UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF EPICHLOROHYDRIN FROM GLYCEROL

HERLIATI

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By

HERLIATI

Thesis Submitted to the School of Graduate Studies, University Putra Malaysia, in Fulfillment of the Requirement for the Degree of Doctor of Philosophy

May 2013

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DEDICATED TO

MY DEAREST MAS MULYONO, PARENTS,

MY LOVELY SONS BINTANG, GILANG and BIMA

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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May 2013

Chair : Professor Robiah Yunus, PhD

Faculty: Engineering

Glycerol is the main byproduct of the biodiesel production. Recently, the market has been flooded by the crude natural glycerol due to the rapid growth in biodiesel industry. Since this crude glycerol has a very low value because of its impurities, the development of new technology to convert glycerol to more valuable chemicals is become an interesting study. Among the various possibilities, a technology to convert glycerol to epichlorohydrin has caught our attention. Epichlorohydrin (EPCH), an important raw material for the production of epoxide resins was successfully synthesized via two-stage process. The first stage is hydrochlorination reaction of glycerol with aqueous hydrogen chloride as a chlorination agent to

produce 1,3-dichloropropanol (1,3-DCP) in the presence of carboxylic acid as the catalyst. The next stage is dehydrochlorination reaction where 1,3-DCP produced from the previous reaction was reacted with sodium hydroxide (NaOH) to form EPCH without the presence of any catalyst. This study includes both simulation and experimental works.

Process simulation is crucial in many chemical process development studies to facilitate the analysis, and optimization of technical processes. It allows the designer to test the performance of process under different conditions and provide feedback quickly. In this study, process simulations were conducted prior the experimental study on both the 1,3-dichloropropanol preparation, and the epichlorohydrin preparation using the ASPEN Plus^{TM} simulation software. The synthesis of 1,3-dichloropropanol occurred through hydrochlorination process, was modeled and simulated using RBatch block which is suitable for a semi-batch reactor process (SBSTR). The simulation was conducted at different temperatures (80 to 120^{o}C); different molar ratio and different concentration carboxylic acid catalyst at atmospheric pressure. The optimum temperature, optimum molar ratio glycerol:HCl, and optimum concentration of the catalyst were found at 110^{o}C, 1:16, and 8 percent by mol of glycerol fed respectively. Subsequently, the synthesis of epichlorohydrin took place via dehydrochlorination reaction was simulated using the reactor block RBatch at different temperatures (20 to 60 ^{o}C) and atmospheric pressure without presence of catalyst. The optimum temperature and optimum molar ratio 1,3-DCP:NaOH were found 60^{o}C (333 K) and stoichiometric respectively. The results from simulation studies shed insights of the performances of these reactions in terms of conversion,

selectivity and yield. The results from these simulations were used to minimize the experimental and scale-up efforts and enable the process optimization to be conducted in wider range of conditions which might not be possible by the experimental study.

Experimental study on hydrochlorination reaction was carried out under operating temperatures ranged from 80 to 120^{o}C and atmospheric pressure, reactant molar ratio from 1:16 to 1:32, and different types of carboxylic acid catalyst. The amount of catalyst required was 8 percent by mol of the total mol of glycerol intake. The optimal reaction conditions were: temperature, 110^{o}C; reactant molar ratio glycerol to HCl, 1:24; catalyst, malonic acid; duration, 3 hours. Quantitative analyses of the reaction products were performed using GC-MS.

Furthermore, experimental studies on dehydrochlorination reaction were carried out under temperatures (50 to 80^{o}C) and reactant molar ratios (1:1 to 1:9). Basic solution of NaOH was added in the reactor, followed by 1,3-DCP as soon as the reaction temperature was reached. The optimal reaction conditions were: temperature, 70^{o}C; reactant molar ratio 1,3-DCP to NaOH, 1:5; duration at 3 minutes. Analysis of the reaction products was also performed using GC-MS.

The kinetics study on dehydrochlorination of dichloropropanol and sodium hydroxide to epichlorohydrin was investigated. The effect of temperatures (50 to 80^{o}C) at different times on such reaction was observed. The reaction rate was found to be pseudo first order with respect to dichloropropanol concentration. The reaction

rate constants at these temperatures were 0.0056; 0.008; 0.012; and 0.021 respectively. Subsequently, the activation energy was determined at 38.85 kJ/mol and the pre-exponential factor A was 1.62×10^4 sec^{-1}. In the presence of excess water and at temperature above 70°C, epichlorohydrin can be easily converted to glycerol thus lower the yield of epichlorohydrin. Therefore, not only choosing the optimal operating conditions but maintaining low amount of water and short contact time are important factors in the design of the reactor for epichlorohydrin of DCP.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS EPIKLOROHIDRIN DARIPADA GLISEROL

Oleh

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May 2013

Pengerusi: Profesor RobiahYunus, PhD

Fakulti: Kejuruteraan

Gliserol merupakan hasil sampingan utama di dalam pengeluaran biodiesel. Sejak kebelakangan ini, gliserol mentah semula jadi telah didapati membanjiri pasaran berikutan pertumbuhan pesat industri biodiesel. Gliserol mentah ini mempunyai nilai yang sangat rendah disebabkan faktor ketidaktulenan, maka pembangunan teknologi baru untuk menukar gliserol kepada bahan kimia yang lebih bernilai adalah satu kajian yang menarik. Di antara pelbagai kemungkinan, teknologi untuk menukar gliserol kepada epiklorohidrin telah menarik perhatian untuk kajian ini. Epiklorohidrin (EPCH) yang merupakan salah satu bahan mentah yang penting untuk pengeluaran resin epoksida telah berjaya dihasilkan melalui dua peringkat proses. Peringkat pertama adalah tindak balas penghidroklorinan gliserol bersama larutan berair hidrogen klorida sebagai agen pengklorinan untuk menghasilkan 1,3-dikloropropanol (1,3-DCP) dengan asid karboksilik sebagai pemangkin. Peringkat seterusnya adalah reaksi penyahhidroklorinan di mana 1,3-

DCP yang dihasilkan daripada tindak balas sebelumnya ditindak balas dengan natrium hidroksida (NaOH) untuk membentuk EPCH tanpa menggunakan pemangkin. Kajian ini melibatkan kedua-dua kerja simulasi dan eksperimen.

Simulasi proses adalah penting dalam kajian-kajian pembangunan proses kimia bagi tujuan memudahkan analisis dan pengoptimuman proses-proses teknikal. Ia membolehkan pereka untuk menguji prestasi proses di bawah keadaan yang berbeza dan mampu memberi maklum balas dengan cepat. Dalam kajian ini, simulasi proses menggunakan perisian Aspen Plus^{TM}telah dijalankan terlebih dahulu sebelum kajian eksperimen untuk penyediaan 1,3-dikloropropanol danepiklorohidrin dilakukan. Sintesis 1,3-dikloropropanol yang berlaku melalui proses penghidroklorinan, telah dimodel dan disimulasikan dengan menggunakan blok RBatch yang sesuai untuk proses reaktor separa kelompok (SBSTR).Simulasi telah dijalankan untuk suhu yang berbeza (80°C hingga 120°C); nisbah molar yang berbeza dan kepekatan pemangkin asid karboksilik yang berbeza pada tekanan atmosfera. Nilai optimum untuk suhu, nisbah molar gliserol:HCl, dan kepekatan pemangkin ditemui masing-masing pada 110°C, 1:16, dan 8 peratus mol nilai suapan gliserol. Selepas itu, sintesis epiklorohidrin melalui tindak balas penyahhidroklorinan pula disimulasi dengan menggunakan blok reaktor RBatch pada suhu yang berbeza (20 – 60^{o}C) dalam tekanan atmosfera tanpa kehadiran pemangkin. Suhu dan nisbah molar 1,3-DCP: NaOH yang optimum ditentukan masing-masing pada 60°C (333 K) dan stoikiometri. Keputusan daripada kajian-kajian simulasi ini telah memberikan maklumat tentang pencapaian tindak balas-tindak balas ini dari segi pemilihan, penukaran,

dan penghasilan. Keputusan-keputusan yang diperoleh dari simulasi ini telah digunakan untuk meminimumkan usaha eksperimen dan skala naik serta membolehkan pengoptimuman proses dijalankan dalam pelbagai keadaan yang tidak boleh dilakukan melalui kajian eksperimen.

Kajian eksperimen bagi tindak balas penghidroklorinan telah dijalankan pada julat suhu operasi dari 80°C hingga 120°C pada tekanan atmosfera, nisbah molar bahan tindak balas dari 1:16 hingga 1:32, dan beberapa jenis pemangkin asid karboksilik. Jumlah mangkin yang diperlukan adalah 8 peratus mol dari jumlah mol suapan gliserol. Keadaan tindak balas yang optimum adalah: suhu 110°C, nisbah molar gliserol kepada HCl 1:24; pemangkin asid malonik; tempoh 3 jam. Analisa kuantitatif bagi produk tindak balas telah dilakukan dengan menggunakan GC-MS.

Selanjutnya, kajian eksperimen untuk tindak balas penyahhidroklorinan telah dijalankan pada suhu (50°C hingga 80°C) dan nisbah molar bahan tindak balas (1:1 hingga 1:9). Larutan NaOH dimasukkan dalam reaktor, diikuti oleh 1,3-DCP sebaik sahaja suhu tindak balas dicapai. Keadaan tindak balas yang optimum adalah: suhu 70°C; nisbah molar bahan tindak balas 1,3-DCP NaOH, 1:6; tempoh 3 minit. Analisa produk tindak balas juga dilakukan dengan GC-MS.

Kajian kinetik tindak balas bagi proses penyahklorinan dikloropropanol dan natrium hidroksida kepada epiklorohidrin telah disiasat. Kesan suhu (50°C hingga

80°C) pada tempoh yang berbeza untuk tindak balas itu telah diperhatikan. Kadar tindakbalas didapati mematuhi tertib pseudo-pertama berdasarkan kepekatan dikloropropanol. Pemalar kadar tindak balas pada suhu ini adalah masing-masing 0.0056; 0.008; 0.012 dan 0.021. Kemudian, tenaga pengaktifan telah ditentukan pada 38.85 kJ/mol dan faktor pra-eksponen A adalah 1,62 x 10^7 $saat^{-1}$. Dalam kehadiran air yang berlebihan pada suhu di atas 70°C, epiklorohidrin boleh bertukar kepada gliserol dengan mudah, justeru mengurangkan penghasilan epiklorohidrin. Oleh itu, faktor penting dalam reka bentuk reaktor untuk sintesis epiklorohidrin daripada DCP tidak sahaja terhad kepada keadaan operasi yang optimum,bahkan adalah penting juga untuk mengekalkan jumlah air yang rendah dan masa sentuhan yang pendek.

ACKNOWLEDGEMENTS

In the name of Allah the Most Merciful and Most beneficient, to whom I express all thankfulness and gratitude as if not HIM I would not able to finish this work.

I would like to express my deepest gratitude and appreciation to my supervisory Professor Dr Robiah Yunus for providing invaluable advice, untiring assistance, encouragement, motivation and support that enabled me to accomplish the PhD's program smoothly. I also thank to my co-supervisor Associate Professor Dr. Zurina Zainal Abidin, Dr. Intan Salwani Ahamad for their kindness assistances, support, and suggestions so that this work could be completed properly.

My high appreciation also goes to all lecturers, administration staff, and technician at the Department of Chemical and Environmental Engineering, Universiti Putra Malaysia for their kind cooperation in providing all necessary facilities throughout my study.

I am also special thanks to all my colleagues at the Departement of Chemical and Environmental Engineering, Dr. Azhary, Dr. Shanty Farida Saleh, Dr. Chong Gun Hean, Dr. Ferra Naidir, Hamidah, Yusof Harun, Saiful and others for their constant support, encouragement, and motivation during the progress of this research.

My heartfelt and sincere appreciate goes to my lovely children; Bintang Akbar Maulana, Gilang Lukman Hakim, Mohammad Bimasakti, my father, H.

Abdurrahman Salam and other relatives and friends who always encourage and supported me during the study period. Last but not least, my special thanks to my dearest husband, Drs. Mulyono, M.Kom, for his love, his, constant encouragement, sacrifice, patience, and understanding that enabled me to finish the study.

I certify that a Thesis Examination Committee has met on 13 of May 2013 to conduct the final examination of Herliati on her Doctor of Philosophy thesis entitled "**Synthesis of Epichlorohydrin from Glycerol**" in accordance with the University and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy,

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia or other institutions.

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HERLIATI

Date:

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LIST OF ABBREVIATIONS

EPCH	Epichlorohydrin
DCP	Dichloropropanol
PCT	Patent Cooperation Treaty
HSDB	Hazardous Substances Data Bank
WHO	World Health Organization
IARC	International Agency For Research on Cancer
CAS	Chemical Abstracts Service
GUI	Graphical User Interface
ASPEN	Advanced System for Process Engineering
EOS	Equation Of State
BSTR	Batch Stirred Tank Reactor
SBSTR	Semi Batch Stirred Tank Reactor
GC-MS	Gas Chromatography Mass Spectrometry
ICIS	International Construction Information Society

CHAPTER 1

INTRODUCTION

1.1. Background

Epichlorohydrin (EPCH) is an important raw material for making epoxide resins. Approximately 76% of the world's consumption of EPCH is used to make epoxy resins, in the form of synthetic elastomer. Epoxide resins have a large number of applications in the car, housing, boating and leisure industries. Other applications of epichlorohydrin include sizing agents for paper-making industry, textile, ion exchange resin, water treatment chemicals, polyols, a variety of glycidyl derivatives, and more (Solvay C. , 2003; Dow, 2007).

Today, biodiesel as an alternative, environmentally friendly, and renewable energy has been produced on a large scale (Azhari, 2010) However one of the main problems in the production of biodiesel is the formation of significantly high amount of glycerol (10 wt %) as a by-product (Michael, Andrew, Winnie, & Thomas, 2006) As the production of biodiesel increases, the quantity of crude glycerol generated will also be considerable, and its utilization will become an urgent topic. According to (Zheng, Xiaoloong, & Yinchu, 2008), glycerol markets have reacted strongly to the increasing availability of glycerol. Although the global production of biodiesel is still very limited, the market price of glycerol has dropped rapidly. If the production of biodiesel increases as predicted, as a rough rule of thumb for every 9 kg of biodiesel produced, about 1 kg of a crude glycerol byproduct will also be produced. As a consequence, the supply of glycerol will be in excess of demand. These aspects

have attracted attention from many researchers to develop alternative routes to utilize glycerol in the production of useful intermediates or final products.

Several opportunities for glycerol transformation, as show at Figure 1.1, have been identified since it can readily be oxidized, reduced, halogenated, etherified, and esterified to obtain value-added compounds such as dihydroxyacetone, mesoxalic acid, 1,3-propanediol, 1,3-dichloropropanol, glyceryl ethers, glycerol carbonate, and glyceryl esters (Zheng, Xiaoloong, & Yinchu, 2008).

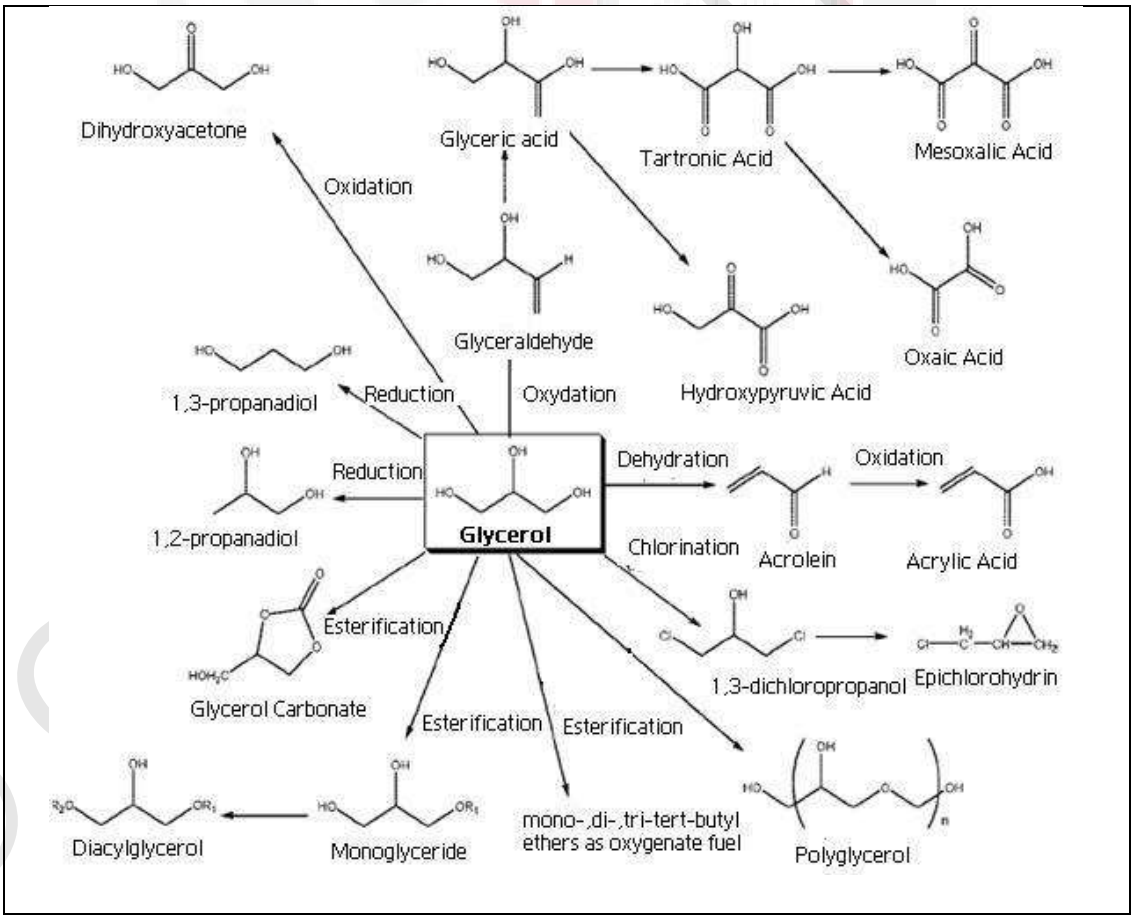


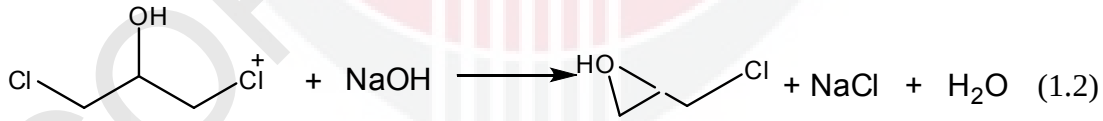
Figure 1.1 Commodity Chemicals from Glycerol (Zheng, Chen, & Shen, 2008)

Dealing with a strong growing demand for epichlorohydrin which is expected to exceed the existing global production capacity by 2013, studies of glycerol

halogenation process or glycerol hydrochlorination process to produce 1,3-dichloropropanol, which is an intermediate in epichlorohydrin synthesis, will be imperative . Based on the estimated production of biodiesel, it appears that bio-based glycerol conversion to epichlorohydrin offers an alternative route to existing process.

Originally, epichlorohydrin was formed by Berthelot in 1854 and by Clarke and Hartman (1941), using caustic soda with α,γ-dichlorohydrin or α,γ-dichlorohpropanol. (α,γ-DCP) is a product of the reaction between an aqueous solution hydrogen chloride and synthetic glycerol, in the presence of acetic acid as a catalyst, at temperature ranged from 80 – 100°C. The reaction schemes involved can be seen below in Eq. 1.1 and 1.2 : (Clarke & Hartman, 1941)

(1.1)



(1.2)

Unfortunately, according to Siano (Siano, et al., 2006), these old processes are characterized by considerable drawbacks, such as the following:

- the loss of catalyst during the reaction due to the relatively low boiling point of acetic acid (117 °C);

- the slowing of the reaction caused by the introduction of water in the reaction mixture, due to the use of aqueous hydrochloric acid, and the failure to remove the water that is formed as a consequence of the reaction itself;
- and the difficult separation of α,γ-dichloropropanol from the reaction mixture.

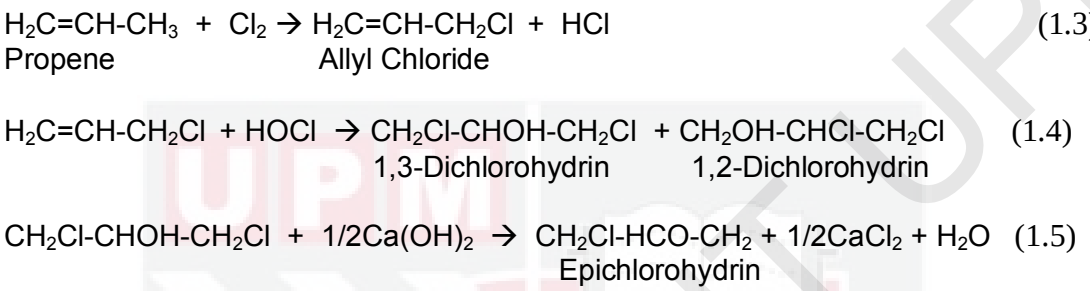
These drawbacks, together with the high cost of synthetic glycerol, have prevented this process from becoming established.

Although several routes are known for epichlorohydrin manufacture (Nexant, 2006), conventional technology is made from propylene and chlorine as primary raw materials in a four-step process which comprises of (Bijsterbosch, Das, & Kerkhof, 1994):

- Preparation of allyl chloride through chlorination of propene or propylene at a high temperature, 500 – 520^{o}C. This step results in low selectivity in which by-products such as mono- and dichloroprene and mono- and dichloropropane are formed.
- Preparation of dichloropropanols by addition of hypochlorous acid to allyl chloride. This step is performed in water at a temperature of 30^{o}C. The low solubility of allyl chloride in water requires the use of a large amount of water and
- Dehydrochlorination of dichloropropanols with an alkali aqueous solution to epichlorohydrin at a temperature 90^{o}C. Epichlorohydrin must be immediately removed from the solution in order to prevent formation of mono-chloropropanol and also glycerol.

- Preparing HOCl solution which is used in the dichloropropanol synthesis. It is prepared by reacting chlorine with calcium hydroxide.

The reaction equations for the aforementioned synthesis of epichlorohydrin can be seen in Eq. 1.3 to 1.5 as below: (Bijsterbosch, Das, & Kerkhof, 1994)



Basically, those routes are used in very large scale production, but it suffers from some undesirable features such as low chlorine atom efficiency. Only one of four chlorine atoms employed in the manufacturing of epichlorohydrin by this route is retained in the product molecule, the remainder emerged as a by-product hydrogen chloride or waste chloride anion. In addition, high unit consumption of energy; high unit of waste water; and use of hazardous evaporated chlorine in the process have prompted the search for alternative routes that are more efficient and environment-friendly (Kubicek, Sladek, & Buricova, 2005). The escalating cost of petrochemical raw material such as propylene has also contributed to the accelerated search for processes that employ less expensive raw material (Bruce M, et al., 2008).

Increase in propylene price in the early 2000s contributed to economically unsustainable situation in the production of chlorinated organic. In contrast, at that time the price of glycerol, which was produced from epichlorohydrin, was falling down. Solvay, as a manufacturer, therefore halted the production of synthetic

glycerol from epichlorohydrin in 2005. Solvay, traditional glycerol and epichlorohydrin manufacturer, have been trying to reverse the procedure by converting the plant to produce epichlorohydrin from glycerol as shown in Figure 1.2.

In 2007, Solvay, was the first company to start production of epichlorohydrin from glycerol at their 10 000 ton plant in France. Glycerol was obtained from a French supplier as a by-product of the biodiesel manufacturer from rapeseed oil. Furthermore, Solvay also already has the planned investment of 100,000 ton/year plant on its integrated site at Map Ta Phut, Thailand, where production was started in the middle 2010.

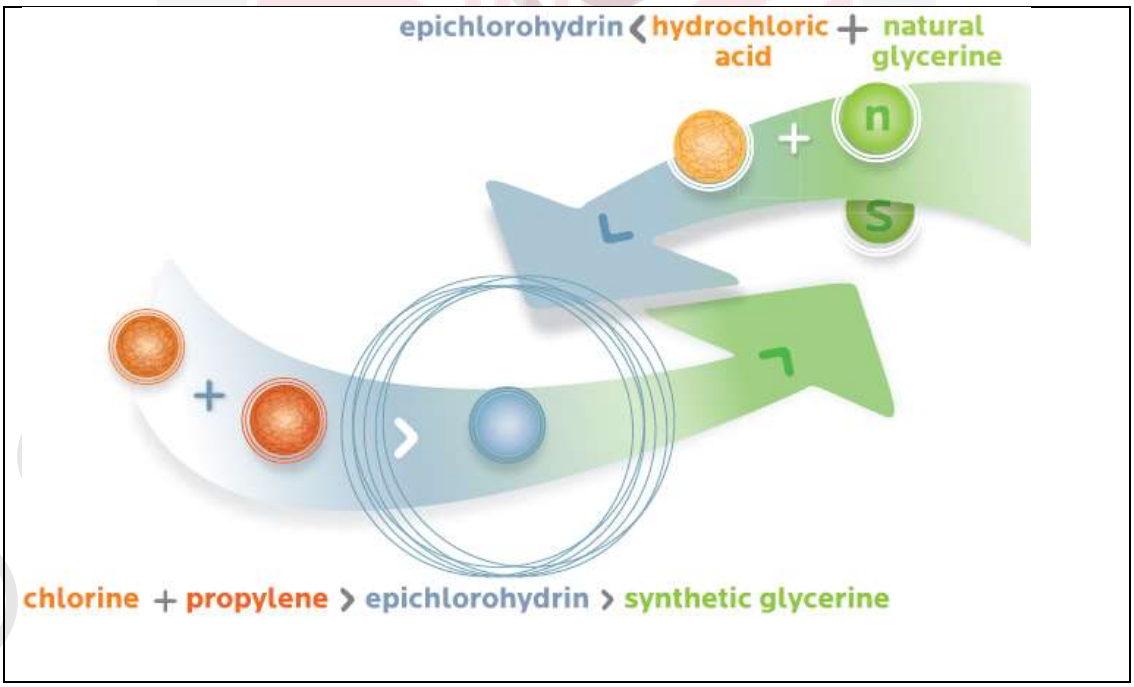


Figure 1.2 Reverse process from glycerol to epichlorohydrin (Solvay, 2007)

According to Solvay, the new glycerol-based process shows crucial advantages over the existing propylene route as follows:

- it does not require a solvent;
- the size of the reactor can be reduced related to higher selectivity;
- the kinetic is much faster;
- hydrogen chloride is consumed rather than produced;
- chlorine consumption is reduced by 50% and water by 70%; and
- chlorinated residues are 80 % lower.

Like Solvay, Dow also has announced the construction of a large glycerol to epichlorohydrin plant in China, which started the production in 2010. The company has selected the Shanghai Chemical Industry Park for its 150,000 ton plant. In this case, glycerol is purchased from the local producers of biofuels, which in China are typically obtained from rapeseed and palm oil. Dow also has decided to build a 100,000 ton liquid epoxy resin plant at the Shanghai location. The Dow production facility reduce waste water by more than 70% compared to conventional propylene-based technology and will almost completely avoid the formation of organic byproducts.

Kubicek (Kubicek, Sladek, & Buricova, 2005) investigated the proprietary process for producing epichlorohydrin from glycerol using an organic acid catalyst. Optimal reaction occurred using anhydrous hydrochloric acid with 30 % (mol) caprilic acid as a catalyst at above 120^{o}C. This would ensure only a limited fraction (10 %) of the catalyst evaporated from the reactor. Siano (Siano, et al., 2006) have also invented a

process for production of 1,3-dichloropropanol (DCP) from glycerol and hydrogen chloride, which is an intermediate of epichlorohydrin production. This reaction is carried out in the liquid phase under temperature of around 100^{o}C in the presence of acetic acid as catalyst. In order to avoid corrosion of the glass-lined steel reaction vessel, the manufacture of DCP is carried out keeping the inner wall of the vessel which lies above the level of the liquid medium at a temperature of 120^{o}C, at which corrosion of the enameled steel is minimized (Krafft, Franck, Andolenko, & Veyrac, 2007). This process can be run either batch-wise or continuously (Kruper, et al., 2008)

Even though the hydrochlorination process as explained above, showed very high reaction conversion of glycerol (almost 100%) (Kubicek et al., 2005; Krafft et al., 2007; Tesser et al., 2007; Kruper et al., 2008; Bruce et al., 2008), it still has low value in selectivity in terms of 1,3-DCP where only 30 to 56 percent of selectivity was achieved (Tesser et al., 2007; Bruce et al., 2008; Lee et al., 2008; Krafft et al., 2007). As reported by Tesser et al. (2007), hydrochlorination process of reaction between glycerol and hydrogen chloride results in formation of other different organochlorines, hence promote multiple parallel reactions. Therefore, the evaluation of product selectivity i.e., conversion of the reactant to the desired product divided by the overall conversion of the reactant or the rate of conversion of the feed to the desired product, is more desirable than the conversion itself (Froment et al., 1979). Moreover, process parameters affecting the selectivity such as temperature and pressure, molar ratio of reactant and catalyst concentration should be thoroughly investigated and analyzed. Therefore, investigations on the effect of those

parameters are important in order to improve the hydrochlorination process specifically on selectivity toward 1,3-DCP. This would ensure that the glycerol byproduct can indeed be used as the starting material in the production of epichlorohydrin. Since, very little information is available on this subject, computer aided process simulation using ASPEN Plus™ software was conducted to minimize the experimental and scale-up efforts. The simulation study would also enable the process optimization to be conducted in wider range of conditions which might not be possible by the experimental setup. In addition, the potential of using cheap basic solution namely sodium hydroxide in the dehydrochlorination of 1,3-DCP to produce .epichlorohydrin also be investigated. Since, the reaction was hypothesized to be very fast, kinetics study on this dehydrochlorination was also performed to investigate its mechanism and rate equations.

1.2. Objectives and Scopes of Work

The objectives of this research are:

1. To simulate the effects of operating conditions such as feed molar ratio, temperature and catalyst concentration on synthesis of both 1,3 Dichloropropanol and Epichlorohydrin using ASPEN Plus.
2. To investigate effect of various experimental condition such as effect of feed molar ratio Glycerol to HCl, reaction temperature, and type of catalyst on hydrochlorination of glycerol and muriatic acid to 1,3 Dichloropropanol in order to obtain optimum process conditions.

3. To investigate effect of various experimental condition such as effect of feed molar ratio 1,3-Dichloropropanol to NaOH and reaction temperature on dehydrochlorination process 1,3-Dichloropropanol and NaOH in order to obtain optimum process conditions and to study its kinetics parameters.

This research includes two consecutive processes consist of

1. Preparation of 1,3-DCP through chlorination of crude biodiesel-based glycerol. The scopes of work are directed toward assesing the effects of operating parameters on the reaction conversion, selectivity, and yield. The parameters considered in this process were namely feed molar ratio, reaction temperature, and catalyst concentration. The reaction was between crude biodiesel-based glycerol and hydrochloric acid using malonic acid as catalyst. Malonic acid was selected due to its high activity and high selectivity (Tesser et al., 2007);
2. and followed by dehidrochlorination of 1,3-DCP to produce EPCH. Assesing the effects of operating parameters, on both the reaction conversion and yield of EPCH, such as reaction temperature, and feed molar ratio were the scopes of work for this part. The reaction was between 1,3-DCP and sodium hydroxide without catalyst.

1.3. Thesis Outline

The thesis consists of six Chapters. Chapter 1 is on the introduction, which highlights the background of the problem and the significance of the research work in the field of glycerol hydrochlorination. Chapter 2 covers the literature reviews on the subject where extensive review, analysis and synthesis are given to the reported works of various authors. The review provides the basis not only for the simulation sections but also for the experimental sections of the thesis. The reviews about kinetic models proposed by prior works are also discussed in this Chapter. From Chapter 3 onwards, each Chapter contains its own background, materials and methods, results and discussions, and conclusions.

Chapter 3 covers the simulation for both synthesis of the 1,3-Dichloropropanol (1,3-DCP) and synthesis of epichlorohydrin using ASPEN Plus^{TM}. The experimental work on dichloropropanol synthesis from glycerol and aqueous hydrochloric acid, 37 %, and analytical technique are described in the Chapter 4. In Chapter 5 was describing the kinetics of dehydrochlorination reaction of dichloropropanol and sodium hydroxide solution to epichlorohydrin. Finally, the summary of the report and recommendation for the future works are included in the conclusion and recommendation section in Chapter 6.

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