# PRODUCTION OF ETHYLENE GLYCOL

## Manufacturing processes

The different processes followed for the production of ethylene glycol are as follows:

Ethylene carbonate process:

In this method, ethylene oxide is converted to an intermediate, ethylene carbonate, by reaction with carbon dioxide, which is then hydrolyzed by water to give ethylene glycol. This process was in use in the 1970s, but this process was replaced later by combined ethylene oxide-glycol plants.

Halcon Acetoxylatin Process:

Two reaction steps were used in the Oxirane plant. In the first, ethylene glycol diacatate was obtained by the oxidation of ethylene in an acetic acid solution, catalyzed by tellurium and a bromine compound. The reaction complex, which is quite complicated, is believed to proceed via a tellurium-bromoethylene complex. The oxidation, which is carried out at 90-200 $^{\circ}$C and 20-30 atm pressure, results in a mixture of acetates due to partial hydrolysis of the diacetate. The reaction liquid effluent is withdrawn and processed to recover glycol acetates and glycol and provide the recycle streams back to oxidation. In the second step of the process, the glycol acetates are hydrolyzed to ethylene glycol and acetic acid.

The process however is not popular due to operating difficulties. A plant started at Channelview to produce 800 million lb/yr of ethylene glycol was shut down after difficulties in startup.

Teijin Oxychlorination Process:

The Teijin process, which has not been commercialized yet, produces ethylene glycol by the reaction of ethylene with thallium salts in the presence of water and chloride or bromide ions. A redox metal compound (such as copper) oxidizable with molecular oxygen is added to the reaction medium to permit the regeneration of the thallium salt.

Union Carbide Syngas Process:

The following process developed by Union Carbide, Inc. Uses synthesis gas for the production of ethylene glycol. Glycerol and propylene oxide are the major by-products. Methanol, methyl formate and water are also produced. An expensive rhodium based catalyst catalyzes the reaction. The process is yet to be commercialized. Union Carbide has already started work on a modified process in association with Ube Industries. It plans to set up a commercial scale plant soon.

Hydrolysis of Ethylene Oxide:

This method is by far the most widely used method for the production of ethylene glycol. The simplicity and reliability of the process makes it popular. Furthermore, it can be used in plants that manufacture ethylene oxide and glycol together. This process has been selected in the following Design Thesis and will hence be dealt in detail.

Chemistry of the Reaction:

The reaction chemistry is quite simple, and can be summarized as follows: ethylene oxide reacts with water to form ethylene glycol, and then further reacts with ethylene glycol and higher homologues in a series of consecutive reactions as shown in the following equations:

$$(CH_2)_2O + H_2O \rightarrow (CH_2OH)_2 \quad \Delta H = -21.8 \text{ kcal}$$

Monoethylene Glycol

$$(CH_2)_2O + (CH_2OH)_2 \rightarrow HOCH_2CH_2OCH_2CH_2OH$$

Diethylene Glycol

$$(CH_2)_2O + HOCH_2CH_2OCH_2CH_2OH \rightarrow HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

Triethylene Glycol

The formation of these higher glycols is inevitable because ethelene oxide reacts faster with ethylene glycols faster than with water. The effects of reaction conditions of the glycol distribution from the hydrolysis reaction are shown in the fig 3.1. The most important variable is the water-to-oxide ration, and in commercial plants the production of diethylene glycol (DEG) and triethylene glycol (TEG) can de reduced by using a large excess of water.

The reactor product distribution is essentially unaffected by temperature and pressure over the ranges (90-200 $^{\circ}$C, 1-30 bars) which are normally of commercial interest. Reaction velocity constants for acidic-neutral conditions are shown in the fig 3.2.

**Process Description of Ethylene Glycol Plant**

The schematic flow diagram of a commercial ethylene oxide hydration plant, designed to produce a maximum quantity of ethylene glycol, is represented in fig 3.3.

The raw materials to a free standing glycol plant are refined ethylene oxide and pure water. These are mixed with recycle waters and pumped into the hydration reactor after being preheated by the exit product stream. In the glycol reactor, sufficient time is provided to react all the ethylene oxide. The operating pressure of the reaction is controlled at a level, which limits or avoids the vaporization of ethylene oxide from the aqueous solution. Literature shows that commercial reactors operating at 190-200 $^{\circ}$C will be at pressures 14-22 atm depending on the initial concentration of the oxide.

The water-glycol mixture from the reactor is fed to the first stage of a multiple stage of the evaporator, which is reboiled with steam. The remaining stages operate at successively lower pressures, with the final stage normally under vacuum. The evaporated water is recovered as condensate and recycled back to the glycol reaction feed mixing tank. The water free glycol solution is sent to a series of vacuum distillation towers to produce purified monoethylene glycol and by-product di- and triethylene glycol.

**Quality specifications**

Since ethylene glycol is produced in relatively high purity, differences in quality are not expected. The directly synthesized product meets the high quality demands (polyester grade glycol). The quality specifications are given in the table below. The UV absorption of fiber-grade ethylene glycol is often used as an additional parameter in quality control.

| | |
|---|---|
| Color, Pt-Co, max | 5 |
| Suspended matter | Free |
| Diethylene Glycol, wt% max | 0.08 |
| Acidity, as acetic acid, wt% max | 0.005 |
| Ash, wt% max | 0.005 |
| Water, wt% max | 0.08 |
| Iron, ppm wt max | 0.07 |
| Chlorides, ppm wt max | <0.2 |
| Distillation Range, ASTM at 760mm Hg, °C, max | 200 |
| Odor | Mild |
| UV Transmittance, %min at: | |
| 220 nm | 70 |
| 250 nm | 90 |
| 275 nm | 95 |
| 350 nm | 99 |
| Specific Gravity, 20/20 °C | 1.1151-1.1156 |
| Water solubility | Complete |

Table 3.1 Product Specifications of Fiber-Grade Ethylene Glycol

Industrial grade ethylene glycol has a less stringent specification than fiber-grade, with a slightly larger boiling range, higher allowable iron content and no UV transmittance test.