unreacted methane and hydrogen chloride.

These last mentioned materials are separated from the chloromethanes by scrubbing the reacted gases with a mixture of liquid chloromethanes usually a refrigerated mixture of chloroform and carbon tetrachloride. Methane and hydrogen chloride are not absorbed and go overhead. They are subsequently separated in water absorber methane recycled. The chloromethane absorbent, enriched with the chlorinated products removed from the reaction gases, is led to a stripping column. Methyl chloride and some methylene dichloride go over head. They are condensed and then purified by a hot water wash (to remove residual hydrogen chloride). An alkali wash, and a strong sulfuric acid wash (to dry the solvent mixture). The methyl chloride, methylene dichloride and any heavy ends are separated by fractional distillation.

Not all of the bottoms from the stripping column are recirculated to the reaction effluent absorber. A considerable portion of the liquid is fed to a secondary reactor, where more chlorine is added and a chlorination reaction is again carried out photochemically, but this time in the liquid phase. Hydrogen chloride vented from the reactor. The reaction products are purified and separated by a sequence similar to that used for methyl chloride and methylene dichloride, except that any product less chlorinated than chloroform is recycled. Desired quantities of chloroform are removed by distillation and the remaining material chlorinated in a third reactor to produce carbon tetrachloride.

Another methane chlorination process is directed specifically to methyl chloride; it makes use of a high methane chlorine ratio (10 to 1 by volume) and a catalyst such as partially reduced cupric chloride deposited on pumice. The gases are mixed and passed through a chlorination furnace operated at about 450°C. The contact time varies but is usually maintained in the range of 1 to 20 sec.

The reaction gases pass through a water scrubber to remove the hydrogen chloride formed and are then led through a series of water-cooled and refrigerated condensers under pressure, the mixture of chlorinated hydrocarbons condenses, and unreacted methane is recycled to the mixing chamber. Practically all the chlorine reacts with the methane, so that little or no chlorine remains in the reaction gases.

Crude methyl chloride is distilled under pressure to yield pure methyl chloride of

refrigerant grade. Approximately 85 to 90 per cent of the condensate distills between - 23 and -23°C (atmospheric pressure) to give a yield of methyl chloride of about 80 per cent based on the chlorine charged.

3.0.1.4 Uses

➤ Methyl chloride

	Per cent
Silicones	58
Tetramethyllead	16
Butyl rubber	12
Methyl cellulose	07
Miscellaneous	<u>07</u>
	100

➤ Methylene dichloride

	Per cent
Paint remover	50
Photographic film	15
Degreasing solvents	13
Aerosol propellants	10
Miscellaneous	<u>12</u>
	100

3.1 CHLOROFORM

3.1.1 From acetone and bleaching powder

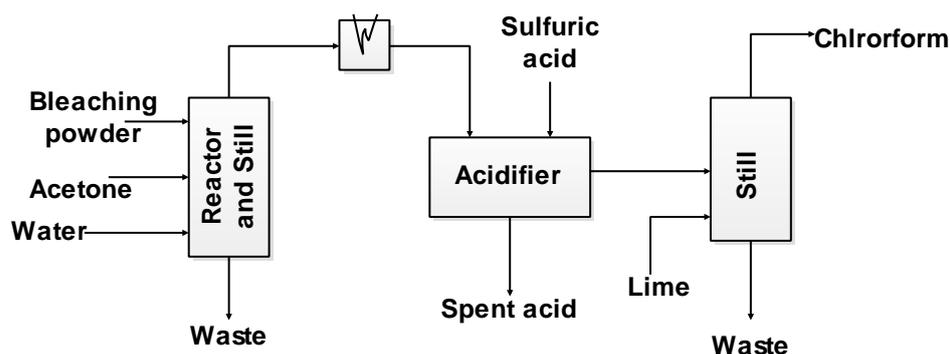


Figure: Production of Chloroform from acetone and bleaching powder

3.1.1.1 Raw material

Basis-1 ton chloroform

Chlorine	3,560 lb
Methane (STP)	6,000 cu ft

3.1.1.2 Reaction



3.1.1.3 Manufacture

The action of bleaching powder ($\text{CaOCl}_2 \cdot \text{H}_2\text{O}$) on acetone, acetaldehyde or ethyl alcohol yields crude chloroform, which may readily be purified by chemical treatment and distillation.

In the older, more common batch process, water is run into a mixing tank. Using good agitation, bleaching powder containing about 34 per cent available chlorine is slowly charged to the mixer in the ratio of about 3 lb per gal of water. The suspension of bleaching powder in water is strained into a cast-iron still, fitted with efficient agitation, cooling coils, and heating coils.

Acetone is slowly run into the still (approximately 0.1 lb of acetone per lb of bleaching powder), and the temperature is maintained below 110°F by the cooling coils and rate of addition. When all the acetone has been added the pot temperature is raised to 134°F, where chloroform begins to distil. By gradually increasing the temperature to 150°F practically all the chloroform formed is distilled over. The vapor are passed through a condenser and collected in a tank fitted with an agitator. The crude material (crude chloroform and water)

is purified by agitation with concentrated sulfuric acid in a weight ratio of about 2 lb of crude chloroform (distillate) per lb of sulfuric acid. After 2 to 3 hr agitation, the crude chloroform (which does not impart any colour to clear concentrated sulfuric acid) is decanted from the acid and charged to a still, where it is distilled over calcium oxide (lime). The purified chloroform assays over 99 per cent and is obtained in an 86 to 91 per cent yield based on the acetone charged. A yield of 80 per cent of chloroform may be realized using acetaldehyde. A 20 per cent aqueous solution of acetaldehyde is charged into a solution of bleaching powder containing 9 to 10 per cent active chlorine. After vigorous stirring of the solution maintained at 110 to 115°F, the product is neutralized and chloroform is separated by distillation and purified as described previously.

These processes may be run on a continuous basis and also may utilize a mixture of acetone and acetaldehyde as the raw material. Industrial ethyl alcohol has been used to make chloroform and was the basis for the original bleaching powder process. By employing a method similar to those previously, 1 ton of chloroform is produced from 19,400 lb of bleaching powder (35 per cent available chlorine), 225 gal of 25 per cent alcohol and about 40 tons of steam.

3.1.1.4 Uses

	Per cent
Fluorocarbon refrigerants	55
Fluorocarbon resins	30
Propellants	05
Pharmaceuticals and miscellaneous	<u>10</u>
	100

3.2 CARBON TETRACHLORIDE

3.2.1 From carbon disulfide and chlorine

3.2.1.1 Raw materials

Basis – 1 ton carbon tetrachloride

Carbon disulfide	1100 lb
Chlorine	2300 lb

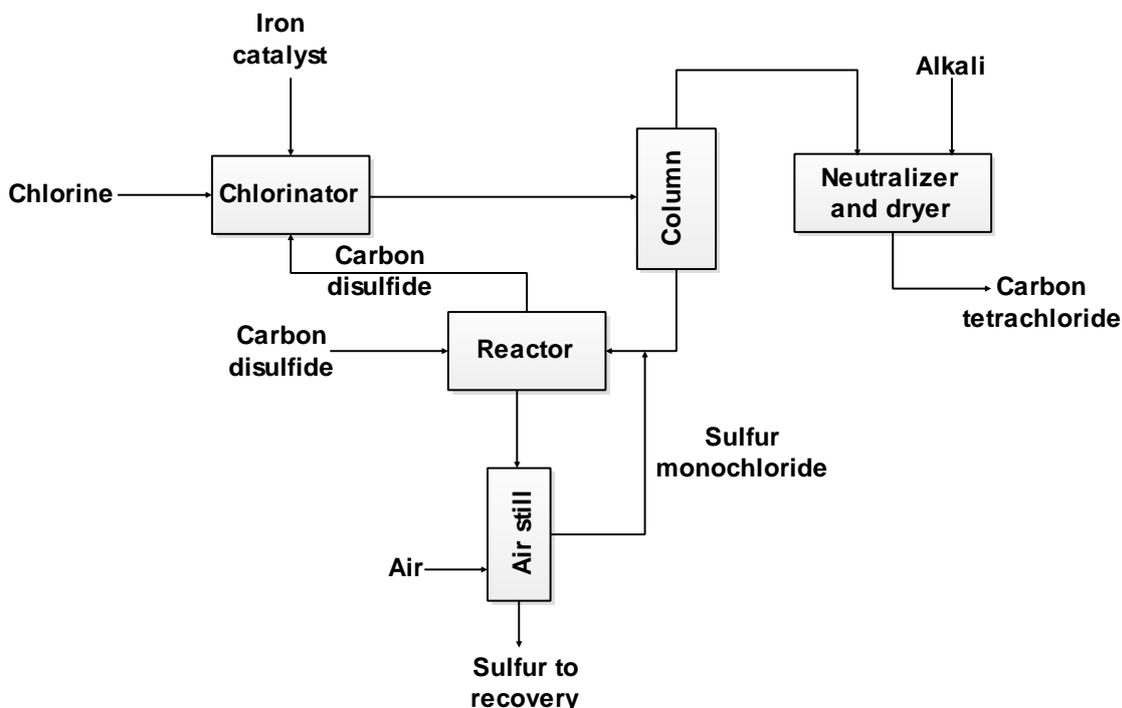
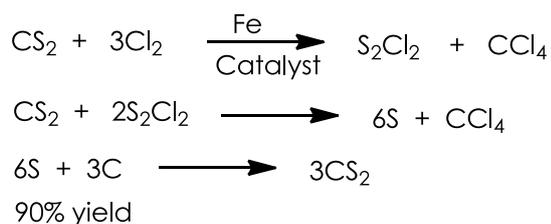


Figure: Production of Carbon tetrachloride from carbon disulfide and chlorine

3.2.1.2 Reaction**3.2.1.3 Manufacture**

A solution of carbon disulfide in carbon tetrachloride (approximately 40 per cent carbon disulfide, 50% carbon tetrachloride, and 10% sulfur monochloride) is charged into a lead-lined chlorinator fitted with cooling coils. Chlorine is bubbled through the solution, which contains iron borings or powder as a catalyst. The iron remains in the chlorinator from batch to batch and is replenished when warranted. The temperature is maintained around 30°C by cooling water. An excess of chlorine is used to insure complete conversion of carbon disulfide (about 0.5% remains unchanged)

The reaction products, consisting of carbon tetrachloride (60 per cent) and sulfur monochloride (40%), are passed to distilling column, where they are separated, the carbon tetrachloride distillate, containing less than 1 per cent sulfur monochloride is sent to a neutralizer and dryer, where acidic material are neutralize by agitation with alcoholic sodium hydroxide solution or by passage over alkaline desiccant. The moisture content is also decreased. Desiccants that may be used include anhydrous calcium chloride, sodium carbonate and silica gel. The dried material may be redistilled it warranted to give carbon tetrachloride of 99.8 – 99.9% purity.

The residue from the distillation column contains about 85 per cent sulfur monochloride and 15 per cent carbon tetrachloride. This mixture is reacted with carbon disulfide at 60°C in a lead-lined reaction kettle fitted with an agitator. At the end of the reaction, the carbon tetrachloride and most of the sulfur monochloride produced are distilled off. The distillate containing the above-mentioned two compounds and unreacted carbon disulfide (about 40%) is charged to the chlorinator to start the cycle, The residual sulfur, containing 10 to 15 per cent sulfur monochloride, is discharged to an air still. The monochloride is removed by blowing with air and is recycled to the reactor with coke.

Several modifications of this process are existent. One such modification is the indirect chlorination of carbon disulfide with sulfur dichloride to produce carbon tetrachloride and sulfur. Less sulfur is produced by this method than by the direct chlorination since the following is the main reaction:



The latter is chlorinated ($4\text{S} + 4\text{Cl}_2 \longrightarrow 2\text{SCl}_2$) to yield sulfur dichloride, which is reacted with fresh carbon disulfide to complete the cycle. The carbon tetrachloride is removed from the sulfur by distillation and is purified as previously. The yield of carbon tetrachloride is approximately 90 per cent based on the weight of carbon disulfide.

3.2.1.4 Uses

	Per cent
Fluorocarbons	85
Grain fumigant	08
Solvents	05
Miscellaneous	02
	100

Carbon tetrachloride is by far the most important of the chlorinated methanes. It is one of the older commercial organic chemicals and has been a dominant factor in various fields during the past forty years. Some of the newer chemicals, more satisfactory for a specific use, have displaced carbon tetrachloride in some of its major uses, but production has continued to increase as "carbon tetrachloride" has invaded new fields. In the dry cleaning field it has been largely replaced by perchlorethylene; in industrial decreasing to a

Further possible reactions to tetraethanolammonium hydroxide or the monoglycol ether of triethanolamine do not play any role in the synthesis. The kinetics of these reactions has been studied.

All the reaction steps have about the same activation energy and show a roughly quadratic dependence of the reaction rate on the water content of the ammonia-water mixture used. Therefore, product composition depends solely on the molar excess of ammonia and not on water content, reaction temperature or pressure. The product distribution as a function of the molar ratio of the reactants is shown in figure.

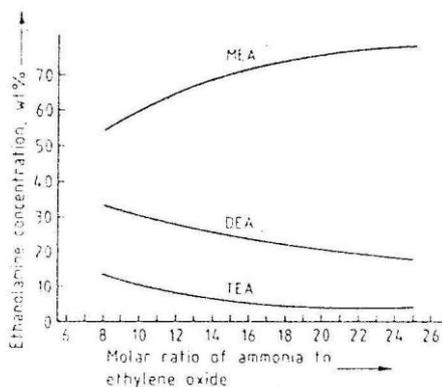


Figure: Product distribution of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) as a function of the molar ratio of ammonia to ethylene oxide (concentration of the aqueous ammonia solution ca. 85%).

Unconsumed ammonia and water fed in as a catalyst are separated from the end products in a distillation line downstream of the reactor and are recycled. In large-scale continuous single-line plants, the requirement for low energy use (i.e., operation with minimum steam consumption) determines both the transport of heat from the reactor and the design of the thermally integrated distillation line. The ethanolamine mixture is worked up in vacuum distillation columns to give the pure products (Figure).

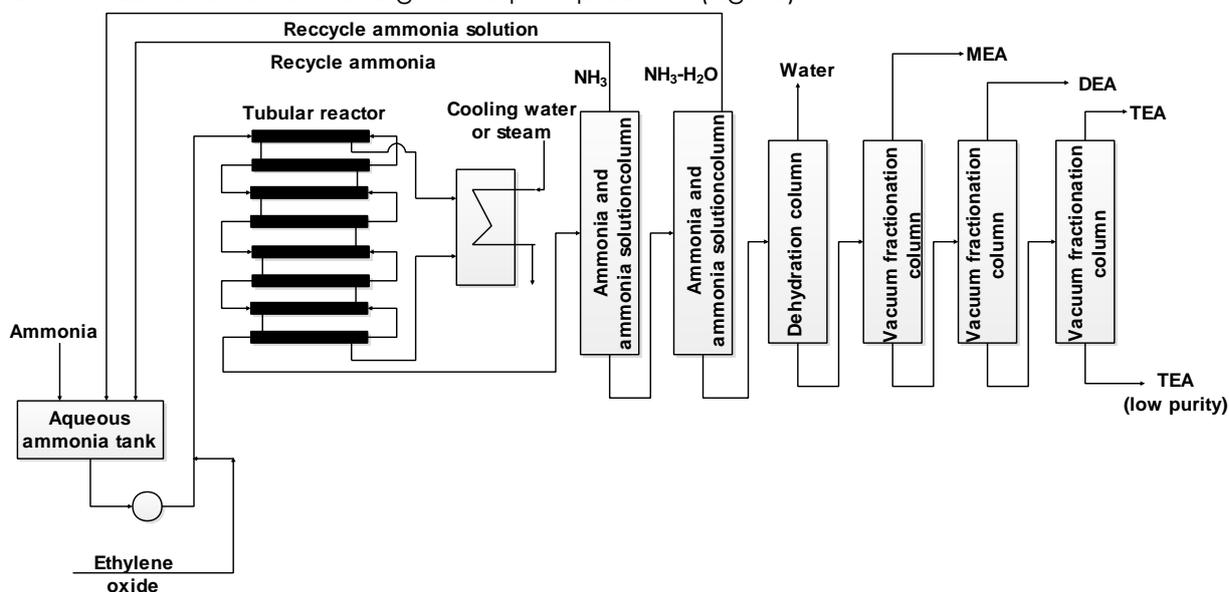


Figure: Production of ethanolamines from ammonia

Figure: Flow sheet for the production of ethanolamines a) Aqueous ammonia tank; b) Tubular reactor c) Ammonia and ammonia solution columns; d) dehydration column; e) Vacuum fractionation columns.

Product distribution of the three ethanolamines can be controlled by appropriate

choice of the ammonia: ethylene oxide ratio. A higher diethanolamine or triethanolamine content can also be obtained by recycling monoethanolamine or diethanolamine to the reactor or by reacting them with ethylene oxide in a separate unit.

For safety reason ethylene oxide must be metered into the ammonia stream; in the reverse procedure, ammonia or amines may cause ethylene oxide to undergo an explosive polymerization reaction. In all large scale processes virtually complete conversion to the three ethanolamines, without significant formation of by-products is achieved. Therefore feedstock costs are independent of the type of production process. On the other hand, manufacturing costs depends to large extent on the product composition desired plant design and degree of thermal integration.

3.3.2 Uses

The most important uses of ethanolamines are in the production of emulsifiers, detergent raw materials, and textile chemicals; in gas purification processes; and in cement production, as milling additives. Monoethanolamine is an important feedstock for the production of ethylenediamine and ethylenimine.

➤ Surfactants

Ethanolamines are used widely as intermediates in the production of surfactants which have become commercially important as detergents, textile and leather chemicals, and emulsifier. Their uses range from drilling and cutting oils to medicinal soaps and high quality toiletries.

Ethanolamine-based surfactants can be formulated as weakly basic or neutral products and are, therefore, particularly well tolerated by the skin; this is especially true for triethanolamine soaps. Moreover, they are noncorrosive and can be used on virtually all textiles without damage. Ethanolamine soaps prepared from oleic acid, stearic acid, lauric acid, or caprylic acid are constituents of many toiletries medicinal soaps.

Ethanolamine soaps produced from fatty acids are among the most industrially important emulsifiers. They are used in cosmetics, polishes, shoe creams, car care products, drilling and cutting and pharmaceutical ointments. Ethanolamine soaps combined with, wax and resins are used as impregnating materials, protective coatings, and products for the care of textile and leather goods.

Ethanolamine soaps obtained from alkylarylsulfonic acids, preferably alkylbenzene sulfonic acids, preferably alkylbenzenesulfonic acids, or from alcohol sulfates are growing steadily in importance and dominate the market for household cleansers. The use of linear alkyl groups instead of branched chains these products has resulted in greater biodegradability.

Fatty acid ethanolamides and products obtained by further ethoxylation have foam stabilizing ability and are, therefore, important additives for detergents. Diethanolamides obtained from coconut fatty acids and from oleic acid are used industrially.

In the manufacture of leather, ethanolamine based chemicals are used for dressing, dyeing and finishing. For paints and coatings, ethanolamines are employed both in production and in softeners and paint removers.

➤ Corrosion Inhibitors

Diethanolamine and triethanolamine are important components of corrosion inhibitors, particularly in coolants for automobile engines, as well as in drilling and cutting oils. They are also employed as additives in lubricants.

When the corrosion inhibitor sodium nitrite and diethanolamine are used together, N-nitrosamines may form. These nitrosamines are carcinogenic; therefore, sodium nitrite and diethanolamine or triethanolamine should not be used simultaneously,

➤ Gas Purification

Large amounts of ethanolamines, principally diethanolamine, are used in absorptive purification to remove weakly acidic components. For example, hydrogen sulphide and carbon dioxide are removed from natural gas, refinery gas, and synthesis gas.

➤ Intermediates

A substantial portion of the monoethanolamine is used as a starting material in the preparation of ethylenimine and ethylenediamine. Ethylenimine is converted to polyethylenimine, an important chemical in paper technology. Diethanolamine is used in the

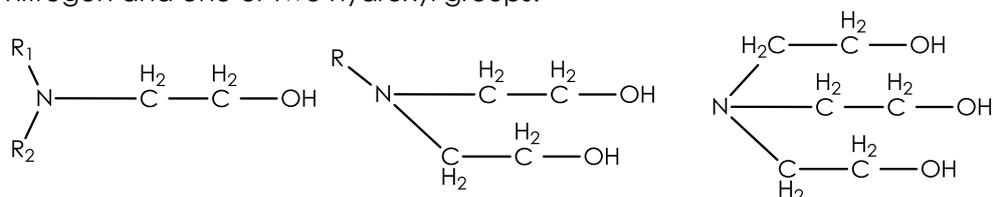
production of morpholine.

➤ **Cement Additives**

Aqueous solutions of triethanolamine and triethanolamine acetate have been used as milling additives in cement production. During grinding of the clinker in ball mills, the small amount of triethanolamine added prevents agglomeration and cushioning of the grinding medium by saturating surfaces of the freshly broken particles. Like other milling additives (e.g., various glycols), they reduce the power required for milling the clinker. Today, the milling of virtually all high-quality Portland cement involves milling additives. In addition to assisting the milling process, triethanolamine also improves the flow properties and setting behavior of the cement.

3.4 N-ALKYLATED ETHANOLAMINES

N-Alkylated ethanolamines are amino alcohols that contain secondary or tertiary nitrogen and one or two hydroxyl groups.



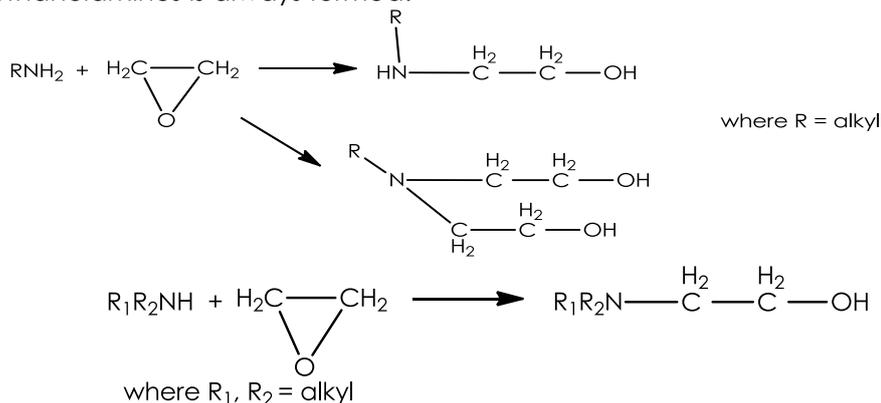
where $R_1 = \text{alkyl or H}$
 $R_2 = \text{alkyl}$
 $R = \text{alkyl}$

Numerous compounds with different properties and uses can be synthesized by varying the alkyl radical.

3.4.1 Manufacture

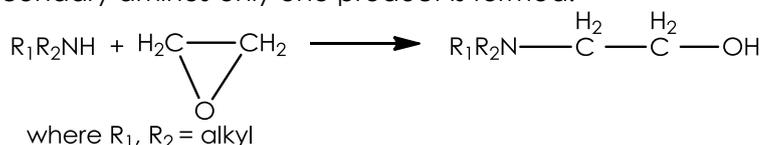
Industrially, N-alkylated ethanolamines are produced almost exclusively by batchwise or continuous reaction of primary, secondary, or tertiary amines with ethylene oxide. For safety reasons, ethylene oxide must be added to the amine, never vice versa. Depending on the product involved, reaction temperature varies from 50 to 170°C and pressure from 0.2 to 4 MPa (2 to 40 bar). Water accelerates the reaction.

When primary amines are used, a mixture of N-alkylethanolamines and N-alkyldiethanolamines is always formed:



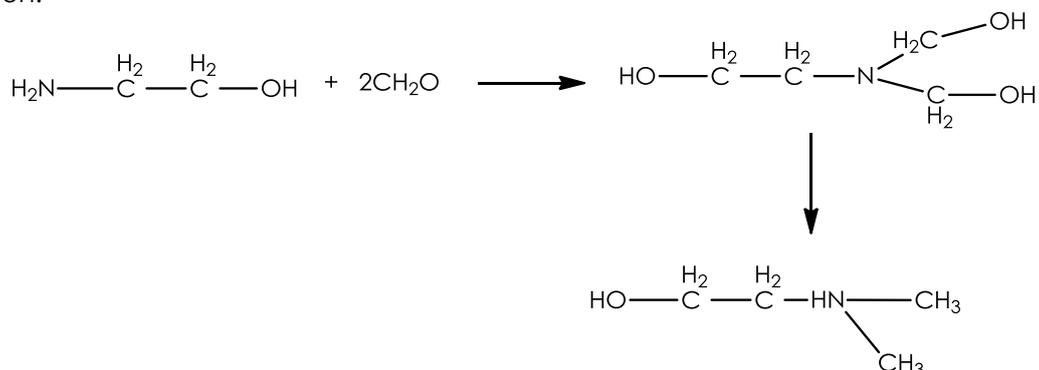
The larger the excess of amine, the lower is the proportion of N-alkyldiethanolamines. If N-alkylethanolamines are desired, a continuous process is usually preferred for economic reasons. Excess amine is distilled from the reaction product and recycled.

With secondary amines only one product is formed:



Another common method of preparing N-alkylethanolamines is by N-alkylation of

ethanolamines. Methyl derivatives can also be obtained by reacting monoethanolamine or diethanolamine, or their homologues, with formaldehyde and then reducing the hydroxymethyl compound. Pure components are obtained from the crude products by distillation.



The reaction of epichlorohydrin with amines to give N-alkylethanolamines is today of only minor commercial importance.

3.4.2 Uses

Alkylethanolamines are used mainly as intermediates, especially in the production of pharmaceuticals such as the local anesthetics procaine (diethylethanolamine 4-aminobenzoate) and tetracaine; (dimethylethanolamine 4-butylaminobenzoate); crop protection agents, flocculants (dimethylethanolamine acrylate and diethylethanolamine acrylate). They are also important in the preparation of chemicals for the paper and leather industries. Use of N-alkylethanolamines in the production of plastics has risen substantially in recent years.

Direct uses of N-alkylethanolamines, especially methyldiethanolamine, include gas purification methods for removing acidic gases (CO₂, H₂S).