ETHYLENE GLYCOL

Introduction:
Wurtz first prepared Ethylene Glycol in 1859 by the hydrolysis of Ethylene glycol diacetate. It did not achieve its commercial production until the world war – I, when it was used in Germany as a substitute for the glycerol in explosives manufacture.

Ethylene Glycol and its lower polyglycols are colorless and odorless, high boiling, hygroscopic liquids completely miscible with water and many organic liquids. Ethylene Glycol gets oxidizes to form a number of aldehydes and carboxylic acids by oxygen, nitric acid and other oxidizing agents.

Manufacturing of EG from Ethylene Oxide:
Currently only one method is predominantly used world wide for the production of Ethylene Glycol. This method is hydrolysis of Ethylene Oxide. Ethylene Oxide is obtained by the direct oxidation of Ethylene with air and Oxygen in presence of Silver catalyst.

After the reactor, the mixture of Ethylene Glycol and Water is passed through successive distillation columns with decreasing pressure. Which first separates excess water and returned back to the reactor. Mono, Di and Tri Ethylene Glycols are separated by vacuum distillation. This is the most common method for the manufacturing of Ethylene Glycol but it has certain drawbacks.

1. The selectivity of ethylene Oxide hydrolysis is low. 10 % is converted to di and tri Ethylene Glycols.
2. Energy consumptions for the distillation of the large amount of excess water is high.

The selective synthesis of Ethylene Glycol via the intermediate Ethylene carbonate seems to be a promising alternative. This compound is obtained in high yield (98%) by reacting Ethylene Oxide with carbon monoxide and can be selectively hydrolysed to give a high yield of ethylene Glycol.

Alternative Process

1. Hydrolysis of Ethylene Chlorohydrin which is produced by the reaction of chlorine and water gives Ethylene Glycol when reacts with sodium carbonate

\[
\begin{align*}
\text{CH}_2\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} & = \text{CH}_3\text{OH} \cdot \text{CH}_2\text{Cl} + \text{HCl} \\
\text{CH}_3\text{OH} \cdot \text{CH}_2\text{Cl} + \text{NaHCO}_3 & = \text{CH}_3\text{OH} \cdot \text{CH}_3\text{OH} + \text{NaCl} + \text{H}_2\text{O}
\end{align*}
\]
Passing Ethylene and chlorine into water at 50 to 120°F produces the Ethylene Chlorohydrin. The Chlorohydrin solution is also concentrated to 35 to 40%. And reacted with the theoretical amount of sodium bicarbonate solution in a closed stirred steam jacketed vessel. At the temperature of 70 to 80°C the hydrolysis proceeds. It is very difficult to separate the salt and Ethylene Glycol, it is always better to make Ethylene Oxide and then Hydrolyze it to make Ethylene Glycol.

2. From synthesis Gas:
   Greatest cost component of a chemical process is the raw material. For synthesis gas, the level of purity, usable concentration and pressure are the three variables that influence cost appreciably. The production of synthesis gas is determined by the raw material, the processing cost and the purification. Most commonly used raw material is natural gas and petroleum resides. Petroleum resides main advantage is its low feed cost with high handle ability. For the Ethylene Glycol manufacturing with synthesis gas is basically affected by two factors:
   
   a. Purity of synthesis gas
   b. Whether the synthesis gas can be used directly or must be separated or have its \( \text{H}_2 / \text{CO} \) ratio adjusted.

In the synthesis of Ethylene Glycol from synthesis gas, using noble metals as catalyst, purity is of paramount importance. Sulfur impurities are very detrimental to the catalyst performance.

Manufacturing of Ethylene Glycol from synthesis gas has five different roots of production,

a. Direct oxidation of Synthesis gas

\[
3\text{H}_2 + 2\text{CO} = \text{HOH}_2\text{C.CH}_2\text{OH} \quad (\text{Rh catalyst at } 3400 \text{ atm. And } 230^\circ\text{C})
\]

b. Reductive hydroformylation of formaldehyde to Ethylene Glycol

\[
\text{H}_2\text{CO} + \text{CO} + \text{H}_2 = \text{HOH}_2\text{C.CH}_2\text{OH} \quad (\text{Rh catalyst at } 4350 \text{ psi and } 150^\circ\text{C})
\]

c. Hydroformylation of formaldehyde to Glycolaldehyde
d. Carbonylation of formaldehyde
e. Oxidative coupling of carbon monoxide
2. From methanol:

Methanol is uniquely cost effective for the glycol synthesis. The cost component of the methanol are:

a. Raw material cost of the carbon source processes to synthesis gas
b. The capital and utilities cost of the producing and purifying the synthesis gas
c. The capital and utilities cost of the producing methanol and purifying it.

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{CO} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} \quad \text{......... 1} \\
\text{CH}_3\text{OH} + \text{HCOH} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} \quad \text{......... 2} \\
\text{CH}_3\text{OH} + \text{CH}_3\text{OH} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} + \text{H}_2 \quad \text{......... 3}
\end{align*}
\]

All the three reactions shown above worked in the presence of free radicals. Reaction 1 works slowly but the other two can be made to work very well. Reaction 3 dehydrodimerization, uses cheaper starting materials but requires stoichometric oxidant. Reaction 2 uses a higher valued raw material for part of the stoichometric and catalytic in free radicals.

Methanol can represent from 120% to 60% of the raw material requirements (on syngas basis) for Ethylene Glycol production, depending on whether the dehydrodimerization or addition reaction is used. Similarly the formaldehyde requirements are from 0 to 44-48% of the Ethylene Glycol Production.

**Process Selection:**

The unit operations involved in the manufacturing of Ethylene Oxide manufacturing from the hydration of Ethylene Oxide is described below and there respective significance in the manufacturing process is briefed below.
**Ethylene Glycol from Ethylene Oxide**

**Reactor:**
We feed Ethylene oxide and water to the reactor and the hydration of Ethylene Oxide take place in this reactor. The Ethylene Oxide is thermally hydrolyzed to Ethylene Glycol without any catalyst presence. Ethylene Oxide water mixture is preheated to 200 °C. Whereby Ethylene Oxide is converted to Ethylene Glycol. For the commercially operating reactors the operating temperature is 190-200°C and pressure is 14-22 atm depending upon the initial concentration of Ethylene oxide. In this Hydrolysis process the formation of higher homologous are inevitable because Ethylene Oxide reacts with Ethylene Glycol much faster than it does with water. To minimize this excess water almost 20 times more is used, almost 90% of the Ethylene Oxide can be converted to Mono Ethylene Glycol the rest is converts to higher glycols.

The most important variable is the water to Ethylene oxide ratio and in commercial plants the production of diethylene glycol and triethylene glycol can be reduced considerably by using excess amount of water. As the molar ratio of water to ethylene oxide increases the selectivity of the Ethylene glycol decreases in the reactor outlet. *(ref: page 240 of encyclopedia of chemical processing and design vol. 20)*. The reference figure from which the data was interpreted is considered as theoretical, operating data from commercial plants which generally show that heavy glycols at high water/EO ratios is somewhat greater than shown in the ref figure. The beneficial effects of increasing the water recycle on MEG yields starts decrease rapidly above water/EO ratio of 10 to 15. In the design of economically optimum glycol plant the improved MEG yields resulting from increasing the water recycle are balanced against increased capital and utility costs.

The rate of hydration is greatly affected by the temperature and the catalytic action of acids. The use acid catalysts in the hydration reaction permits it to be operated...
at lower temperature and pressures than the unanalyzed reaction, but the reaction solution becomes highly corrosive and requires acid removal.

**Evaporators:**

The water glycol mixture from the reactor is fed to the first stage of a multiple stage evaporator, which is reboiled using high-pressure steam. The remaining stages normally of the evaporator operate at successively lower pressure, with the final stage normally under vacuum. The evaporate water is recovered as condensate and recycled back to the glycol reacting feed mixing system.

**Distillation:**

The VDU (Vacuum Distillation Unit) takes the residuum from the ADU (Atmospheric Distillation Unit) and separates the heavier end products such as vacuum gas oil, vacuum distillate, slop wax, and residue. The liquid from the feed furnace enters the tower bottoms, where it is collected and sent for further processing. Steam is injected into the base of the tower to reduce the hydrocarbon partial pressure by stripping some light boiling components from the bottoms liquid.

Ethylene glycol and the water mixture is fed to the final column for purification of ethylene glycol by vacuum distillation method. From the top of the column we get pure Ethylene Glycol and from bottom we get higher glycols.

**Uses of Ethylene Glycol:**

1. Ethylene Glycol lowers the freezing point of water. Its ease of handling makes it perfect antifreeze, which accounts for over 50% of its commercial uses.
2. Commercial antifreezes based on glycol also contain corrosion inhibitors and are used for example in motor vehicles, solar energy units.
3. Ethylene Glycol is also a commercially important raw material for the manufacture of polyesters fibers chiefly poly ethylene terephthalate. This application consumes 40% of total consumption of Ethylene Glycol.
4. It is also used for the production of recyclable bottles.
5. Other uses are humectants (moisture retainer), plasticizer, softener, hydraulic fluid and solvent.