INTRODUCTION

Ethylene glycol, 1-2 ethanediol, HOCH2CH2OH, usually called glycol, is the simplest diol. It was first prepared by Wurtz in 1859; treatment of 1,2-dibromoethane with silver acetate yielded ethylene glycol acetate, which was then hydrolyzed to ethylene glycol.

Ethylene glycol was first used industrially in place of glycerol during World War I as an intermediate for explosives (ethylene glycol dinitrate), but has since developed into a major industrial product.

The worldwide capacity for the production of ethylene glycol via the hydrolysis of ethylene oxide is estimated to be 7x10^6 ton/a.

Ethylene glycol is used mainly as antifreeze in automobile radiators and as a raw material for the manufacture of polyester fibers.

CURRENT PRODUCTION METHOD

Only one current method is currently used for the industrial production of ethylene glycol. This method is based on the hydrolysis of ethylene oxide obtained by direct oxidation of ethylene oxide obtained by direct oxidation of ethylene with air or oxygen. The ethylene oxide is thermally hydrolyzed to ethylene glycol without a catalyst. Fig. 1 shows a simplified scheme of a plant producing ethylene glycol by this method. The ethylene oxide-water mixture is preheated to a temperature of 200 °C, whereby the ethylene oxide is converted to ethylene glycol. Di-, tri-, tetra-, and polyethylene glycols are also produced, but with respectively decreasing yields.

The formation of these higher homologues is inevitable because ethylene oxide reacts with ethylene glycols more quickly than with water; their yields can however, be minimized if an excess of water is used- a 20-fold molar excess is usually employed. Thus, in practice almost 90% of the ethylene oxide can be converted to monoethylene glycol, the remaining 10% reacts to form higher homologues:

\[ C_2H_4O + H_2O \rightarrow C_2H_6O_2; \Delta H = -79.4 \text{ kJ/mol} \]

\[ nC_2H_4O + C_2H_6O_2 \rightarrow HO(CH_2CH_2O)_{n+1} - H \]

\[ n = 1,2,3 \]

After leaving the reactor, the product mixture is purified by passing it through successive distillation columns with decreasing pressures. Water is first removed and returned to the reactor, the mono-, di-, and triethylene glycols are then separated by vacuum distillation. The yield of tetraethylene glycol is too low to warrant separate isolation. The heat liberated in the reactor is used to heat the distillation columns.

The shape of the reactor affects the selectivity of the reaction. Plug-flow reactors are superior to both agitator-stirred tanks and column reactors.
Figure 1. Flow Diagram for a Glycol Plant
a) Reactor; b) Drying Column; c) Monoethylene Glycol Column; d) Diethylene Glycol column; e) Triethylene Glycol Column; f) Heat Exchanger

ALTERNATIVE METHODS FROM ETHYLENE OR ETHYLENE OXIDE

The most promising alternative methods for industrial-scale application are the following.

- Selective synthesis of Ethylene Glycol via the Ethylene Carbonate (1,3-dioxolan-2-one)

This seems to be a promising alternative. Ethylene carbonate is obtained in high yield (98%) by reacting ethylene oxide with carbon dioxide and can be selectively hydrolyzed to give a high yield of ethylene glycol. Only double the molar quantity of water is required.

\[ C_2H_4O + H_2O \xrightarrow{\text{cat}} C_3H_4O_3 \xrightarrow{H_2O} C_2H_6O_2 + CO_2 \]

According to a Halcon patent, ethylene oxide can be extracted from the aqueous solution, formed during its production, with supercritical carbon dioxide. An ethylene oxide-carbon dioxide solution is obtained, which reacts to form ethylene carbonate then yields ethylene glycol. Possible catalysts for this reaction are quaternary ammonium and phosphonium salts. Problems such as product
separation and catalyst feedback still need to be resolved but this method seems to be the most promising for industrial application.

- **Direct oxidation of Ethylene**

  Catalytic oxidation of ethylene with oxygen in acetic acid gives a yield of ethylene glycol (>90%) which is much higher than that obtained in the more indirect route via the ethylene oxide. It has already been used on an industrial scale, but this method was soon abandoned due to problems caused by corrosion. These methods use the following reaction.

\[
\begin{align*}
C_2H_4 + AcOH & \xrightarrow{O_2, \text{HBr}, 160\degree C, 2.5\, MPa} AcOCH_2CH_2OAc \\
AcOCH_2CH_2OAc & \xrightarrow{H_2O} C_2H_6O_2 \\
Ac & = CH_3OH
\end{align*}
\]

A more recently developed catalyst system is based on the use of PD(II) complexes. In recent years, increasing attention has been paid to Pd(II) systems as catalysts for the direct oxidation of ethylene to ethylene glycol. In spite of the widespread interest in this alternative, industrial applications have yet to be realized.

**ALTERNATIVE METHODS FROM SYNGAS**

Industrial research emphasis has been placed on five generalized methods of ethylene glycol production (see table 1):

- **Direct production from syngas**

  Without doubt, the direct approach of using syngas to effect all 4 C-H, 2 O-H and 1 C-C bonds simultaneously would be without competition if no unusual requirements of feed-stocks or processing were required. Pruett and colleagues at Union Carbide unquestionably achieved a magnificent feat in production ethylene glycol directly from syngas.

  After we bestow accolades on this technical achievement we must return to a realistic assessment. From a raw materials cost viewpoint, the system is far from ideal. Purity and pressure add appreciably to syngas cost, and with rhodium as the catalyst, the syngas must be ultra-low in sulfur. Processing costs associated with capital are extremely high due to the very high pressure of the synthesis and the very slow rate of reaction.

  Besides Union Carbide, others active in this area with rhodium include Mitsui Petrochemicals. Some work, on the direct use of syngas with ruthenium catalysts has been published by Texaco.
- **Carbonylation**

  The granddaddy of all syngas-based processes to ethylene glycol is the old Du Pont process, which produced glycolic acid from formaldehyde and CO at high pressure in the presence of strong mineral acids. The glycolic acid was converted to methyl glycolate and then was hydrogenated at high pressures to ethylene glycol and methanol. This process was operated commercially by Du Pont many years ago.

  There have been refinements to this process. Chevron has explored the use of hydroformylation while Exxon has used Du Pont Nafion membrane, a perfluoro sulfonic acid resin. Raw material analysis suggests that about 60% (3 mol syngas) of the raw materials requirements must be a methanol-free grade of formaldehyde. The syngas must be separated or at least concentrated in each component because of the high pressure reactions of CO in glycolic acid formation and of H₂ in reduction of glycolate. These separated components constitute the final 60% (1 mol CO and 2 mol H₂) of the raw material cost. The other processing costs are not extraordinary.

- **Hydroformylation**

  Converting formaldehyde to glycoaldehyde followed by reduction to ethylene glycol seems to be the pathway chosen by many corporations. Invariably, the hydroformylation catalyst of choice is rhodium used with mild coordinating compounds such as triphenylphosphine. The formaldehyde source, representing 60% of the raw materials, is usually the very expensive trioxane or paraform. The syngas to meet the balance (60%) of the raw materials requirements would be the most purified possible to avoid the lowest levels of sulfur, which can deactivate and poison the rhodium.

  Most of the work by Mitsui, Shell ad National Distillers is typified by very slow reaction rates. Glycolaldehyde production rates are around 0.1 mol/L/h. The first apparent break from the pack of very low rates is shown by the work of Carroll and Chan at Monsanto. They were able to hydroformylate paraformaldehyde to glycoaldehyde at a rate of 2.5 mol/L/h at 110 °C under 4000 psig pressure using a 1:1 H₂/CO gas mixture.

- **Oxidative coupling of CO.**

  This reaction in the presence of primary alcohols has been used extensively examined in Atlantic Richfield and Ube Industries. This reaction can be affected either in the liquid or vapor phase but always uses palladium as the primary oxidation catalyst. A variety of cocatalysts or promoters reoxidize the palladium. Arco chose more traditional reoxidants metallic palladium such as copper salts in the liquid phase and very high levels of alkyl nitrite in the vapor phase to act in the reoxidation.

  Raw materials costs in this process are high since the process requires separation of the syngas into its components. The CO must be free of hydrogen and at high pressures for oxidative coupling. The H₂ is likewise used at very high pressures for the difficult reduction of the oxalate diester to ethylene glycol. In the
oxidative coupling of CO, it is obvious that all hydrogen present in the CO as an impurity will be effectively oxidized to water. This increases raw materials costs and adds further processing burden, since water is detrimental to the desired oxidation, especially in the Arco version. The stoichiometry of the reaction represents 120% of the theoretical syngas to ethylene glycol, 2 mol CO and 4 mol H₂.

- **Formaldehyde condensation.**

  Weiss et al. describe an ethylene glycol process that condenses 2 mol of formaldehyde to glycoaldehyde over zeolite catalysts in the presence of sodium hydroxide. The glycoaldehyde is then reduced to ethylene glycol over a nickel catalyst under relatively mild conditions. Essentially, all of the ethylene glycol raw material is supplied by the medium-priced aqueous formaldehyde. Low levels of methanol in the formaldehyde should be tolerable in the reaction. Processing costs in the condensation are minimal.

  Major deficiencies in the process are high theoretical molar syngas requirements, the need for medium-cost formaldehyde, selectivity loss to sodium formate, and base and salt handling.

**INDUSTRIAL USES OF ETHYLENE GLYCOL.**

Ethylene glycol lowers the freezing point of water. Its ease of handling makes it a perfect antifreeze, which accounts for over 50% of its commercial uses.

Commercial antifreezes based on glycol also contain corrosion inhibitors and are used, for example, in motor vehicles, solar energy units, heat pumps, water heating systems, and industrial cooling systems. Protection against freezing is directly related to the 60% glycol prevents freezing down to a temperature of –55°C. There is little point using higher concentrations because the freezing points starts to increase.

Ethylene glycol is also a commercially important raw material for the manufacture of polyester fibers, chiefly poly (ethylene terephthalate) (fibers, synthetic organic). This application consumes 40% of the total ethylene glycol production. Polyesters are, however, used for other purposes, e.g., for producing recyclable bottles. Other minor uses of ethylene glycol are as a humectant (moisture-retaining agent), plasticizer, softener, hydraulic fluid and solvent.
Figure 1. Block processing of syngas ethylene glycol processes
PROCESS ANALYSIS

One process alternative is to produce ethylene glycol from ethylene oxide. The minimal requirements for such an alternative include one reactor, two separators and one distillation column.

The reactor is the unit where the hydrolysis of the ethylene oxide occurs and it’s converted to ethylene glycol. Di-, tri-, tetra and polyethylene glycols are also produced, but with respectively decreasing yields. The operating temperature range is (190 – 200 °C) and pressure (14 – 22 atm).

The kinetic data for the uncatalyzed reactions are obtained from Corrigan and Miller, and Lichtenstein and twigg. The rate of production for the main reaction is:

\[
C_2H_4O + H_2O \rightarrow C_2H_6O_2
\]

\[
r_a = 3.255 \times 10^{12} \exp(-9547.7/T)X_aX_bV,(mol/s)
\]

The rate for the production of diethylene glycol as the secondary reaction is:

\[
C_2H_6O_2 + C_2H_4O \rightarrow C_4H_{10}O_3
\]

\[
r_a = 5.93 \times 10^{12} \exp(-9547.7/T)X_aX_cV,(mol/s)
\]

Where \( X_a, X_b, X_c \) are the mole fractions of ethylene oxide, water and ethylene glycol in the liquid phase, respectively, \( V(m^3) \) is the volume of the liquid phase and \( T \) is the temperature.

Also, it’s required to control the \( H_2O:C_2H_4O \) molar ratio to get the desired conversion of ethylene oxide. For a 90% conversion we need to operate at a 20 \( H_2O:C_2H_4O \) molar ratio.

The separators are used remove water from the mono-, di-, tri-, tetra-, and polyethylene glycols mixture.

The distillation column is used to separate monoethylene glycol as the final product by controlling the temperature profile and pressure. The di-, tri-, and polyethylene glycols mixture comes out as the bottom product.

The model of the distillation column will consist of a system of differential and algebraic equations.

The following processing units might be included to have a more detailed analysis of the process:

- Preheater of the ethylene oxide-water mixture.
- Temperature controller in the preheater in order to maintain the temperature of the ethylene oxide-water mixture.
- Temperature and pressure controller in the distillation columns to obtain purified ethylene glycol as the final product.
- Heat exchangers of the distillation column.

A complete model would give us the chance to:

- Analyze the possible changes of a good number of variables and/or parameter and their influence on the ethylene glycol process.
- Determine the optimum operating conditions to achieve the best quality in the final product.
- Determine the optimum controlling methods that should be used to obtain the best profits.
- Determine what kind of equipment is best for the process (e.g. plug flow reactors).
- Develop troubleshooting procedures.
- Determine future developments we can introduce into the process.

REFERENCES

- CHEMTECH, August 1984, 504-511.