

## Production of Glycol

<sup>1</sup>J. Soji Adeyinka, <sup>2</sup>C. Ijogbemeye Oseghale and <sup>2</sup>Oke Bamidele

<sup>1</sup>Department of Chemical Engineering, University of Port Harcourt,  
P.M.B. 5323, Port Harcourt, Nigeria

<sup>2</sup>Department of Chemical Engineering, University of Abuja, P.M.B.117, Abuja, Nigeria

---

**Abstract:** The study presents a novel route for production of propylene glycol using chlorination and dechlorination of alcohol. Isopropyl alcohol was reacted with hydrochloric acid where chlorine substituted hydroxyl group in the alcohol. This chlorinated propyl was peroxidated using hydrogen peroxide to produce propylene glycol in a two stage reaction. Observation from product yield showed a profound yield of propylene glycol when chloropropane was peroxide by hydrogen peroxide at a temperature of 4°C and a flow rate of 2.5 mL min<sup>-1</sup>.

**Key words:** Glycols, chloropropane, hydrogen peroxide, organic phase, optimal product

---

### INTRODUCTION

Glycols are dihydric alcohol in which two hydroxyl groups are bonded to different carbon atoms. Although, glycols may contain heteroatom, those that will be discussed here are composed solely of carbon, hydrogen and oxygen. Simple glycols are attached to an otherwise unsubstituted hydrocarbon chain as represented by the formula C<sub>n</sub>H<sub>2n</sub>(OH)<sub>2</sub> (Jones, 2002).

The simple ethylene and propylene glycols are odorless and colourless when pure. They have relatively high boiling point, freeze well below 0°C and are very hygroscopic. They are miscible in all proportions with water and possess excellent solvent properties for dyes, synthetic resins etc. (Othmer, 1979; Scheeline and Oko, 1988).

Isopropyl alcohol is a chemical compound widely used as automotive antifreeze (coolant). In its pure form, it is odourless, colourless, syrup liquid with a sweet taste. Isopropyl alcohol is toxic and its accidental ingestion should be considered a medical emergency. Ethylene glycol was first prepared in 1859 by the French chemist Charles Wurtz. It was produced on a small scale during World War 1 as a coolant and as an ingredient in explosives (Othmer, 1979).

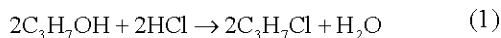
Isopropyl alcohol has a melting point of 12.9°C, boiling point of 197.3°C and a density of 1.1132×10<sup>3</sup> kg m<sup>-3</sup>. It has become increasingly important in the plastic industry to use ethylene oxide in the manufacture of polyester fibers and resins including polyethylene terephthalate which is used in the

production of plastic bottles for soft drinks. The antifreeze capability of ethylene glycol has made it an important component of verification mixtures for low-temperature preservation of biological tissue and organs (Lide, 1993; Scheeline and Oko, 1988).

Chlorination of olefins such as ethylene, by the addition of chlorine is commercially important and can be carried out either as a catalytic vapour-phase or as a liquid-phase process (Othmer, 1978; Adeyinka, 2000). Hydrocarbon chlorination can be carried out in vapour or liquid phase and source of chlorine could be hydrochloric acid, chlorine gas, numerous organic or inorganic chlorides such as SO<sub>2</sub>Cl<sub>2</sub>, PCl<sub>5</sub> and so on (Adeyinka and Okoye, 2000; Adeyinka and Mamedov, 2000). Generally, the means of initiating this reaction could be thermal (heat), photochemical (light) or by use of catalyst. (Nwokeabia, 1998).

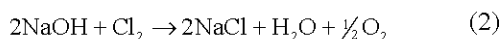
### MATERIALS AND METHODS

Pure 36% hydrochloric acid (100 mL) was measured into a two necked round bottom flask then isopropyl alcohol was gradually dosed drop wise with a regulator into the reactor at a constant flow rate of 2.5 mL min<sup>-1</sup> Eq. 1. The second hole was fitted with a thermometer to monitor the temperature gradient in the reactor as the reaction proceeded. The experiment proceeded with initial temperature of 33°C for 1 h 45 min (105 min) with a total volume of 254 mL of isopropyl alcohol used to neutralize 100 mL of hydrochloric acid. The temperature of the reaction rose up to 35.7°C in indicating an exothermic reaction with an energy increase of 2.554×10<sup>3</sup> kJ.

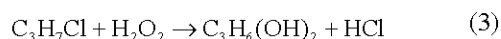


The heat of reaction and the temperature control was achieved using instant reactor cooling by submerging it in a cold water bath. This technique was particularly useful in the extreme case of run-away temperature (Oseghale and Adeyinka, 2004).

The reaction product was left in the reactor for 1 h to cool the mixture to an ambient temperature (25°C). The products of the reaction in the reactor exhibited both organic and inorganic phases using a separation funnel. The inorganic phase was separated from the organic phase. An organic phase volume of 230 and 117 mL of inorganic phase were separated for analysis. The reaction was repeated with the reactor kept inside a condenser to maintain at -15°C. Isopropyl alcohol (254 mL) was again using the earlier method at a feed rate of 2.5 mL min<sup>-1</sup>. The product from the chlorination process contained 234 mL organic phase. This organic phase was separated. From this organic phase, 50 mL of Chloropropane (organic phase) was used in another reactor for peroxidation reaction the reactor was kept inside a condenser at a temperature of 4°C. Sodium hydroxide (NaOH) was reacted with the chloropropane at a feed rate of 1 mL min<sup>-1</sup> to neutralize the chlorine adsorbed. The experiment proceed for 50 min using a total of 50 mL of Sodium hydroxide to completely remove the chlorine in the organic phase. After the reaction, the product was left for 5 min before the temperature reached an ambient temperature. White sediments at the bottom of the reactor was separated for physical analysis. A total of 68 mL of product was realized which was a white sediment at the bottom of the reactor.



After separation of the NaCl, the organic phase was the reacted with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which was supplied through the second feed line at a feed rate of 0.5 mL min<sup>-1</sup> for 40 min. Using a flow regulator a total volume of 20 mL of H<sub>2</sub>O<sub>2</sub> was used. After the reaction, the product was left for 30 min before bringing it out from the condenser (Eq. 3).



Physical analysis was carried out on the product to determine the boiling point and density.

**Qualitative analysis of the organic phase:** The organic product was subjected to various qualitative tests in order to ascertain the type(s) of organic compositions and the

functional groups present in the solution. The identification of gases evolved in experimental processes greatly assist in identifying the acid radical (anion) present in the given substance. The chloride was carried out tests.

**Chlorine test:** The inorganic phase was titrated with Sodium thiosulphate for total Chlorine reaction; a total of 26.7 mL of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used. The total absorbed chlorine in the inorganic phase was 59.4 mL.

**Hydrogen chlorine test:** A colourless gas was observed with pungent and irritating smell. When in contact with damp blue litmus paper, it changed deep blue litmus paper into red in ferring acidic gas.

**Action with NH<sub>3</sub>:** Dipping a glass rod in NH<sub>3</sub> solution and holding it to the mouth of the reactor 2 white dense fumes are formed. These two tests confirmed presence of hydrogen chloride gas in the process.

## RESULTS AND DISCUSSION

It was observed that the reaction of hydrochloric acid and Isopropyl alcohol at room temperature was exothermic. Since there was an increase of 12°C temperature during the reaction. On analysis, the physical composition of the products (organic and inorganic phases) at room temperature (117 mL inorganic and 230 mL organic) and 4°C conditions (113 mL inorganic and 234 mL organic) are similar. From Table 1, it was also observed that there was lower unreacted Chlorine in organic phase of the experiment (at -4°C) but more Chlorine in the organic phase of the experiment at room temperature condition (Condenser) was observed.

From Table 2, it was observed that the organic product (Chloropropane) obtained at -4°C condition has similar physical properties with Chloropropane from Literature (PPG Industries, 1975). A pure yield was obtained at a reduced temperature condition than that at room temperature.

Table 1: Product yields at room temperature conditions

Physical composition	Products at 25°C	Products at -4°C
Inorganic phase	117 mL	113 mL
Organic phase	230 mL	234 mL

Table 2: Physical properties of organic product compared with chloropropane from literature

Physical properties	Chloropropane from literature	Organic phase at low temperature	Organic phase at room temperature
Boiling point (°C)	45-50	48.000	43.000
Density (g mL <sup>-1</sup> )	0.885-0.890	0.893	1.009

**Table 3: Physical properties of propanol**

Physical properties	Propanol literature	Propanol experiment
Boiling point (°C)	96-99	91.000
Density (g mL <sup>-1</sup> )	0.803-0.806	0.889

**Table 4: Physical properties of propylene glycol and ethylene glycol**

Physical properties	Propylene glycol experiment	Propylene glycol literature	Ethylene glycol literature
Boiling point (°C)	131.000	188	198
Density (g mL <sup>-1</sup> )	0.998	1.035-1.037	1.112-1.115

When the organic product was reacted with sodium hydroxide, white precipitate was formed. Physical analysis of the product confirmed that the product was propanol as shown in the Table 3.

When the organic product (Chloropropane) reacted with hydrogen peroxide, a clear colourless liquid was produced which we assumed to be propylene glycol. The physical property was analyzed to compare it with those from literature (PPG Industries, 1975) as shown in Table 4.

It was observed that the product exhibited similar properties (Density: 0.998 g mL<sup>-1</sup>, B. pt: 131°C) with Propylene glycol with (Density: 1.036 g mL<sup>-1</sup>, B. pt: 188°C) with a difference of about 3.6% variation. This variation we assumed was due to presence of impurities in the chloropropane (the product of the first reaction) used in this process.

### CONCLUSION

This research presents the necessary steps for using careful kinetic and reaction condition, pure materials and homogenous systems to improve increase yield in the production of glycol. The chlorination and dechlorination of alcohol in the production of glycol shows that the physical parameters obtained during the reaction indicated that lower temperature favoured the production of propylene glycol. The variation in boiling point of propylene glycol from the experiment and that obtained from literature was a result of impurities in the product obtained and the unstable condition of the condenser. The results of the research have proved that reaction temperature and process route exercised profound influence on chlorination and dechlorination process aimed at producing propylene and ethylene glycol, respectively lower temperature suits optimal product

formation for industrial implementation of the process. Further research on enhanced catalyst is currently on going to develop optima (H<sub>2</sub>O<sub>2</sub>) catalyst activity and establish impurity route for the reaction.

### ACKNOWLEDGEMENT

The Department of Chemical Engineering (University of Port Harcourt, Port Harcourt, Nigeria) is gratefully acknowledged.

### REFERENCES

- Adeyinka, J.S. and B.B. Mamedov, 2000. Effect of H<sub>2</sub>O<sub>2</sub> as catalyst on product distribution on Ar-H Oxychlorination at low temperature. *Global J. Pure Applied Sci.*, 6: 697-704.
- Adeyinka, J.S. and R.O. Okoye, 2000. Effect of CuO on H<sub>2</sub>O<sub>2</sub> in homogeneous catalyzed oxy-chlorination of Kerosene. *AMSE*, 61: 31-54.
- Adeyinka, J.S., 2000. Influence of CuO on H<sub>2</sub>O<sub>2</sub>-catalyzed Oxy-chlorination of Benzene. *JNSChE*, 19: 68-71.
- Jones, M., 2002. *Organic Chemistry*. 2nd Edn., W.W. Norton and Co., New York.
- Lide, R.D., 1993. *Handbook of Chemistry and Physics*. 73rd Edn., Chemical Rubber Publishing Co., Boca Raton.
- Nwokeabia, I.T., 1998. The effect of temperature on the production of Lindane by H<sub>2</sub>O<sub>2</sub>-HCL Oxychlorination of benzene using ALCL<sub>3</sub> as co-catalyst. B.Eng. Thesis, University of Port Harcourt.
- Oseghale, C.I. and S.J. Adeyinka, 2004. Thermodynamic analysis of co-catalytic oxychlorination of phenol. *Int. J. Sci. Technol. Res.*, 1: 124-131.
- Othmer, K., 1978. Hydrogen Chloride. In: *Encyclopedia of Chemical Technology*, Othmer, K., R.E. Kirk and D.F. Othmer (Eds.). 3rd Ed., John Wiley and Sons, New York, pp: 335.
- Othmer, K., 1979. Chlorocarbons and Chlorohydrocarbons. In: *Encyclopedia of Chemical Technology*, Othmer, K. (Eds.). 3rd Edn., John Wiley and Sons, New York, pp: 668-676.
- PPG Industries, 1975. Process for preparing monoethylene glycol and ethylene oxide. United States Patent 3904656. <http://www.freepatentsonline.com/3904656.html>.
- Scheeline, H.W. and T. Oko, 1988. Ethylene glycol process economics programme. Report No. 70, 70A, 70B, SRI International, Menlo Park, Fovatin, Cal.