HERLIATI

DOCTOR OF PHILOSOPHY

2013

UNIVERSITI PUTRA MALAYSIA

BERILMU BERBAKTI

SYNTHESIS OF EPICHLOROHYDRIN FROM GLYCEROL

HERLIATI

DOCTOR OF PHILOSOPHY
UNIVERSITI PUTRA MALAYSIA

2013

SYNTHESIS OF EPICHLOROHYDRIN FROM GLYCEROL

By

HERLIATI

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

May 2013

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

SYNTHESIS OF EPICHLOROHYDRIN FROM GLYCEROL

By

HERLIATI

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 x 10^4 sec^{-1}. In the presence of excess water and at temperature above 70^{o}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

HERLIATI

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.

ACKNOWLEDEGMENTS

In the name of Allah the Most Merciful and beneficent, 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 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 Universities 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,

Members of the Thesis Examination Committee were as follows:

Mohd. Halim Shah bin Ismail, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Y.Bhg. Thomas Choong Shean Yaw, PhD
Professor, Ir
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Dayang Radiah binti Awang Biak, PhD
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Y. Bhg. Vahid Nassehi, PhD
Professor
Loughborough University
United Kingdom
(External Examiner)

_____

NORITAH OMAR, PhD
Assoc. Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 26 June 2013

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 were as follows:

Robiah Yunus, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Zurina Zainal Abidin, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Intan Salwani Ahamad, PhD
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Dzulkefly Kuang Abdullah, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 11 Jul 2013

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.

HERLIATI

Date: 13 May 2013

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABREVIATIONS

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).

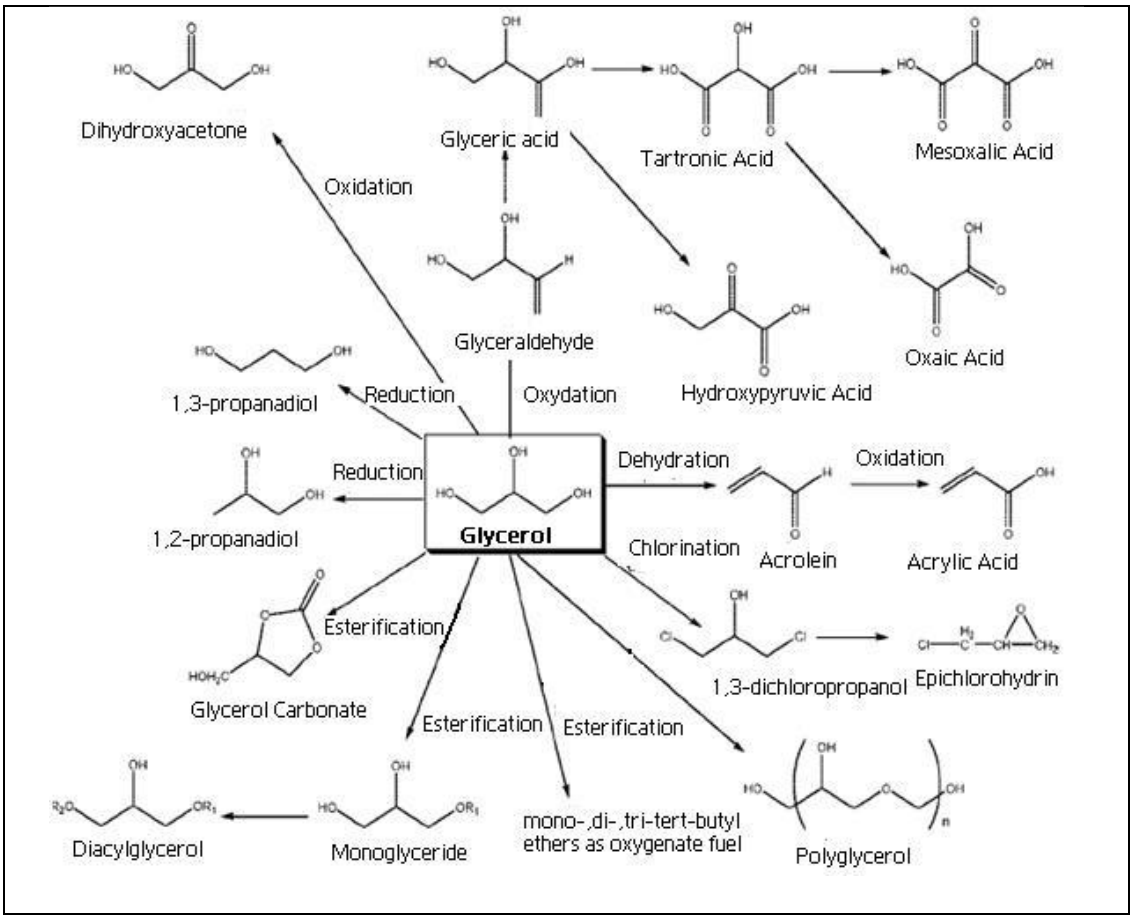


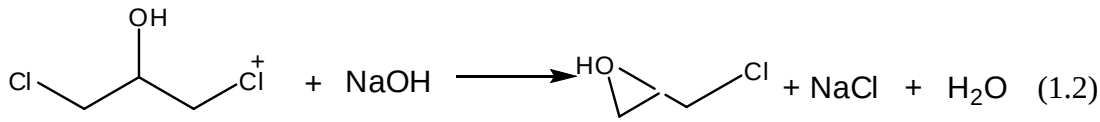
Figure 1.1 Commodity Chemicals from Glycerol (Zheng, Chen, & Shen, 2008)

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^{o}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.

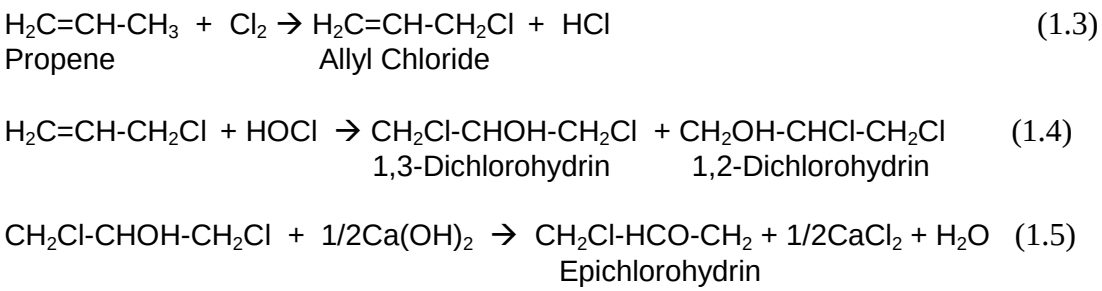
These drawbacks, together with the high cost of synthetic glycerol, have prevented this process from becoming established.

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.

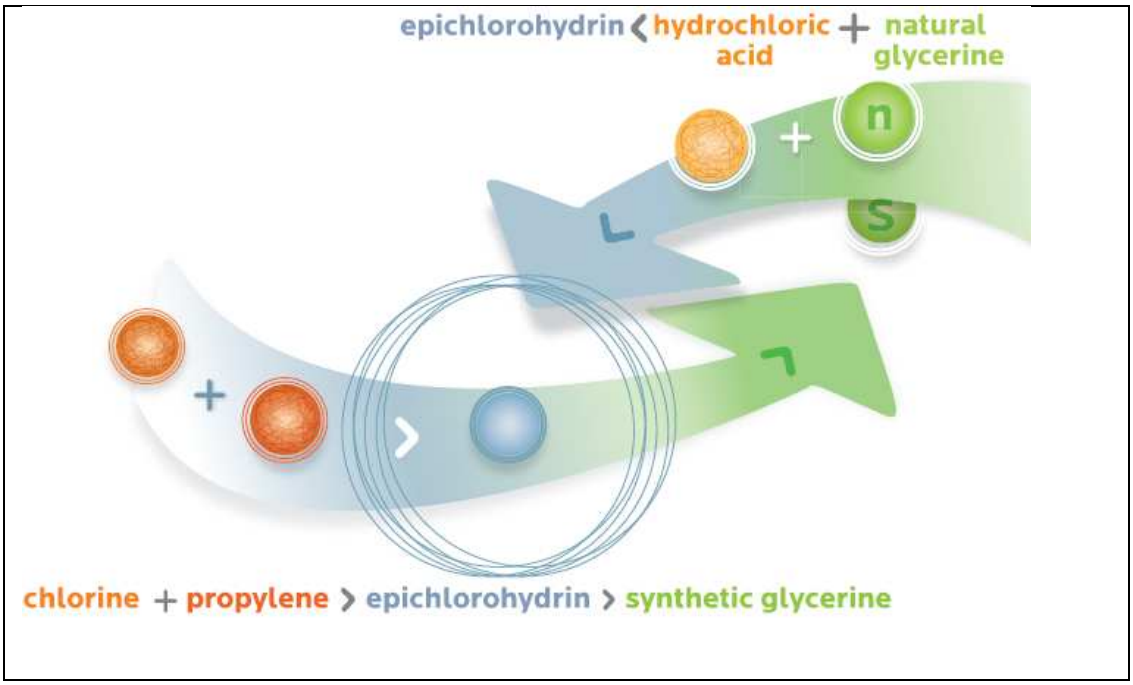


Figure 1.2 Reverse process from glycerol to epichlorohydrin (Solvay, 2007)

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 been 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.

CHAPTER 2

LITERATURE REVIEW

The availability of large amount of glycerol by-product from biodiesel production has encouraged ongoing development of technologies that utilize glycerol as a raw material for producing commodity chemicals. It has been known for decades that glycerol can be made to react with hydrogen chloride to form an intermediate dichloropropanol, which can then be converted to epichlorohydrin. Unfortunately, this chemistry has not been used commercially to any significant extent because of the high cost of glycerol compared to propylene. The availability of bio-based glycerol and the tight propylene market has reversed this situation.

Recently published world and U.S. patent applications disclosed technologies that claim improvements to the old art for producing epichlorohydrin from glycerol. In this literature review international patents published were described under the Patent Cooperation Treaty (PCT) (invented by Kubicek et al., 2005; Krafft et al., 2007), U.S. patent application (invented by Krafft et al., 2007; Kruper et al., 2008) and some information from the journal articles regarding the technology of preparing epichlorohydrin from glycerol. In general, the principle of the process is a reaction of glycerol with hydrogen chloride in the presence of carboxylic acid as catalysts, producing 1,3-dichloro-2-propanol (1,3-DCP) or dichlorohydrins and water. This reaction is carried out in the liquid phase under temperature around 100^{o}C while pressure can be either atmospheric or elevated. Under this condition, the solubility of HCl in the reaction mixture will be increased. Subsequently, this 1,3-DCP will be converted to epichlorohydrin by adding basic solution.

2.2. HISTORICAL DEVELOPMENT

Originally glycerol has been known as a raw material for epichlorohydrin production. Its principle is glycerol reacts with hydrogen chloride to form an intermediate 1,3-dichloropropanol which can then be converted to epichlorohydrin by adding basic solution. Unfortunately, this process suffers setback due to the high cost of synthetic glycerol compared to propylene at that time (Kraftt, 2007).

Figure 2.1 shows several routes for epichlorohydrin production. Epichlorohydrin was first introduced in the mid-1930s by Shell using a process based on the high temperature chlorination of propylene to form allyl chloride and byproduct hydrogen chloride. At lower temperatures, the predominant reaction is the addition of chlorine to the double bond to produce dichloropropane or allyl chloride. Allyl chloride was then converted to glycerol chlorohydrin (dichloropropanol) by reaction with hypochlorous acid (HOCl). It was obtained by reaction of chlorine and water where byproduct hydrogen chloride is also formed. Dehydrochlorination is a reaction between dichloropropanol with a base such as calcium hydroxide to produce epichlorohydrin and byproduct calcium chloride. This classical chemistry, shown as Route 1 in the Figure 2.1, is still in use today for the manufacture of epichlorohydrin.

In the mid-1980s, Showa Denko commercialized a process based on the chlorination of allyl alcohol, as illustrated by Route 2 in the Figure 2.2 (Nexant, 2006). Showa Denko's route to allyl alcohol is by oxidative acetoxylation of propylene to allyl acetate, followed by hydrolysis. Allyl alcohol can also be obtainable from the isomerization of propylene oxide. Allyl alcohol is then chlorinated in aqueous

hydrogen chloride to obtained dichloropropanol. This intermediate is subsequently dehydrochlorinated with base as previously described.

Route 3 depicts a reaction sequence patented by Dow that goes through acrolein as an intermediate. Propylene is oxidized to acrolein in the first step, with some further oxidation to acrylic acid. In the second step, acrolein is chlorinated to 2,3-dichloropropanal. Subsequent hydrogenation of this aldehyde gives 2,3-dichloropropanol, which is then dehydrochlorinated with base as previously described.

A patent by Solvay discloses the epoxidation of the double bond of allyl chloride using hydrogen peroxide at low temperature. Designated as Route 4, this path skips the formation of dichloropropanol and goes directly from allyl chloride to EPCH. Acetone is the key intermediate in Route 5. According to an Asahi patent, acetone, produced from propylene via cumene hydroperoxidation and cleavage with phenol as co-product, can be chlorinated to obtain dichloroacetone (Yohei, 2011).

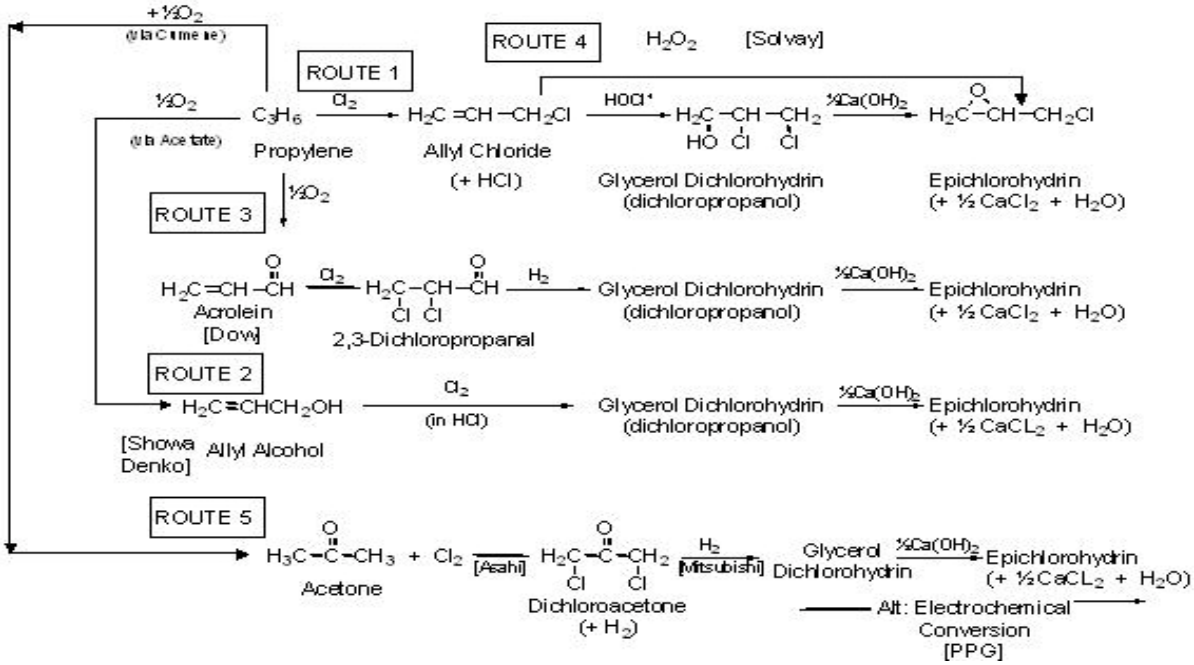
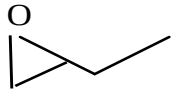


Figure 2.1 Epichlorohydrin process route (Nexant, 2006)

However, epichlorohydrin is still commercially derived indirectly by chlorohydrination of allyl chloride, which is obtained by high temperature chlorination of propylene, Equation 2.1 (Bijsterbosch et al., 1994). Byproducts of chlorination are cis- and trans-1,3-dichloropropene and 1,2-dichloropropane. Glycerol dichloropropanol are made from allyl chloride, Equation 2.2, with 1,2,3-trichloropropane being obtained as a byproduct. Finally, epichlorohydrin is produced from the glycerol-dichloropropanol mixture by treatment with a basic solution, Equation 2.3. The reactions are as follows:

$$CH_2=CHCH_3 + Cl_2 \rightarrow CH_2=CHCH_2Cl + HCl \quad (2.1)$$

$$2CH_2=CHCH_2Cl + 2HOCl \rightarrow HOCH_2CHClCH_2Cl + ClCH_2CHOHCH_2Cl \quad (2.2)$$

$$ClCH_2CHOHCH_2Cl + NaOH \rightarrow \text{  } + NaCl + H_2O \quad (2.3)$$

Increase of propylene price in the early 2000s resulted in an economically unsustainable situation in the production of chlorinated organic. In contrast, at that time the price of glycerol, which was produced from epichlorohydrin, was declined. Solvay, as a manufacturer, therefore halted production of synthetic glycerol from epichlorohydrin in 2005. Solvay, traditional synthetic glycerol and epichlorohydrin manufacturer, have been trying to reverse the procedure by converting the plant to produce epichlorohydrin from glycerol as shown in Figure 2.2. (Solvay, 2007)

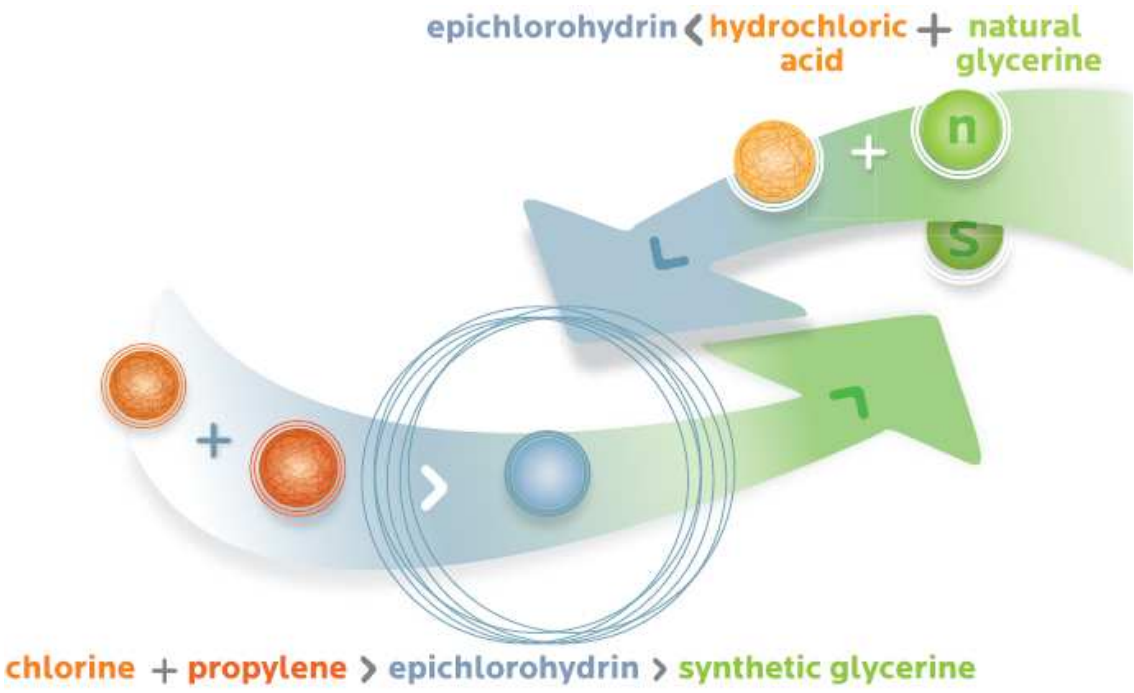
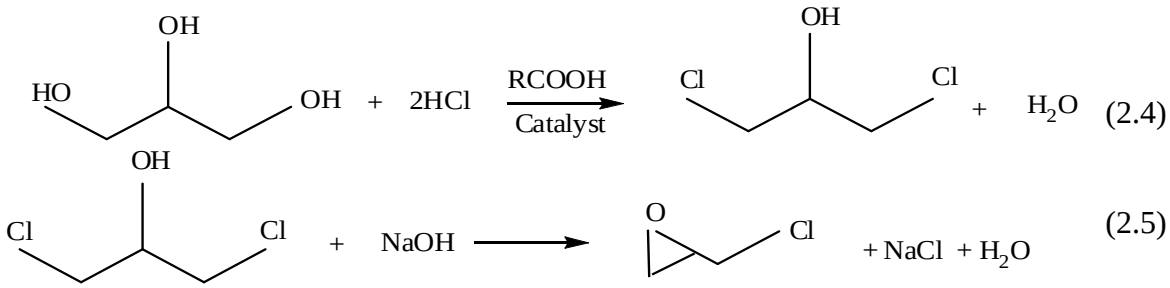


Figure 2.2 Glycerol to Epichlorohydrin

The said process is the transformation of glycerol, a by-product of the manufacturing of biodiesel through what they called Epicerol process. The reactions involved are as follows: (Solvay, 2007)



Epichlorohydrin

The first reaction, Equation 2.4, is a chlorination process, which glycerol is transformed to 1,3-dichloropropanol then this compound subsequently is converted to epichlorohydrin through dehydrochlorination process, Equation 2.5.

In 2007, Solvay was the first to start production of epichlorohydrin from glycerol at their 10 000 ton plant in France. Glycerol was obtained from a French source as a by-product of the manufacture of biodiesel from rapeseed oil. Furthermore, Solvay also already planned investment in a 100 kilo ton unit on its integrated site at Map Ta Phut, Thailand, where production began in the middle 2010. (Solvay, 2009)

Another big chemical company that also has announced the construction of a large glycerol to epichlorohydrin is Dow. The company has selected the Shanghai Chemical Industry Park for its 150 kilo ton plant. In this case, glycerol will be purchased from local producers of biofuels, which in China are typically obtained from rapeseed and palm oil. Dow also has decided to build a 100 kilo ton liquid epoxy resin plant at the Shanghai location. The Dow production facility reduces waste water by more than 70% compared to conventional propylene-based technology and will almost completely avoids the formation of organic by product. (Dow, 2007)

The global epichlorohydrin capacity is currently estimated at 1.4 million ton/year, and glycerol-based epichlorohydrin have accounted for roughly 50,000 ton/year in 2007 which is roughly 3.5% (Cargill, 2007). According to UK-based market research firm Merchant Research & Consulting Ltd. (2008), the rate of consumption of these chemicals largely exceeds their production rate, which puts an upward pressure on epichlorohydrin prices. Especially in China, epichlorohydrin capacity has been growing about 20 percent per annum (China report, 2003). The following graph, Figure 2.3, illustrates supply and demand for epichlorohydrin over the world:

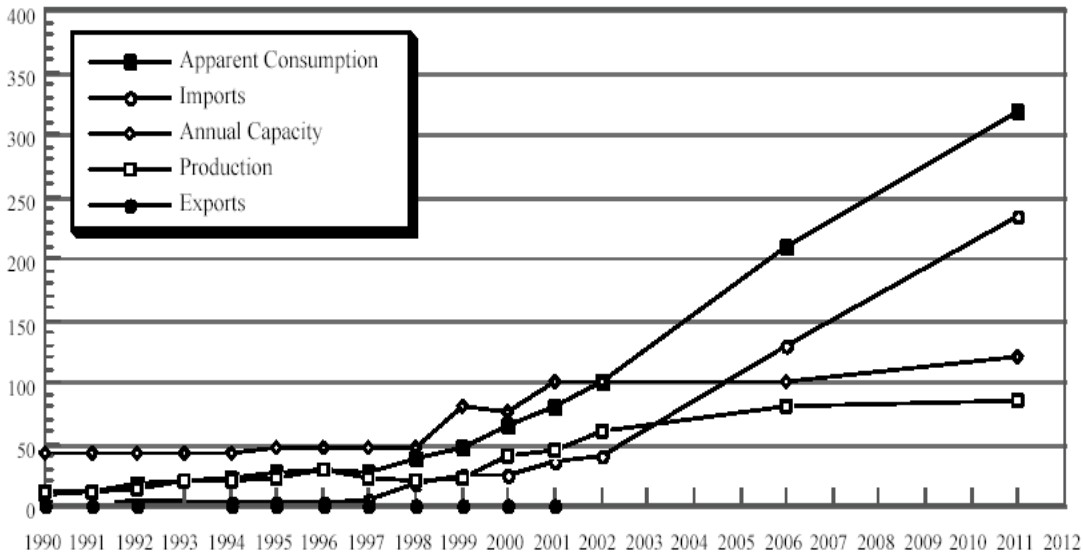


FIGURE 2.3 Supply and Demand for Epichlorohydrin (Thousands metric tons) (Report, 2008)

2.3. GLYCEROL FEEDSTOCK

Glycerol is the simplest triol that is also called glycerin or 1,2,3-propanetriol or glycil alcohol. It is the backbone component of all natural fats and oils in the form of fatty

acid esters and is an important intermediate in the metabolism of living organisms. Glycerol is obtained as a major byproduct of transesterification reaction of fats or seed oils such as, sunflower, peanut, olive oil, soya bean oil, rapeseed and sunflower oils, palm oil and coconut oil to obtain biodiesel (Barnwal & Sharma, 2005). Glycerol can also be produced by fermentation and chemical synthesis. Microbial production of glycerol has been known for 150 years. During World War I, glycerol was produced commercially with microbes. It can be easily modified by reacting the OH functional groups (Carine et.al, 2006).

A number of microorganisms are capable of producing glycerol by fermentation, including yeasts such as *Saccharomyces cere*V*isiae*, *Candida magnoliae*, *Pichia farinose*, and *Candida glycerologenes*, bacteria such as *Bacillus subtilis*, and algae such as *Dunaliella tertiolecta* (Wang et.al, 2001). Over expression of the genes associated with glycerol formation has been attempted in efforts to improve glycerol synthesis by microorganisms, which is based on channeling the glycolytic flux toward glycerol formation and on decreasing the activities of the pathways for dissimilation of glycerol. Triose phosphate isomerase is a key enzyme in the glycolysis that directs dihydroxyacetone phosphate to glyceraldehyde-3-phosphate after the split of fructose-1,6-bisphosphate. When the triose phosphate isomerase gene (TPI) of *Saccharomyces cere*V*isiae* is deleted, the mutant is able to attain a high glycerol yield from glucose (80-90% of the theoretical yield) and glycerol productivity [1.5 g/(L h)] without the need for a steering agent (Compagno, 1996). However, the mutant strain grows poorly due to an energy deficiency and shows genetic instability on the glucose medium. The NAD+-dependent glycerol-3-phosphate dehydrogenase is a key enzyme for glycerol formation in *S. cere*V*isiae*

and many other yeast strains, and the overexpression of the GPD1 gene in yeast increases glycerol production. In a strain of *S. cere*V*isiae*, the glycerol yield exhibiting 20-fold increased Gpd1p activity resulting from over expression of GPD1 gene was 6.5 times of that the wild type (Nevoight, 1996). Over expression or disruption of GPD1 could also modulate glycerol and ethanol yields during alcoholic fermentation in *S. cere*V*isiae*. Mutants with gpd1D exhibited a 50% decrease in glycerol production and increased ethanol yield. On the other hand, over expression of GPD1 in strains resulted in a substantial increase in glycerol production at the expense of ethanol in broth containing 200 g/L glucose. In 2001, a review was published about the glycerol production with microbial fermentation (Zheng et.al,, 2001).

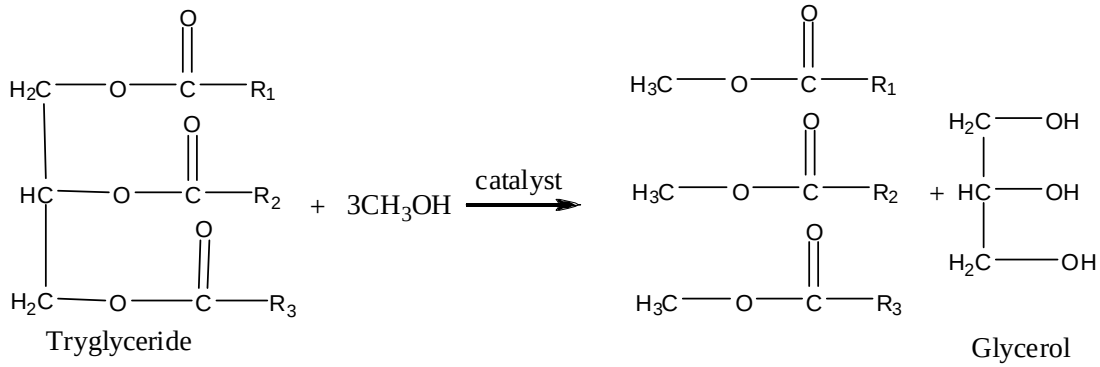
A new energy resource such as biodiesel fuel has grown in importance in recent years. Biodiesel (composed of fatty acid methyl esters) is an efficient, clean, 100% natural energy alternative to petroleum fuels (Gerpen, 2004). The many favorable aspects of biodiesel fuel include the following: It is safe for use in all conventional diesel engines, it offers the same performance and engine durability as petroleum diesel fuel, it is both nonflammable and non-toxic, and it reduces tail pipe emissions, visible smoke, and noxious fumes and odors. Biodiesel is obtained from natural, renewable sources such as new and used vegetable oils and animal fats (Krafft et al., .2007a) On the basis of these advantages; biodiesel technology is making the transition from a research endeavor to a worldwide commercial enterprise. In support of this increasing consumption, there have been substantial increases in biodiesel production in recent years, a trend that is expected to continue. Europe and the United States are the leading biodiesel producers at this time, with European

production in 2003 estimated at 1.7 × 109 L (450 million gal) (data from European Biodiesel Board, 2004) and U.S. production in 2004 estimated at 114 million L (30 million gal) (McCoy, 2005).

This growth is the result of the construction of new production plants and the expansion of existing ones (Michael, 2005). Biodiesel can be produced from any material that contains fatty acids, whether they are free acids or linked to other waste greases, and edible oil-processing wastes can be used as feedstock for biodiesel production. The choice of feedstock is based on such variables as local availability, cost, government support, and performance as a fuel. A variety of reaction configurations can be employed in biodiesel synthesis, involving inorganic acid, inorganic base or enzymatic catalysis, biphasic or monophasic reaction systems, and ambient or elevated pressures and temperatures. The choice of such chemical technology to employ in a production plant depends on the type of feedstock and its quality. The choice of conversion technology will in turn influence costs. The scale of operation will also bear upon construction and operating costs. In any case, individuals considering the construction or modification of a biodiesel production facility need the means of estimating the cost of biodiesel production based on the components of the operation and construction costs (Michael, 2005).

During triglyceride transesterification, glycerol separates from the oil phase as the reaction 2.6 shows. The glycerol liberated during transesterification has substantial commercial value if it is purified to USP grade. As a rough rule of thumb, about 1 kg of glycerol is produced for every 9 kg of fatty acid methyl ester. Therefore, increased biodiesel production results in the accumulation of glycerol, which leads to a price

decline. The effect is that the sale of glycerol is becoming the bottleneck of biodiesel production enhancement. Figure 2.4 is a forecast of the development of global glycerol production (Zheng, 2008). It shows an exponential growth of glycerol until 2010.



(2.6)

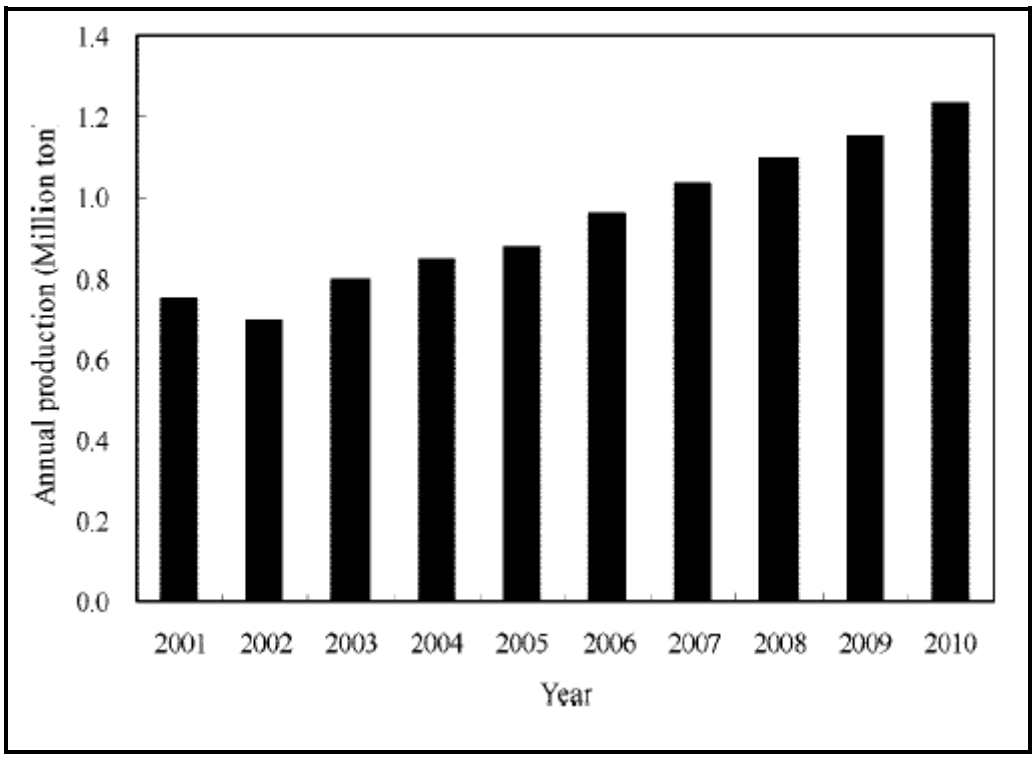


FIGURE 2.4 Projection of Global Glycerol Production (Zheng, 2008)

Glycerol that is used for producing dichloropropanol can be a crude product or purified product (Krafft, Franck, Andolenko, & Veyrac, 2007). When the glycerol is a crude product, it can comprise, for example, water and a metal salt. When purified glycerol is used, that glycerol is obtained by purified crude glycerol using one or more purification operations such as a distillation, an evaporation followed by a separation operating such as settling out, filtration or centrifugation. Krafft mentioned that a distillation operation gives good result. It is also possible to carry out an operation consisting in drying the crude product or the product derived from the purification operations. It is also possible to carry out a purification operation, which comprises treating the crude product or a product obtained from another purification operation, with a resin (Krafft, Patrick, Benoit, & Sara, 2007).

The crude glycerol from biodiesel manufacturing plant can be treated with steam under reduced pressure (Krafft, Patrick, Benoit, & Sara, 2007). For example the operation can be carried out in an arrangement composed of a round-bottomed flask equipped with a pocket having a thermocouple, with a magnetic bar for the stirring, with a dip pipe for the injection of steam, with a distillation head with a pocket having thermocouple, with a side reflux condenser cooled to $0^{o}C$ and with a round-bottomed flask for collecting the evaporate. Crude glycerol contains about 40 % by weight of glycerol while purified glycerol contains 80 % by weight of glycerol. Table 2.1 and Table 2.2 show glycerol properties and crude glycerol content from biodiesel respectively (Maneely, 2006).

Table 2.1 Glycerol Properties (Maneely, 2006)

Property	Description
Boiling point (1 atm)	290^{o}C
Density (25 °C)	1.262 g/ml
Flashpoint (open cup)	176 °C
Solubility	water, ethanol

Table 2.2 Crude Glycerol content from Biodiesel (Maneely, 2006)

Property	Description
Glycerol content	40 to 90%
Water content	8 to >50%
Methanol content	should be less than0.5%
Salt content	0 to 10%

Several opportunities, Figure 2.5, for glycerol consumption have been identified since it can readily be oxidized, reduced, halogenated, etherified, and esterified to obtain alternative commodity chemicals such as dihydroxyacetone, mesoxalic acid, 1, 3-propanediol, 1,3-dichloropropanol, glyceryl ethers, glycerol carbonate, and glyceryl esters (Zheng et al., 2008).

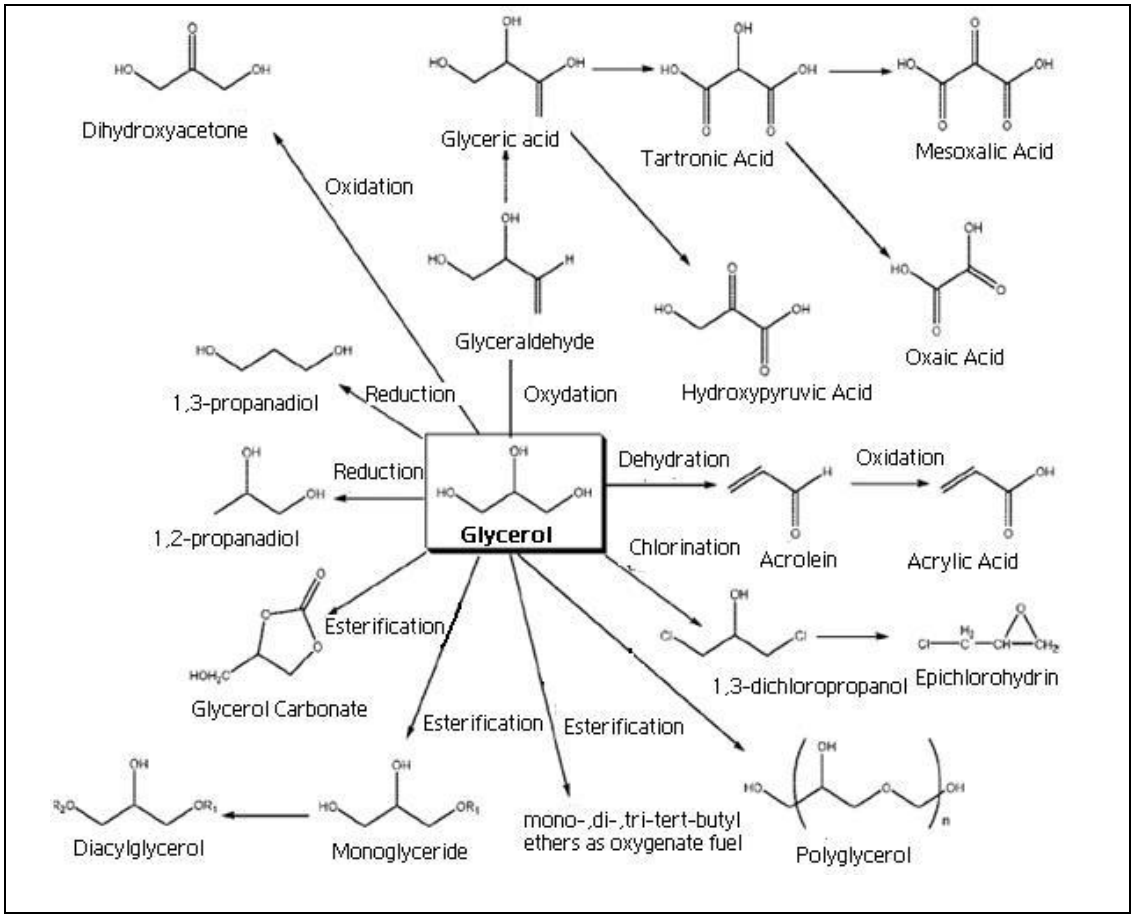


Figure 2.5 Commodity Chemicals from Glycerol (Zheng et al., 2008)

2.4. EPICHLOROHYDRIN PROPERTIES

Epichlorohydrin is a colorless liquid with an irritating, chloroform-like odor. It is slightly soluble in water (6 g/100 ml of water), miscible with alcohol, ether, chloroform, trichloroethylene, and carbon tetrachloride and insoluble in petroleum hydrocarbons (HSDB, 2009). Epichlorohydrin hydrolyzes slowly at room temperature and more rapidly in the presence of heat or traces of acid. When heated to decomposition, epichlorohydrin emits toxic fumes of hydrochloric acid and other

chlorinated compounds. The commercial product is 98% pure with a maximum of 0.2% water.

Epichlorohydrin is a hazardous material due to its toxicity, flammability and reactivity. Appropriate precautions must be taken to safely store, transport, deliver and handle this product. In all cases, international, national, regional and local regulations related to transport, storage, handling, health, safety and environmental protection must be strictly observed (Solvay, 2003).

2.4.1 Physical Properties

The chemical structure of epichlorohydrin is shown in Figure 2.6. Physical properties are provided in Table D.1, Figure D1, and Figure D2 (Appendix). Typical chemical reactions are provided in Table D1. In mixtures with air, the vapor phase can produce a flammable or moderately explosive mixture when the concentration of epichlorohydrin is between 3.8% and 21% (by volume).

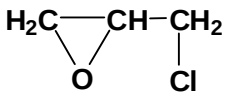


Figure 2.6 Chemical structure of epichlorohydrin

The lower flammability limit (3.8%) is reached when the temperature of the liquid corresponds to that of the flash point (around 31°C).Beyond the upper flammability limit (21%), the mixture is no longer flammable because the concentration in atmospheric oxygen is too low. However, conditions of flammability may be reached

by dilution of the vapors (draught of air, etc.) and from aerolization (Solvay, 2003). In view of the significant risk due to its flammability, it is recommended to handle and store epichlorohydrin under nitrogen. Epichlorohydrin should be kept away from sources of heat, flames and sparks. In addition, when handling epichlorohydrin (pumping, etc.), electrostatic charges may be produced. These may cause sparks, which are a source of ignition. To avoid this risk, it is essential to ensure that all equipment is properly grounded and bonded (Solvay 2003).

Thermal Decomposition

Starting from about 225°C, "dry" epichlorohydrin may polymerize. In the presence of water, even at moderate temperatures, it may undergo thermal decomposition via hydrolysis, especially if the medium is acidic or basic. Epichlorohydrin burns to form water, carbon oxides and hydrogen chloride (HCl: an irritant gas).

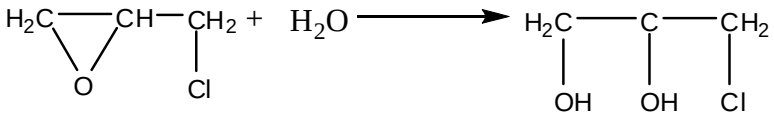
Chemical Reactivity

Epichlorohydrin may react violently in the presence of acids or bases, pure or in concentrated solutions, especially at high temperatures. Principal categories of materials that can react with epichlorohydrin are: acids, bases such as alkalis, amines and ammonia, alcohols, carbon monoxide, metallic oxides and hydroxides, salts, especially metal halides (e.g., $FeCl_3$), and aluminum, magnesium, copper, tin, zinc and their alloys.

Degradation in Aqueous Solutions

Whether or not it contains a base or an acid, epichlorohydrin in an aqueous solution can be hydrolyzed into glycerol in several stages as the following (Solvay, 2003):

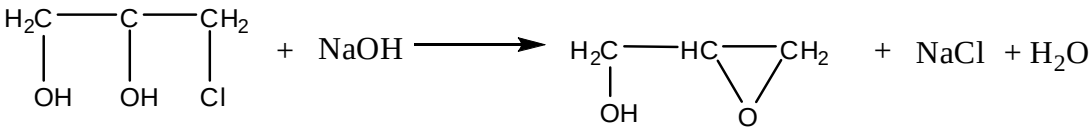
Firstly, epichlorohydrin is hydrolyzed into α-monochloropropanol



(2.7)

Epichlorohydrin α-monochloropropanol

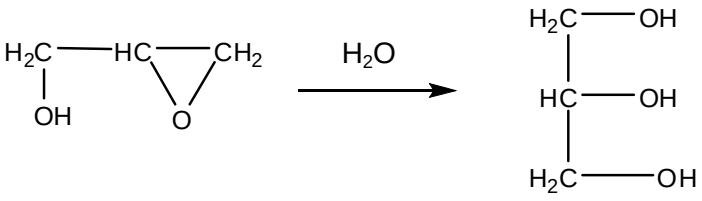
Secondly, reaction of α-monochloropropanol in a basic medium into glycidol



α–monochloroydrin Glycidol

(2.8)

Finally, glycidol is hydrolyzed into glycerol



Glycidol Glycerol

(2.9)

Bases and acids catalyze the hydrolysis of epichlorohydrin in an aqueous solution. Its hydrolysis rate is therefore a function of its concentration and the concentration of either the base or acid. According to Ma et al. (2008), hydrolysis reaction lowers the

reaction yields then, epichlorohydrin produced must be removed as quickly as possible from the reaction environment by designing a suitable distillation column and choosing the optimal operating conditions. They suggested that dehydrochlorination reaction, which reaction between dichloropropanol and sodium hydroxide to produce epichlorohydrin, is performed in a reactive distillation system, and epichlorohydrin is flashed out with stream to shorten the contact time to prevent hydrolysis.

Materials of Construction for Storage

Epichlorohydrin is normally stored and transferred in containers made of mild steel or stainless steel. Corrosion (especially in mild steel) may appear in abnormally damp conditions. Epichlorohydrin has a swelling effect on polymers and elastomers (pipes, gaskets, protective gloves and boots, etc.) that varies with the exact type of material. Polymers may also be used such as polypropylene, polytetrafluoroethylene, and polysulphides (Krafft, Franck, Andolenko, & Veyrac, 2007).

Exposure Control

Although epichlorohydrin has a very high vapor pressure as Table D.1 (appendix D) shows, it can be controlled to maintain vapor concentrations well below occupational exposure limits. This should be achieved through properly designed, leak-tight product handling systems. Good ventilation is important; whenever possible, the epichlorohydrin handling facilities should be located outdoors to maximize natural ventilation. However, good ventilation cannot replace a closed, leak-tight system. All aspects of the handling operation, from delivery through reaction to disposal, must be

carefully scrutinized for exposure potentials. Activities such as sampling should receive particular attention. Measures that prevent exposures should be thoroughly explored (Solvay, 2003; Dow, 2007).

Personal Protective Equipment

In view of the properties of epichlorohydrin, it is essential to take all reasonable precautions to reduce exposure to a minimum. Epichlorohydrin easily penetrates clothing, gloves and shoes. Thus, it is necessary to wear suitable protective clothing whenever handling the product. The materials are recommended based on the permeability testing done according to ASTM method F739-91 such as butyl rubber with protection more than 8 hours, polyvinyl alcohol with protection more than 4 hours, polytetrafluoroethylene with protection more than 4 hours (Solvay, 2003). Epichlorohydrin should not be allowed to come in contact with leather. Contaminated leather may appear dry but the product diffuses to the skin and can lead to chemical burns.

Environmental Issues

During the manufacture of glycerin, epoxy resins, and other chemicals, epichlorohydrin may be vaporized to the atmosphere and diluted in wastewater. In wastewater, groundwater and ambient water, epichlorohydrin has been detected at low levels, (WHO, 1984). Additionally, epichlorohydrin has low stability in the environment because it undergoes hydrolysis rapidly in aqueous media (Bijsterbosch, 1994). However, due to its strong reactivity as mentioned above, spill of epichlorohydrin to environment may give an impact directly.

Thus, it is important to avoid it to disperse and to handle any spills of product by referring to the national, regional and/or local regulations. Fortunately, epichlorohydrin rapidly disappears in the atmosphere and will not accumulate. According to Carra et al., (1979) and Ma et al. (2007), in the presence of water and basic or acid, epichlorohydrin will decompose to glycerol as can be seen in Equation 5.2, thus safer to the environment.

Health Risks

Epichlorohydrin (liquid or gas) is an irritant to the eyes, skin and mucous membranes of the respiratory and digestive tracts. It is absorbed through intact skin and, in some cases, induce allergic reactions. Additionally, it may cause burns, which appears a few hours after exposure. Moreover, epichlorohydrin may affect both nervous systems and respiratory and also affect on abdominal cramps and convulsions (Giri, 1997). Fatigue, headache, chronic respiratory problems and, in some cases, blood and liver complaints are the usual symptoms for chronic toxicity. Carcinogenic effects have been observed with animals only (IARC, 1987).

2.5. APPLICATIONS OF EPICHLOROHYDRIN

Epichlorohydrin is an important raw material for the production of epoxide resins, synthetic elastomer, sizing agents for papermaking industry, textile, ion exchange resin, water treatment chemicals, polyols, and a variety of glycidyl derivatives (Solvay, 2003). In addition, it has also been used to production of Zeospan, a

specialty polyether rubber used for automobile parts, to cure propylene-base rubbers, as a solvent for cellulose esters and ethers and in resins with high wet-strength for the paper industry (IARC, 1999).

2.5.1 Epoxy Resins

Epichlorohydrin is primarily used to manufacture epoxy resins. By reacting a polyhydric phenol with an aliphatic chlorohydrin or simple aliphatic epoxide generally produces epoxy resins. The most familiar epoxy is obtained by condensing epichlorohydrin with bisphenol A (Bhatnagar, 1996).

Epoxy resins are versatile polymers used in the manufacture of adhesives, coatings, and structural parts needed by the automotive, marine, offshore, aerospace and aircraft industries (ICIS, 2012). In the construction industry, epoxy resins are the preferred materials for non-slip, easy to clean and chemicals barrier surfaces. They are the adhesives of choice due to their excellent adhesion onto steel and concrete. Epoxy resins are used in many paints for automotive, refrigerators, and electric household appliances. Major advantages of epoxy resins include corrosion resistance, solvent and chemical resistance, hardness, and adhesion. Epoxy resins have excellent strength and electric insulation properties (Osamu, 1990). They are used in the electronic industry for printed circuits boards (in mixture with fiberglass) and to encapsulate electronic components (to protect them from damage).Storage tanks, pipes, appliances, and food and drink cans all benefit from durable coatings made from epoxy resins. Their adhesive properties are especially useful to combine different materials in sport equipment such as skis, tennis rackets, windsurfer, boats,

etc. Epoxy resins have excellent adhesive properties and are applied in two-component glues, for industry and domestic applications (Lee & Neville, 1967).

2.5.2 Elastomers

Elastomers made from epichlorohydrin offer excellent resistance to oxygen, weather, fuels and oils. This makes them ideal for many automotive applications, especially with the increase instringent emission control regulations and higher quality requirements (Clark, 2005).

2.5.3 Pharmaceutical industry

Epichlorohydrin is used in chemical synthesis of complex molecules for the pharmaceutical industry. Epichlorohydrin is the starting material in the synthesis of glycerol monochloropropanol (1-chloro-2,3-propanediol), used in the manufacture of pharmaceutical products (X-ray contrasting, cough mixtures) (Solvay, 2009).

2.5.4 Papers, Inks, Dyes

Wet-strength paper sizing is prepared from either polyamides modified with epichlorohydrin or from the reaction product of epichlorohydrin and an alkylene amine (Solvay, 2003). Epichlorohydrin polyhydroxy compounds and their esters are useful in the production of special printing inks and textile print pastes. These products yield flexible films that are chemically inert to caustic soda and other chemical solutions. Epichlorohydrin adducts are useful as filler retention aids, paper coatings, flocculants, and anti-static agents. Paper and paperboard products with

improved printability, pigment retention, folding endurance, and gloss also are prepared with epichlorohydrin reaction products. Besides that the paper industry uses polyamine-epichlorohydrin resins to improve paper wet-strength. This grade of paper is found in coffee filters and tea bags (Solvay, 2003).

2.5.5 Textiles

In the textile industry, epichlorohydrin is used to modify the carboxyl groups of wool (Dow, 2007). The resulting product has a longer and improved resistance to moths. Epichlorohydrin is also used to prepare protein-modified, wool-like fibers which have an affinity for acid dyes and which exhibit resistance to both mold and insects. Further, epichlorohydrin is used to prepare dyeable polypropylene fibers and to dye polyolefin, polyacrylonitrile, polyvinyl chloride, polyvinyl alcohol, and other fibers. It is also used to impart wrinkle resistance and to prepare antistatic agents and textile sizing. Derivatives of epichlorohydrin show utility as leveling, dispersion, softening, emulsifying and washing agents (Gerhard, 2009).

2.5.6 Ion Exchange Resins

Epichlorohydrin is used to produce both anion- and cation exchange resins (Dow, 2007). Water-insoluble anion-exchange resins having good stability are prepared by reacting epichlorohydrin with ethylenediamine or a higher homolog. Strong-base anion-exchange resins can be produced by reacting epichlorohydrin with polymeric tertiary amines. Epichlorohydrin-based anion exchangers are used successfully to purify drinking water and to clean polluted air. Cationic-exchange resins are

produced by condensing epichlorohydrin with polyhydroxy phenols and by sulfonating the product (Dow, 2007).

2.5.7 Surface Active Agents

Many epichlorohydrin-based, surface-active agents are synthesized by condensing the epichlorohydrin with a polyamine such as tetraethylene-pentamine, plus a fatty acid such as stearic acid (Dow, 2007). The polyamine and fatty acid may be replaced with an alkali metal, starch, or other reactant. Sulfonated epichlorohydrin is occasionally substituted for epichlorohydrin. Such products find use in cosmetics and shampoos, and as detergents, sudsing agents, water softeners, and demulsifiers.

2.5.8 Plastic foams

Epichlorohydrin can also be used in the synthesis of polyols, reagent for the manufacture of rigid polyurethane foams. These grades of foams are non-flammable and have excellent heat insulation properties for construction industry, and refrigerators (Solvay, 2003)

2.5.9 Water treatment chemicals

Epichlorohydrincan be used in the manufacture of polyamines and polyquaternary ammonium salts, as flocculants in water and waste water treatment and also is used in ion-exchange resins for water treatment and softening (Dow, 2007)

2.5.10 Other Applications

Other applications for derivatives of epichlorohydrin include: Asphalt improvers, corrosion inhibitors, electrical insulation for wire, fire-retardant urethanes, hair conditioning rinses, liners for polyethylene bottles, linoleum and linoleum cements, lubricant additives, petroleum production aids, pharmaceuticals, photographic film bases, rubber latex coagulation aids, waterproofing compounds, and zinc electroplating compounds (Solvay, 2003)

2.6. HYDROCHLORINATION PROCESS

The hydrochlorination reaction is a reaction between glycerol and hydrogen chloride in the presence of carboxylic acid or its derivatives as a catalyst, providing 1,3-dichloropropanol, which is an intermediate of epichlorohydrin synthesis, and water. This reaction is carried out in the liquid phase under temperature around 100^{o}C while pressure can be either atmospheric or elevated, in order to increasing the solubility of gaseous hydrogen chloride in the reaction mixture (Kubicek et al., 2005; Krafft et al., 2007; Bell et al., 2008).

Kubicek et al. (2005) have conducted the hydrochlorination reaction of glycerol with gaseous hydrogen chloride in the presence of acetic acid as catalyst at reaction temperatures range 70 to 140^{o}C and with continuous removal of the water of reaction. Even though distilled glycerol with various content of glycerol can be used, crude glycerol with various content glycerol can also be used. In this case they used the liquid feed containing 50 percent by weight of glycerol. According to them the

mixture of products, apart from containing dichloropropanol also contain water and small amount of acetic acid catalyst and un-reacted hydrogen chloride. The hydrogen chloride can be used without any treatment for the next reaction step in epichlorohydrin synthesis.

Krafft (Krafft, Franck, Andolenko, & Veyrac, 2007) invented a process for producing dichloropropanol from glycerol, which comes from the conversion of animal fats in the manufacturing of biodiesel, with a chlorinating agent in the presence of acetic acid, adipic acid and caprilic acid as the catalysts. As a chlorinating agent, they used either an aqueous solution of hydrogen chloride or anhydrous hydrogen chloride.

They found that when they used acetic acid as catalyst then most of the catalyst (55 %) evaporated from the reaction liquid and was found in the condensate. Furthermore, they replace the acetic acid with the caprylic acid in order to reduce catalyst loss from the reactor. In this way only 10 % of the acid evaporated from the reactor. About the reaction temperature, they found that the best results were obtained above 120^{o}C. All their experiment is shown in Table 2.4

Siano (Siano, et al., 2006) have also reported a method to make dichloropropanol isomers from glycerol. Their technique is based on the reaction of gaseous hydrogen chloride with glycerol in the presence of malonic acid catalyst. Their experiment was carried out at 100°C using 8 mole percent the catalyst (based on glycerol). The conversion of glycerol was 76 percent for 5 hours.

Table 2.4 The Various Control Parameter and Results by Krafft et al. (2007)

		Experiment Number								
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Boiler Temperature	^{o}C	123	121	123.1	130	117.6	146.4	130	119.4	131.6
Conc. aq. HCl	Mole/kg	9.59	9.59	5.29	5.29	5.29	3.95	3.95	3.95	3.94
Nature of the organic acid[1]		aa	Ca	Ca	ca	Ca	Ca	Ca	ca	Ada
Feed Flow Rate										
Glycerol	g/h	30	30	30	30	30	22	22	22	25.6
1,3-DCP	g/h	42	42	42	42	42	0	0	0	0
Organic acid	g/h	3.9	9.41	9.41	9.41	9.41	6.21	6.21	6.21	3.6
Aq. HCl	g/h	79	79.5	149	163	148	98.7	98.7	98.7	153.5
Overall conversions &										
Selectivity										
HCl conversion rate	(%)	57.3	60.7	51.2	45.9	36.3	80.0	91.6	87.4	87.6
Glycerol conversion rate	(%)	87.8	91.8	93.0	95.2	86.4	97.7	96.7	95.0	99.4
Organic acid in distillate/ Organic acid used	mole/mole	0.55	0.02	0.11	0.13	0.16	0.11	0.14	0.20	<0.0005
MCP selectivity	(%)	61.9	56.0	51.0	57.2	47.0	27.8	29.6	25.1	7.4
DCP selectivity	(%)	29.7	27.1	29.5	39.7	20.4	42.8	60.3	55.2	82.3
Oligomer selectivity	(%)	0.9	0.4	0.6	0.8	0.6	1.2	1.6	1.1	

[1]aa: acetic acid; ca:caprylic acid; ada: adipic acid

In addition, Bell et al.. (2008) have carried out an experiment to synthesize dichloropropanol from glycerol. They used 2 wt. % of a carboxylic acid catalyst with hydrogen chloride at slightly above atmospheric pressure (20 psi) and 120^{o}C in a sealed vessel. Based on their results, glycerol is converted initially to α-monochloropropanol (1-MCP) predominantly with much smaller amounts of β-monochloropropanol(2-MCP). Furthermore, 1-MCP is converted mainly to α,γ-

dichloropropanol (1,3-DCP) with much smaller amounts of α,β-dichloropropanol(2,3-DCP). They observed that conversion glycerol to dichloropropanol is low under atmospheric pressure. They proposed some suggestion in order to improve this process such as using bubble system to introducehydrogen chloride gas to the reaction, employing an azeotropic agent to facilitate water removal, and employing multiple reaction stages with interstage water removal. However, either bubble system or azeotropic system to remove water from the reaction medium is expensive and therefore less desirable on a commercial scale.

Moreover, Bell et al. (2008) investigated effect of higher hydrogen chloride concentration on the reaction conversion, rate, and selectivity. They applied pressures of hydrogenchloride gas at range 15 to 110 psi. They observed that at higher pressure the hydrochlorination reaction be faster, and drive the reaction to higher conversion. The best conditions, on their works, were pressure at 110 psi, and temperature at 110^{o}C, 5 mole% of acetic acid as the catalyst for 4 hour. Their results can be seen in Figure 2.7.

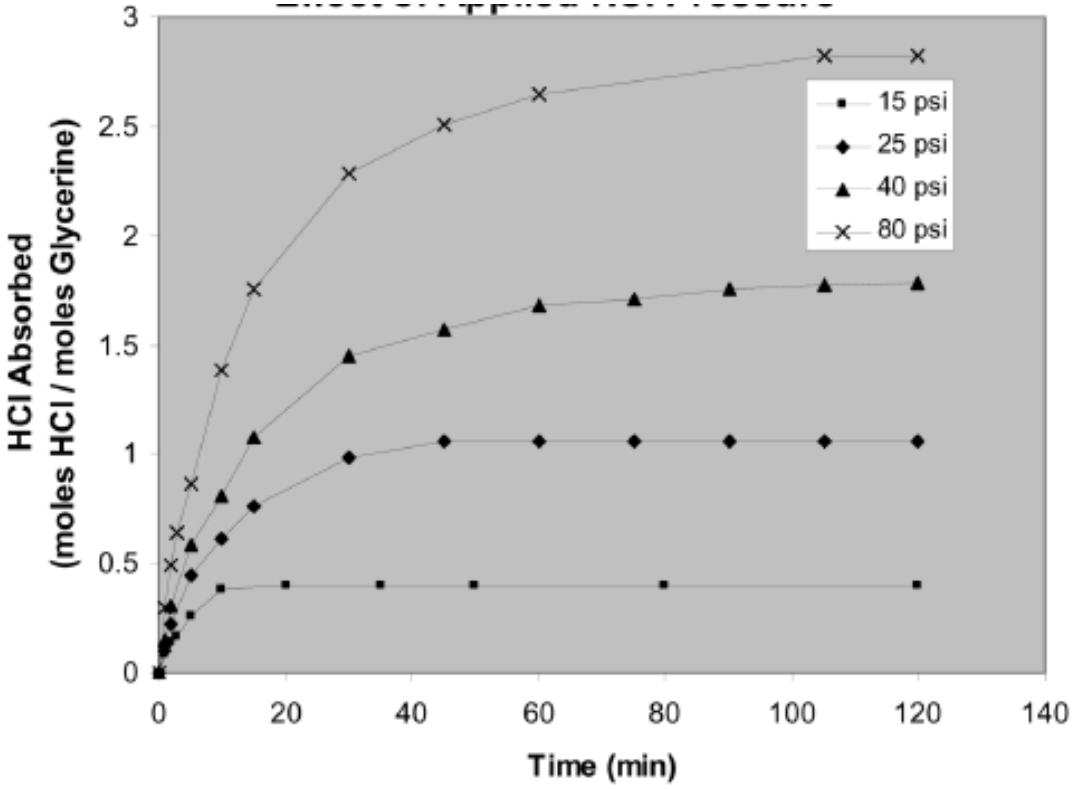


Figure 2.7. Plot Effect of Pressure on HCl absorbed in glycerolhydrochlorination reaction (Bell et al., 2008)

The hydrochlorination can be carried out in a continuously operating one-step circulating reactor or in a cascade of continuous flow reactors of the liquid-gas type (Kubicek et al., 2005). To achieve good conversions of the starting glycerol to the dichloropropanol products, it is also necessary to remove the water of reaction from the reaction environment for the reason of chemical equilibrium, preferably by distillation under reduced pressure. They also mentioned that any reactor for the reaction of the liquid-gas type can be chosen for the reaction itself, such as a stirrer reactor, a bubble tower (column), variously filled columns for the liquid-gas contact, ejectors and the like. In addition, they also have comparedbetween a circulation column reactor, consisting of vertical cylinder with external circulation of the reaction mixture, and a cascade of continuous flow reactors with three reactors of the

cascade without final recovery of the monochloropropanol reactive intermediate as shown in Table 2.5.

Table 2.5 Comparison Circulation Column Reactor and Cascade Continuous flow Reactor (Kubicek et al., 2005)

Parameter	Circulation column reactor	Cascade continuous flow reactor
Glycerol (kg/h)	4.875	4.875
Acetic acid (%)	2	2
Gaseous hydrogen chloride (kg/h)	5	5
Reaction Temperature (^{o}C)	106	95
Pressure in the reactor (kPa)	101	101
Conversion of glycerol (%)	99.8	99.9
Yield of dichloropropanol (%)	95.6	83.1

Krafft (Krafft, Franck, Andolenko, & Veyrac, 2007) conducted their experiment in a reactor, which is equipped by distillation column. In this case glycerol is fed in either a continuous or batch mode via a first line and catalyst via a second line, the feed of hydrogen chloride, anhydrous or in aqueous solution, is carried out continuously or in batch-mode via a third line, a distillation column is fed via a fourth line with vapor produced from the reactor, the residue from the distillation column is recycled via a fifth line to the reactor, a purge from the reactor bottom is fed via a sixth line into a stripper wherein a partial stripping operation is carried out, the gas phase containing most of hydrogen chloride from a stream is recycled via line to the distillation column or via line to the reactor, a distillation or stripping column is fed with the liquid phase arising from the stripper via a seventh line, the main fraction of

dichloropropanol is collected from the top of the column through an eighth line and the column residue is recycled via a nine line to the reactor.

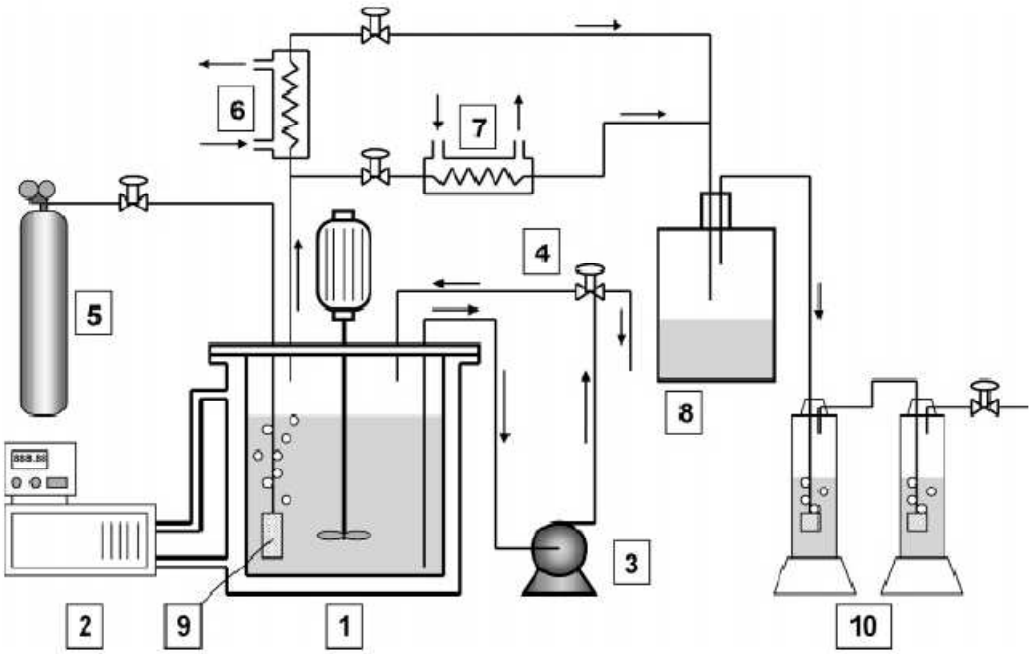


Figure 2.8 Chlorination experimental apparatus by Tesser et al. (2007)

Tesser et al. (2007) investigated glycerol chlorination with gaseous hydrogen chloride for the production of dichloropropanol. They used a jacketed glass reactor operated in batch conditions for the glycerol and continuously for the hydrochloric acid. Their experimental runs have been carried out in a laboratory apparatus schematically represented in Figure 2.8. The flow of hydrogen chloride is fed, from a cylinder, directly into the liquid glycerol phase in the reactor by using a porous ceramic sparger that, together with the stirrer, ensures a good gas-liquid inter-phase contact. The temperature of the reaction mixture is kept constant within ±0.3 °C by means of a thermostat that continuously circulates thermal fluid into the reactor jacket. The reactor is equipped also with an external recirculation line operated by a

peristaltic pump and with a stopping valve for withdrawing samples of the reacting mixture at different times. The peristaltic pump is turned on only when a sample has to be collected and then is stopped.

The other head of the reactor was mounted with two types of condensers, the first is vertical and is used for runs at total reflux in which, practically, and only hydrogen chloride and small amounts of water are allowed to leave the reactive system. The second condenser is placed horizontally and is used only for runs under stripping conditions, when the flow of hydrogen chloride is used as a stripping agent to remove all the volatile components from the reaction mixture. After the condensers, a reservoir tank is provided for collecting the condensed products eventually present, while the gaseous flow, mainly constituted by un-reacted hydrogen chloride, is finally neutralized by bubbling in a series of two or more Drechsel-type bottles containing a solution of sodium hydroxide.

The neutralization of the hydrogen chloride excess is monitored by adding an indicator (phenolphthalein) to the sodium hydroxide solution in a way that, when the solution in a bottle is completely neutralized, the indicator changes color and a further neutralization trap is added. All the runs have been conducted at atmospheric pressure of hydrochloric acid because of the limitation of the adopted glass reactor. The increase of the reaction pressure should result in an increase of reaction rate (Schreck, 2006; Bell et al., 2008) as a consequence of the higher concentration of hydrochloric acid in the liquid-phase mixture.

2.7. DEHYDROCHLORINATION PROCESS

The dehydrochlorination reaction is a reaction between dichloropropanol, either 1,3-dichloropropanol or 1,2-dichloropropanol, with base solution, providing epichlorohydrin, which is applied widely as mentioned before. This reaction was carried out in the liquid phase under temperature range 35to 85^{o}C (Carra et al., 1979; Ma et al., 2007; Zhang et al., 2012) while pressure can be either atmospheric or vacuum, in order to avoid hydrolysis reaction which can lower yield of epichlorohydrin (Carra et al., 1979). A competitive reaction, where the product, epichlorohydrin may be converted back to mono-chloropropanol and glycerol, will eventually occur when reaction temperature exceeds 85^{o}C (Carra et al., 1979; Ma, 2007). The reactions involved during dehydrochlorination process can be seen in Figure2.9 and 2.10 below

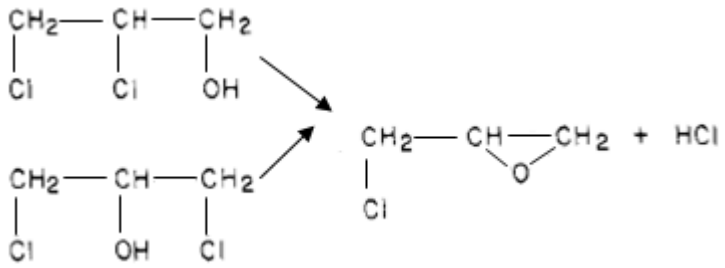


Figure 2.9 Dehydrochlorination reaction (Carra et al., 1979)

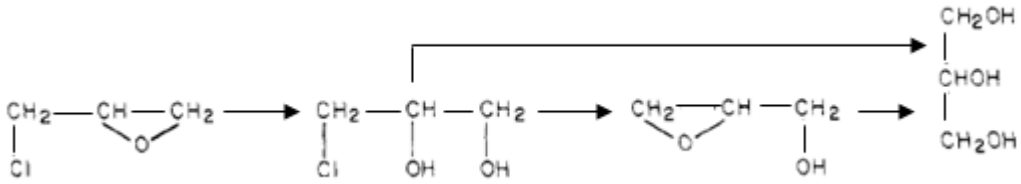


Figure 2.10 Hydrolisis reaction of Epichlorohydrin (Carra et al., 1979)

Carra et al. (1979) have conducted the dehydrochlorination reaction of 1,3-dichloropropanol with calcium hydroxide at reaction temperatures range 35 to 65^{o}C.

They determined the kinetic parameters of 1,3-DCP and 2,3-DCP in an aqueous base solution containing an excess of $Ca(OH)_2$ and offered a kinetic model of the overall system using the techniques of potentiometry and gas chromatography. The reaction was carried out in a stirred batch reactor without the presence of catalyst for 15 minute. Ma et al. (2007) also studied the kinetics of dehydrochlorination of DCP and the side reaction of ECH hydrolysis using the techniques of potentiometry only. However, the said technique was unable to separate the reaction products otherwise only decreasing ion can be measured. The earliest study on kinetic have been carried out by Zhang (2012) which used very small volume of the reactor (0.00215 ml) where using gas chromatography for the analysis.

2.8. REACTION KINETICS

In reaction engineering, the concept of equilibrium can be approached either from the basis of chemical kinetics or thermodynamics equilibrium. While thermodynamic equilibrium emphasizes on minimizing Gibb's energy requirement ΔG_{min} as the criterion, reaction kinetics look at equilibrium in terms of reaction rates. At equilibrium, the rate of appearance of products must be the same as the rate of disappearance of reactants. Ideally, if reactants A and B react to form products C and D, the reaction equation can be written as;

$$aA + bB \rightleftharpoons cC + dD \qquad (2.10)$$

Where rate of reactions of the above reaction can be written as:

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A^{\alpha} C_B^{\beta} \quad (2.11)$$

$$r_C = \frac{dC_C}{dt} = k_2 C_C^{x} C_D^{\delta} (2.11)$$

Where α, β, χ, and δ are orders of reaction with respect to A, B, C, and D respectively. At equilibrium, these rates are the same, $r_A = r_C$ and it may be compounded as

$$r = k_2 C_C^{x} C_D^{\delta} = k_1 C_A^{\alpha} C_B^{\beta} \quad (2.12)$$

Combining gives

$$K = \frac{k_1}{k_2} = C_C^{x} C_D^{\delta} / C_A^{\alpha} C_B^{\beta} \quad (2.13)$$

K is equilibrium constant, k_1 and k_2 are the reaction rate constant and C_A, C_B, C_C, and C_D represent the concentrations of component A, B, C and D respectively.

Studies on reaction kinetics generally focus on the dependency of rate equation, *r* on concentration, via reaction order, n and reaction constant, k. It also establishes the dependency of rate constant, k on temperature via Arrhenius Equation. Equation 2.10 to 2.13 developed so far are mainly for homogenous reactions only. When a solid catalyst, which is in different state of aggregation from the reaction media, catalyzes the reaction, it becomes heterogeneous reaction. The presence of several phase boundaries requires both the transport processes and reaction rate be accounted for in the development of rate equations for these reactions. The rates of adsorption

desorption and surface reactions are combined to give the expression for the overall rate in terms of fluid concentrations. The resultant equations are usually very complex and dependent upon so many variables. The use of many assumptions renders the results to be more meaningful than the simplified approach.

Liquid-solid catalytic reaction, where the catalyst in solid state, is a typical heterogeneous system in the chemical and petroleum industries. In view of uncertainties and lack of knowledge in transport processes to and from catalyst surfaces, the power-law form of the rate equation (Equation 2.12) has been used widely in industrial reactor design (Smith, 1981). This simple empirical approach ignores the adsorption and desorption phenomenon and provides no information on reaction mechanisms. Nevertheless, it has been proven that such rate equation can correlate the experimental data just as accurately, as the detailed methods.

However, in cases where the adsorption and desorption are important, an intermediate approach called Langmuir-Hinshelwood formulation was developed in detail by Hougen and Watson in 1947 based on the method originally proposed by Hinshelwood in 1940 (Levenspiel, 1999). It was based on the Langmuir rate and isotherm expressions, which assume first order relationships for adsorption and desorption processes. The simplicity of this Langmuir-Hinshelwood formulation allows rapid determination of rate equations of acceptable engineering accuracy. The net rate of adsorption and desorption of a component A is given by;

$$r_a = k_a C_A(\bar{C}_m - \bar{C}) - k'_a C_A = k_a[C_A \bar{C}_v - \frac{1}{K_A}\bar{C}_A] \qquad (2.14)$$

$\bar{C}$ is the average of concentration of an adsorbed species and $\bar{C}_m$ representing the concentration corresponding to a complete formation of molecular layer on the catalyst surface. The difference between these two concentrations, $\bar{C}_m$ and $\bar{C}$ equals to the concentration of vacant sites, $\overline{C}_v$. Adsorption equilibrium constant, K_A is the ratio between rate constant of adsorption (k_a) and desorption (k'_a), $K_A = \frac{k_a}{k'_a}$. At equilibrium, the net rate of adsorption, r_a is zero; the concentration of A on the catalyst surface is in equilibrium with the concentration in the fluid, $C_A$given by;

$$(\bar{C}_A) = K_A C_A \bar{C}_V \qquad (2.15)$$

The determination of rate of surface reaction depends on the nature of the reaction on the surface. It can between an adsorbed molecule and another molecule on the surface or between adsorbed molecules on adjacent active sites. For the hydrochlorination reaction of the type given in Equation2.7,in case of using solid catalyst, can be simplified as below:

$$A + B \rightarrow C + D \qquad (2.16)$$

Since approximately 75 % of all heterogeneous reaction mechanism are surface-reaction-limited rather than adsorption or desorption-limited (Fogler, 1992), the reaction between adsorbed glycerol and hydrogen chloride to be reaction-rate-limited was assumed. The reaction mechanism is postulated to be as follows:

Adsorption: $A + S \Leftrightarrow A.S$

$$r_a = k_A(C_V C_A - \frac{C_{A.S}}{K_A}) \quad (2.17)$$

Where C_V is the vacant site of the catalyst

Surface Reaction: B + A.S ⇔ C.S + D

$$r_s = k_s(C_A C_{A.S} - \frac{C_{C.S} C_D}{K_S}) \quad (2.18)$$

Desorption: C.S ⇔ C + S

$$r_d = k_d(C_{C.S} - \frac{C_C C_V}{K_C'}) \quad (2.19)$$

S is the active site on the catalysts. Equation2.17 for the adsorption of reactants on the catalysts, Equation2.18 is the surface reaction and Equation2.19 is desorption of products from the catalysts. For surface-reaction-limited mechanism, it can be seen that replacing $C_{A.S}$ and $C_{C.S}$ in Equation2.18 by quantities was needed that can be measured.

For surface-reaction-limited mechanisms, the adsorption rate equation 2.17 to obtain $C_{A.S}$ was used, because $r_d/k_A = 0$, then

$$C_{A.S} = K_A C_A C_V \quad (2.20)$$

the desorption rate equation2.19 to obtain $C_{C.S}$ was used, then

$$C_{C.S} = \frac{C_C C_V}{K'_C} \quad (2.21)$$

The total concentration of sites $\bar{C}_m$ is

$$\bar{C}_m = C_V + C_{A.S} + C_{C.S} \quad (2.22)$$

Combining Equation 2.18, and 2.20 to 2.22, then obtained

$$r = \frac{\bar{C}_m k_s K_A (C_B C_A - \frac{C_C C_D}{K_e})}{1 + C_A K_A + C_C / K'_C} \quad (2.23)$$

When the reverse reaction is neglected and letting $K_C = 1/K'_C$ and $k = k_s.\bar{C}_m$, we have

$$r = \frac{k K_A C_A C_B}{1 + K_A C_A + K_C C_C} \quad (2.24)$$

If the adsorption is weak for all components, the denominator of Equation 2.24 approaches unity then the rate equation reduces to homogeneous form.

$$r = k C_A C_B \quad (2.25)$$

In our study, the hydrochlorination reaction involving glycerol and hydrogen chloride, the reaction is homogeneous second order reaction.

2.8.1. Kinetics of chlorination of glycerol

Based on the available literature (Thompson, 1963), the chlorination reaction of glycerol with hydrochloric acid in the presence of carboxylic acid catalyst involves three-step mechanism as follows;

a. a nucleophilic substitution on acrylic carbon that consists of an esterification reaction with the formation of a water molecule;
b. the formation of an oxonium group through alkyl-oxygen bond scission, with the aid of a vicinal group and the carboxylic acid release; and
c. the subsequent formation of chlorohydrin by chlorine addition.

Tesser et al. (2007), proposed mechanism kinetic as shown in Figure 2.11:

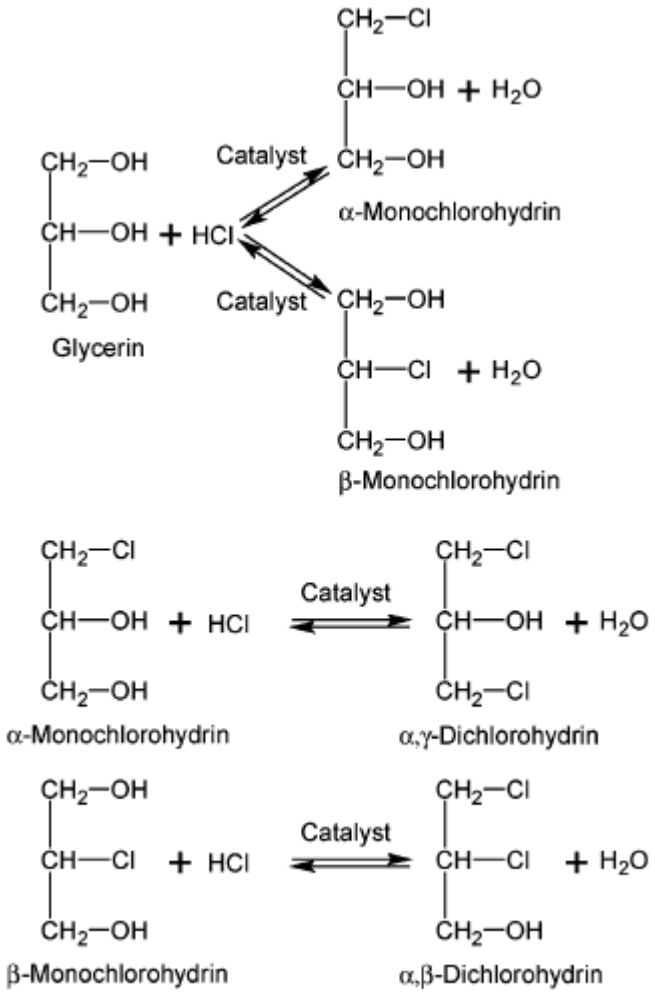


Figure 2.11 Mechanism kinetic of Hydrochlorination (Tesser et al., 2007)

Tesser et al., (2007) illustrated the three-step mechanism as in the following figures, related to glycerol chlorination. The first step is the esterification of glycerol:

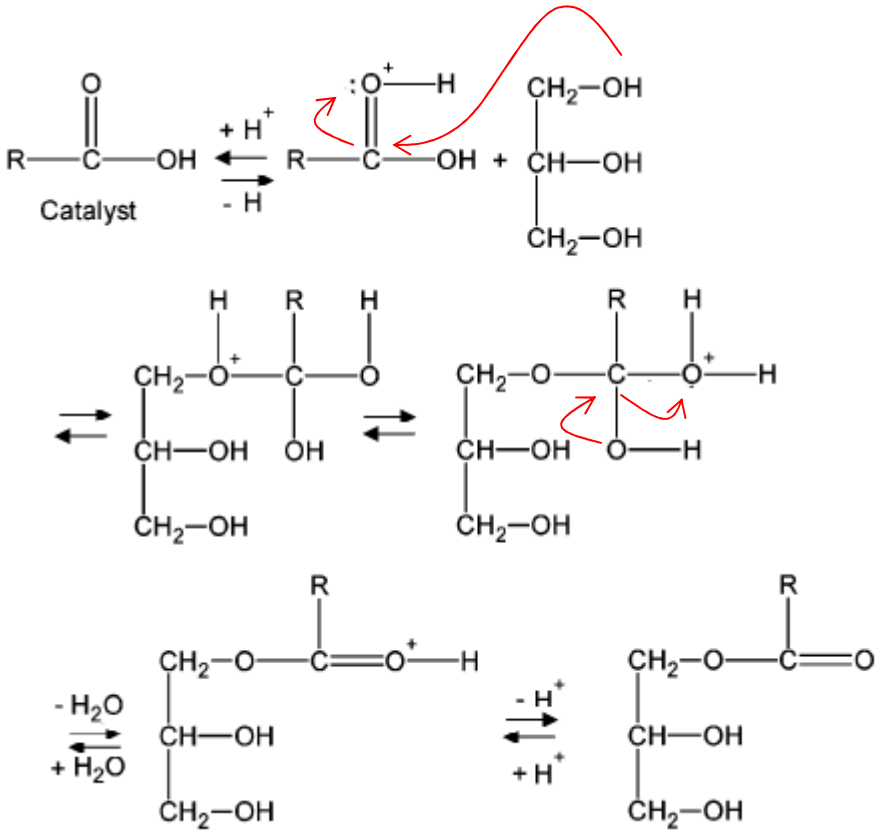


Figure 2.12 Nucleophilic addition reaction (Tesser et al., 2007)

This step is a nucleophilic addition reaction, followed by water elimination, in which glycerol attacks the protonated carbonyl group. This is the classic mechanism, normally accepted for the acid-catalyzed esterification reaction.

The second step of the reaction mechanism heading to the formation of a three-membered ring oxonium group and the catalyst back to its initial form:

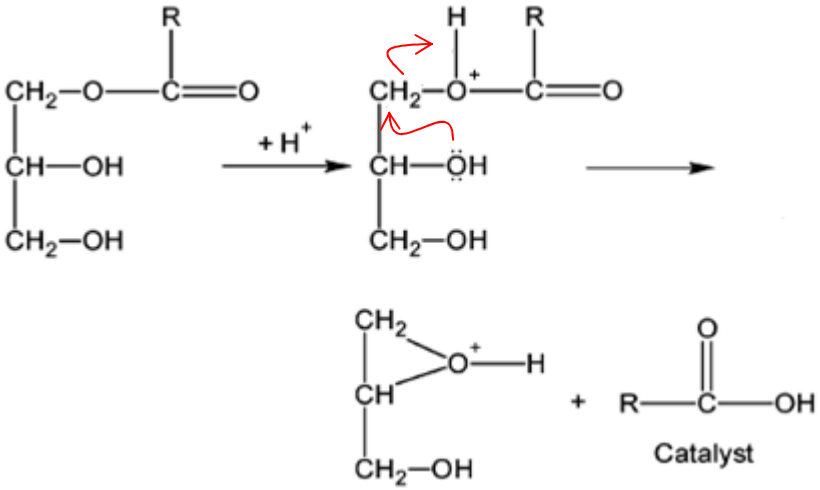


Figure 2.13 Nucleophilic Substitution Reaction (Tesser et al., 2007)

The last step in the reaction sequence is the nucleophilic substitution SN_2 that involves the attack of chlorine anion on the less-substituted carbon atom of the oxonium intermediate (α position):

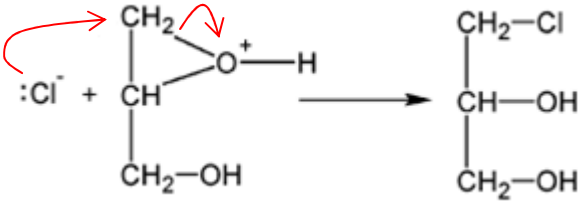


Figure 2.14 α-substitution (Tesser et al., 2007)

Also, the *β*-substitution is possible, even if less probable, giving place in this case to *β*-monochloropropanol according to the following:

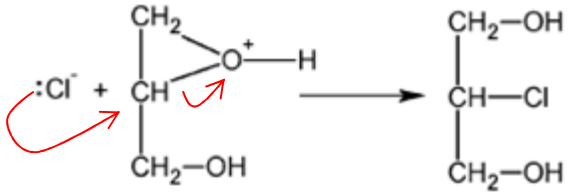


Figure 2.15 β-substitution (Tesser et al., 2007)

Tesser R. et al. (2006), studied the chlorination of glycerol with gaseous hydrochloric acid in the presence of a catalyst, malonic acid. Besides reaction mechanism they also determined both kinetic constants and equilibrium constants at temperature range 80 to 120^{o} C as mentioned above. Based on the experimental results, they strongly agreed with that described reaction mechanism. They found that the amounts of α-monochloropropanol are always higher than those of β-monochloropropanol. Furthermore, the β-monochloropropanol is not able to further react, giving place to the formation of α, β–dichloropropanol. The absence of the vicinal OH group, in this case, prevents the formation of the oxonium ring intermediate and, hence, prevents the second chlorination in the α-position. On the contrary, α-monochloropropanol can undergo a second chlorination with a mechanism similar to the one previously shown.

All these findings can also explain the experimental observation that the concentration of β–monochloropropanol slightly increases during the reaction. This will continue when the glycerol is still present in the reaction medium. At higher reaction times, when glycerol has been almost completely reacted, the concentration of β-monochloropropanol remains nearly constant. On the contrary, α-

monochloropropanol can undergo a second chlorination with a mechanism similar to that expressed by Figure 2.12 to 2.15 that leads to the formation of α,γ- dichloropropanol. On the basis of these considerations, they proposed a reaction scheme as shown in Figure 2.16. Reactions 2 and 4 have been considered irreversible because α-monochlorohydrin accumulates during the reaction and α,γ- dichlorohydrin has been obtained always in small quantity.

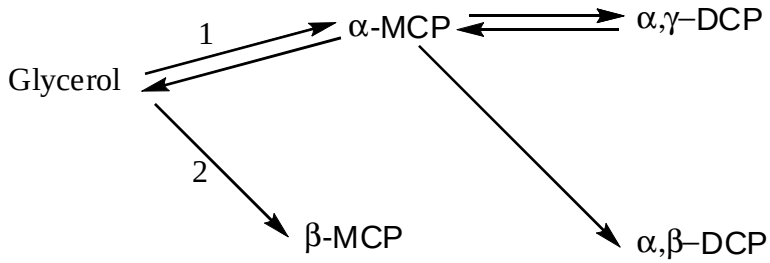


Figure 2.16 (Tesser et al., 2007)

Figure 2.16 furthermore, can be represented by four distinct reactions as follow:

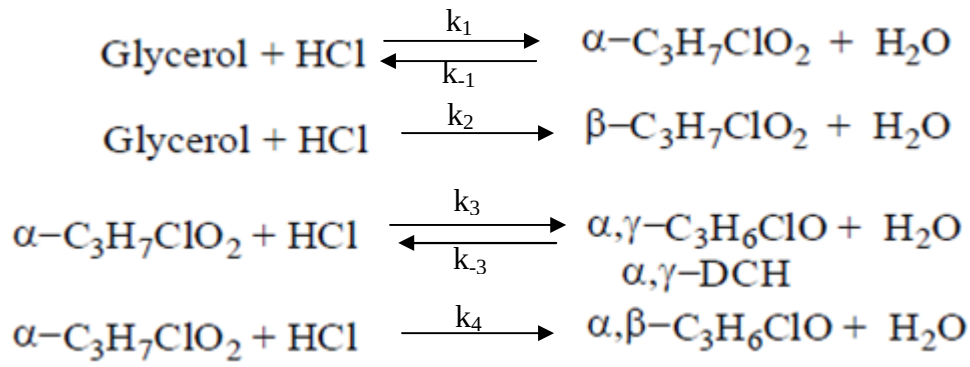


Figure 2.17 Reactions on Hydrochlorinataion Glycerol (Tesser et al., 2007)

The kinetic constant and Arrhenius parameter, and equilibrium constant are reported by Tesser et al. (2007) and are shown in Table 2.6 and 2.7 respectively. While the evolution in time of the composition for the experimental run with malonic acid at 80°C can be seen in Figure 2.18

Table 2.6 Kinetic Constants and Arrhenius Parameters for the Runson Malonic Acid by Tesser et al. (2007)

T (^{o}C)	k_1 [a]	k_2 [a]	k_3 [a]	k_4 [a]
80	7667±940	450±41	714±227	8±3
90	11 704 ±1 272	764 ±60 1	109±307	13 ±5
100	13274±1692	1089±87	1784±407	26±7
110	19 433 ±2 216	465±123	1 2 383 ±532	32 ±9
120	27411±2861	2215±170	2179±685	31±13

	reaction 1	reaction 2	reaction 3	reaction 4
*E*a (kJ mol^{-1})	35.2 ± 0.3	44.3 ±0.2	34.9 ± 0.8	42.1 ±1.0
Ln A	20.9 ± 9	21.3 ±0.7	18.6 ±2.2	16.5 ± 2.8

[a]Kinetic constants are expressed in cm^6/(mol^2 min).

Table 2.7 Equilibrium Constants Evaluated from Standard Gibbs Energy of Formation for the Runs with Malonic Acid by Tesser et al. (2007)

T (°C)	K_{E1}	K_{E3}
80	3846	194
90	3064	167
100	2470	146
110	2015	128
120	1660	113

Based on those kinetics data from Tesser et al., a simulation model using Aspen Plus on hydrochlorination reaction of glycerol with gaseous hydrogen chloride in the

presence of malonic acid as the catalyst (Chapter 3) was developed. Furthermore studied the synthesis of 1,3-dichloropropanol from glycerol with aqueous hydrogen chloride using also malonic acid as the catalyst (Chapter 4) also was done.

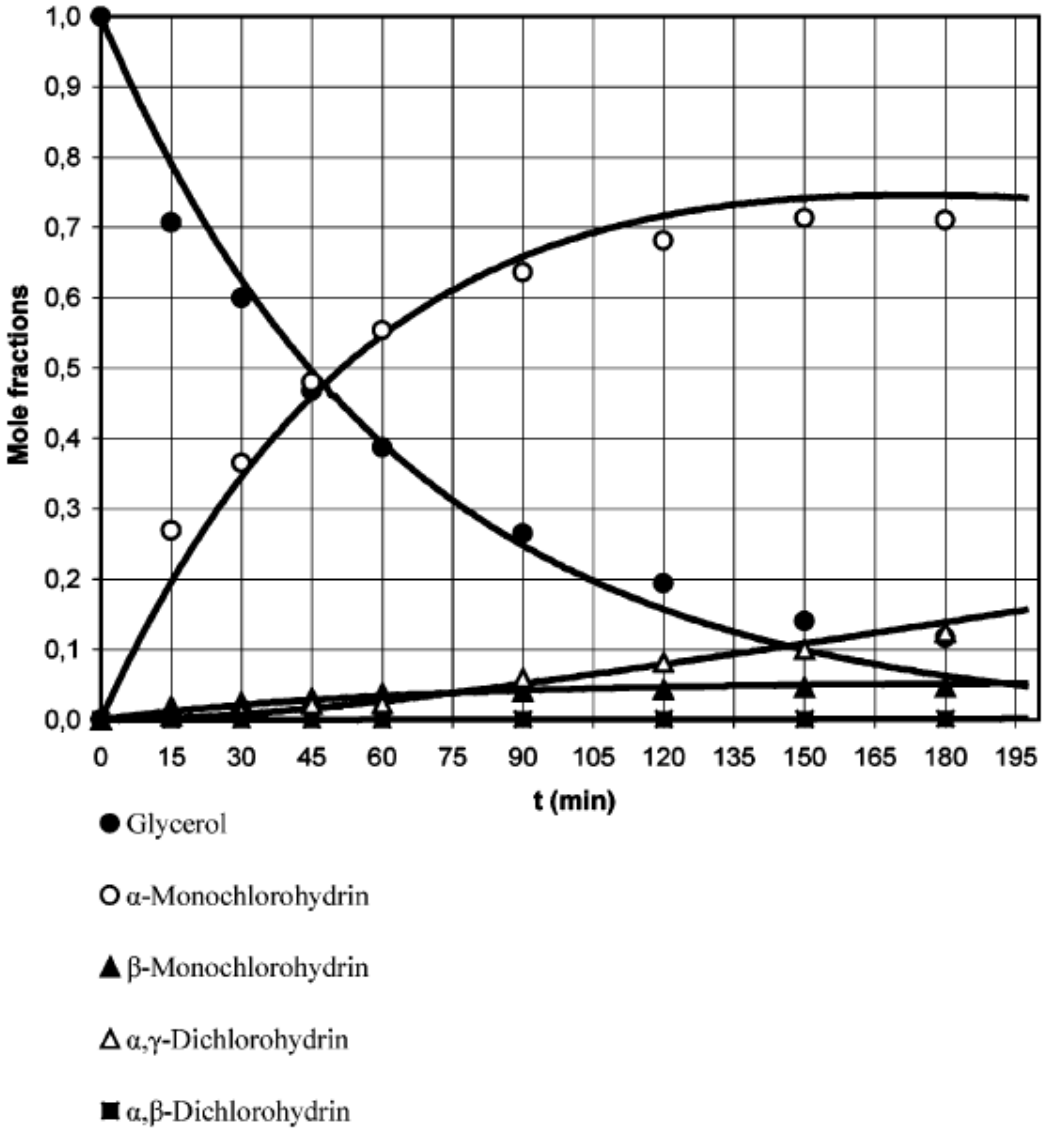


Figure 2.18 Plot of experimental data developed by Tesser et al. (2007)

2.8.2. Kinetics of dehydrochlorination 1,3-dichloropropanol

The dehydrochlorination reaction to produce epichlorohydrin by elimination of hydrogen chloride from dichloropropanol has been reported by Carra et al. (1979), Ma et al. (2007) and Zhang et al. (2012). In this process, described by Zielinski (1964) and Huntress (1948), aqueous NaOH or $Ca(OH)_2$ acts on α,β- or α,γ-dichloropropanol as can be seen in Figure 2.17. Carra et al. described a study of the kinetics of the main reaction involved in epichlorohydrin synthesis with $Ca(OH)_2$ in excess. They offered a kinetic model of the overall system using a potentiometry method and also gas chromatography analysis. The results indicated that the reaction can be modeled as a first order reaction.

They observed that optimum temperature for the highest conversion is at 65^{o}C as can be seen at Figure 2.19, while their kinetics parameter results are tabulated at Table 2.8.

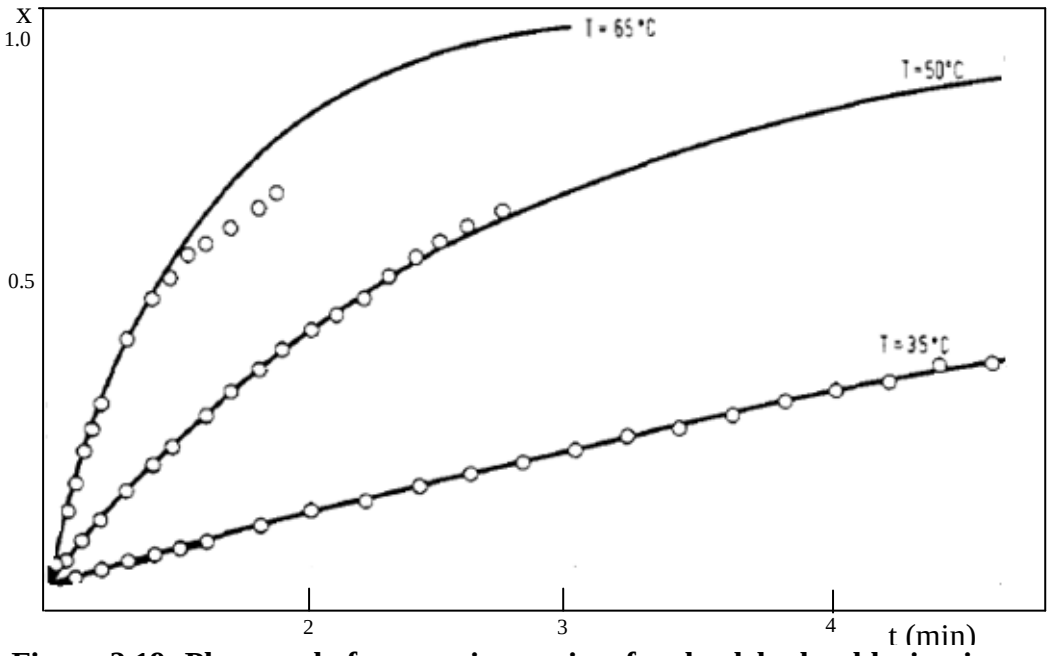


Figure 2.19: Plot trend of conversion vs time for the dehydrochlorination reaction (Carra et al., 1979)

Table 2.8 Kinetic Parameters by Carra et al. (1979)

Reagents	A, s^{-1}	E_a, kJ/mole
1,3-dichloropropanol	10^7	49.21
1,2-dichloropropanol	6,4 x 10^8	71.33

Ma et al. (2007) not only studied the kinetics of dehydrochlorination of dichloropropanol but also studied the hydrolysis of epichlorohydrin in the presence of caustic soda as shown in Equations 2.26 and 2.27. In order to measure the rate of reaction, potentiometric method was used. They reported that both two reactions can be considered as second order reactions.

$$C_3H_6Cl_2O + NaOH \rightarrow C_3H_5ClO + NaCl + H_2O \quad (2.26)$$

$$C_3H_5ClO + NaOH \rightarrow C_3H_8O_3 + NaCl \quad (2.27)$$

In order to eliminate hydrolysis reaction (Equation 2.27), which can lower the yield of product epichlorohydrin, Ma et al. (2007) suggested that the contact time to be shortened and the reactions temperature at below 80^{o}C.

From the dehydrochlorination experimental result, they proposed the rate equation for the dehydrochlorination,

$$r = k[OH^-][DCP] \quad (2.28)$$

Where $k = Ae^{-Ea/RT}$. Substituted into Equation 2.28 then

$$r = Ae^{-Ea/RT}[OH^-][DCP] \quad (2.29)$$

The values for the proposed Equation were determined from the experimental plots to be as follows; A = 1.77 x 10^7; Ea = 172 kJ/mol. The latest kinetics study was done by Zhang et al. (2012), they carried out dehydrochlorination reaction between 1,3-dichloropropanol and sodium hydroxide solution at temperature ranged from 50 to 80^{o}C in a very small volume of reactor (0.002154 ml). Their results indicated that the reaction can be considered as second order reaction where activation energy, Ea, is 36,000 cal/mole and pre-exponential factor, A, is 1.61 x 10^{25}. This study has found that the value of activation energy, Ea, is 38.85 kJ/mol and pre-exponential factor, A, is 1.62 x 10^7/sec. From those results no conclusion could be drawn.

2.8.3. Determination of Rate of Equation from Laboratory Data

The chemical engineer needs a numerical equation for the rate of reaction or reaction kinetics in order to correctly design a commercial-scale reactor. Although the rate equations could be derived from reaction mechanism, it is not essential in cases where the experimental data is available (Smith, 1981). All that is needed is an equation for the rate, which will be accurate over the range of conditions expected in the reactor. The proposed rate equations are verified by comparing them with experimental data. This can be done in three ways namely, integration method, differential method and initial rate methods. The advantageous of each of these methods are discussed in various textbooks on chemical kinetics (Smith, 1981,

Fogler 1992, Levenspiel, 1999). For a single reaction, where rate-controlling mechanism involves the collision or interaction of a single molecule A with a single molecule of B, in reaction A + B → C, then the number of collisions of molecules A with B is proportional to the concentration of reactants in the mixture. Such reactions in which the rate equation corresponds to a stoichiometry and rate are called elementary reactions. On the other hand, when there is no direct correspondence between stoichiometry and rate, then they are called non-elementary reactions.

According to Ma et al. (2007) besides the main reaction, dehydrochlorination of 1,3-dichloropropanol with caustic soda solution to produce epichlorohydrin, epichlorohydrin will also be converted to glycerol via hydrolysis reaction. This reverse reaction can potentially occur but can be avoided by shortening the contact time and using appropriate temperature during the reaction. Furthermore, in this work, for dehydrochlorination step, since the reaction is simple (Figure 2.17) then it can be used simple technique as described by Levenspiel (1999) in which the reaction is considered as a single elementary reaction.

For the dehydrochlorination of 1,3-dichloropropanol to form epichlorohydrin (Figure 2.17), a kinetic rate equation be proposed as given below:

$$-r_{DCP} = -\frac{d[DCP]}{dt} = k[DCP][OH^-] \qquad (2.30)$$

In this work, excess $[OH^-]$ was applied in order to neglect effect of $[OH^-]$on the rate of reaction then the kinetic rate equation is reduced to:

$$-\frac{d[DCP]}{dt} = k[DCP] \quad (2.31)$$

The integral form of Equation 2.30 is given below,

$$\ln\left(\frac{[DCP]_o}{[DCP]}\right) = kt \quad (2.32)$$

In terms of conversion where $[DCP] = [DCP]_o(1\text{-}X_{DCP})$ and $d[DCP]/[DCP]_o = dX_{DCP}$, the rate equation, Equation 2.31 becomes

$$-\frac{dX_{DCP}}{dt} = k(1 - X_{DCP}) \quad (2.33)$$

The integral form of Equation 2.33 is given below,

$$-\ln(1 - X_{DCP}) = kt \quad (2.34)$$

A plot of $\ln\left(\frac{[DCP]_o}{[DCP]}\right)$ or $-\ln(1 - X_{DCP})$ versus time (t) will generate a straight-line plot having a slope of k. The value of k could be obtained from the slope and substituted back in to Equation 2.32 or 2.34 for curve fitting with experimental data.

CHAPTER 3

SIMULATION FOR THE SYNTHESIS OF EPICHLOROHYDRIN USING ASPEN PLUS™

3.1. Introduction

According to Mario (Mario, 2011), process simulation provides good insights to process development activities and enables us to predict the characteristics of such process. Process parameters such as flow rates of the input and output stream, compositions of the product, temperatures, pressures, and sizing of the equipment for all unit operations can be predicted using analysis techniques. According to Fogler (Fogler, Nihat, & Gurmen, 2002), these techniques could be empirical correlations, mathematical models, and numerical solutions assisted by numerous commercially available computer-aided process simulation tools such as PRO/II™, ChemCad™ and ASPEN Plus™. However, empirical analysis technique requires a series of experimental work, where much effort and cost is needed to evaluate and validate the performance of the whole process. While, in process simulation we only require process inputs and flow-sheet which will be used by the simulation to determine process outputs as shown in Figure 3.1. The advantages of using process simulation tool are listed as follows (Mario, 2011):

- It allows the designer to test the performance of process and provide feedback quickly to the process simulation activities;
- The simulation process activity can be coordinated to develop optimum operating condition of such process;

- It minimizes experimental and scale-up efforts which allow evaluation of process in wider range of temperatures and pressures which might not be possible by experiments;
- It capable of explores the process by answering "what-if" questions more flexible and sensitive;
- It also can models the process quantitatively and give quick response on the performance of the process thoroughly.

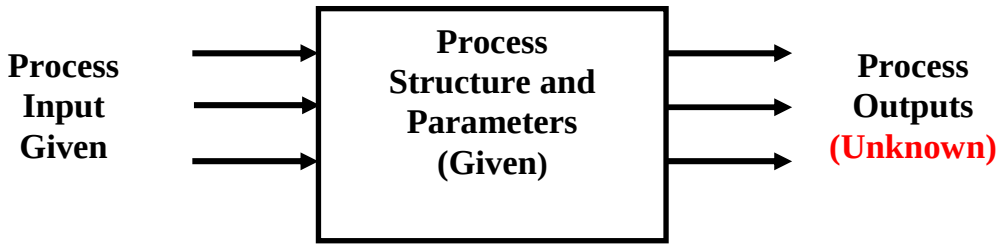


Figure 3.1: Process Simulation Problems (Mario, 2011)

Our study focused on process simulations using ASPEN Plus™, a process simulation tool, which uses the fundamental of physical relationships such as thermodynamic equilibrium, material and energy balances, and reaction rate equations to make a good prediction to process performance and can also be used to develop kinetics models. ASPEN Plus™ provides a very powerful tool for a Chemical Engineer to perform process simulation in various chemical processing fields including oil and gas production, refining, and other chemical processing industries.

In this work, we studied the simulation of epichlorohydrin synthesis which has two-step processes namely the hydrochlorination process for converting glycerol to

dichloropropanol and followed by dehydrochlorination process for converting dichloropronol to epichlorohydrin (Krafft, Gilbeau, Balthasart, & Paganin, 2007; Kubicek, 2005; Ma, Zhu, Yuan, & Yue, 2007; Siano et al., 2006; Tesser, Santacesaria, Di Serio, Di Nuzzi, & Fiandra, 2007). These simulation works enabled us to investigate effects of several parameter affect on said two step process in much less of effort compared to experimental work. Information required for the simulation such as: chemical reactions and kinetics parameter data were obtained from a secondary source namely from Tesser et al. (2007), for hydrochlorination process, and from Carra et al. (1979), for the dehydrochlorination process.

3.2. ASPEN Plus^{TM} for Process Simulation

ASPEN, an acronym for Advanced System for Process Engineering, is strongly suitable for the simulation of steady-state processes. It is also very strong for the simulation of continuous processes systems such as processes involving recycle streams, non-ideal phase, adiabatic operation systems and kinetic on complex reactions that are take too much time to analyze manually by hand calculations. For design of process and optimization, which has what if-type of question, this simulator has been proven ideally suited to give good solution. Matthew et al. (2004) have commercialized this software in 1980's. As a publicly traded company, APENTech has more than 1800 employers over the world and offers an integrated solution to chemical process industries thoroughly (Mario, 2011).

Moreover, in order to design stage including cost and profitability analysis, which are aspects of process engineering, ASPEN Plus also can be used (Fogler, 2002). The robustness of this software that it has a huge data bank integrated with built-in model for many of unit operation such as distillation columns, separators, heat exchangers, reactors, and so on. Moreover, for a specific purpose, a habitual practice or sophisticated models in custom can be determined by its model data bank. These derived models may be created either using subroutines of Fortran language or Excel worksheets then put them into Aspen model library. Additionally, Aspen also has an integrated property databank for thermodynamic properties and physical parameters. During the calculation of the whole streams of the process flow sheet, Aspen able to estimate missing parameters automatically by various group contribution methods.

3.2.1. How to Use ASPEN Plus™

Based on the guidelines described by Mario (2011), the following is guide how to start Aspen Plus version 10.2, **ASPEN Plus™** can be started by clicking on the Windows Start menu, selecting Programs then choosing ASPEN Tech, and then clicking on ASPEN Engineering Suite, then selecting ASPEN Plus (depending on the version that we have), and then ASPEN Plus™ user interface will open. Then the option of opening an existing file or creating a new file will be appeared; in case this for the first time user, we should choose a blank simulation as depicted in Figure 3.2.

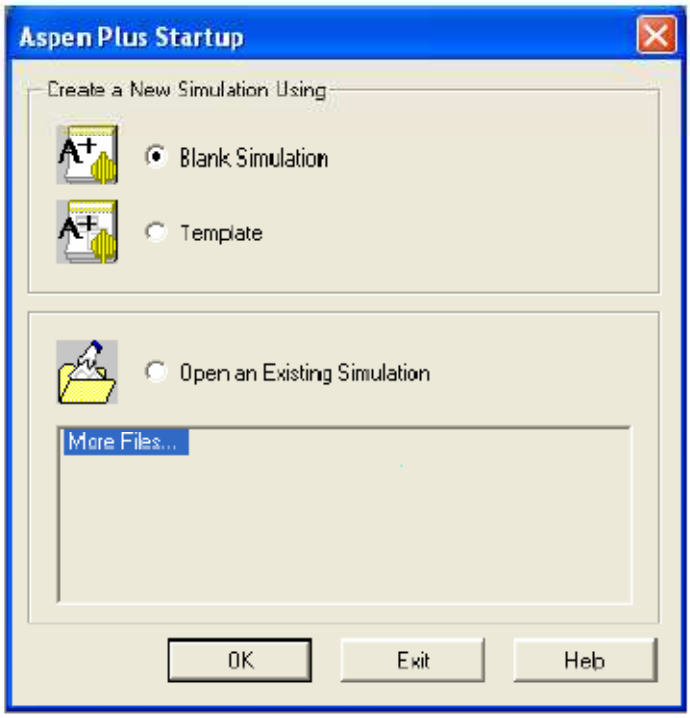


Figure 3.2: Graphical User Interface (GUI) of ASPEN Plus™ version 10.2 (Mario, 2011)

Afterwards, ASPEN Plus™ will display the User Interface as shown in Figure 3.3. Mario (2011) described some characteristics of the User Interface as the following:

• Menus: to state in detail program options and all commands, these tabs are used

• Toolbar: commonly-used functions can be accessed directly by this tab

• Data Browser: folders, forms, and sheets are navigated by data browser.

• Folders: Data browser has many root items called folder.

• Forms: folders contain some forms which are used to input data and to show the results of simulations.

• Sheets: are also inside the folders and are selected using tabs at the top of each sheet.

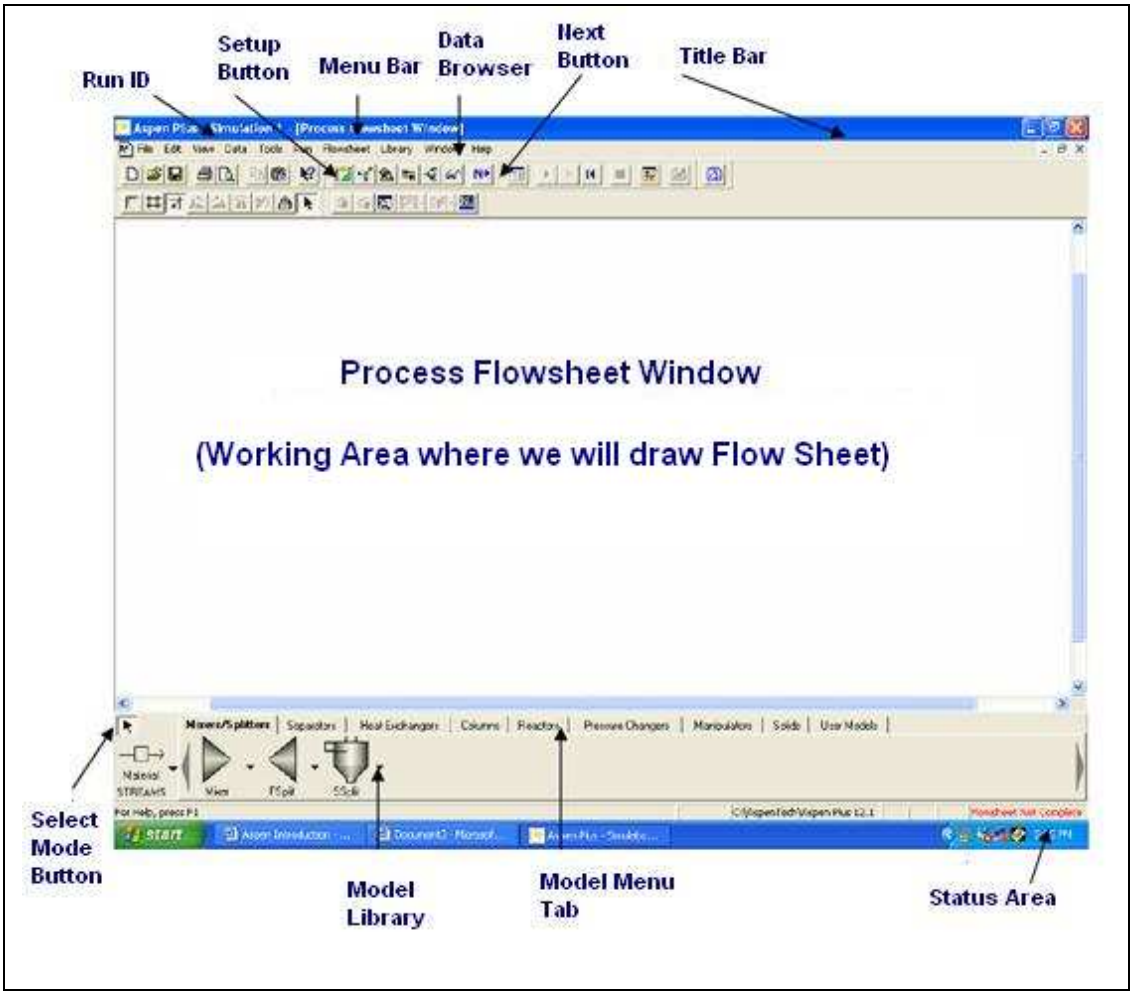


Figure 3.3: User Interface of ASPEN Plus™ version 10.2 (Mario, 2011)

Furthermore, before run the drawing flow-sheet, all required data are needed for the five main folders as below:

1. *Setup*: information on the simulation, like title and description of the project this folder can be specified by using this folder.
2. *Components*: this folder to describe all chemical components involved in the process. When the certain component is not available in Aspen data bank, user can define by drawing the molecule structure of the component which can be linked to specific software like Chemdraw.

3. *Properties*: we can choose a base method, thermodynamic models, to determine all properties involve the process such as pressure vapor of the component using this tab. For selecting a proper thermodynamic model, a search tree developed by Mario (2011) can be followed as depicted in Figure 3.4
4. *Stream*: to input all stream data such as flow rate, composition and operating condition, we can use this folder.
5. *Blocks*: this folder provides data on the process equipment. Reactor for example, here we must setting-up the configuration, phase of reaction, and write all reactions involve. Then we must also input the value of kinetic parameter like reaction rate constant, k, reaction order, and activation energy.

Once those described five folder have been completed by all required data, we are then ready to run the simulation and a simulation report will be provided. One of the useful features in ASPEN Plus™ is that a report containing all information regarding a simulation is provided within a text editor. Since information such as mole composition of components within a stream, which is favorable, is not procured by default ASPEN instead of stream flow-rates, temperatures, and various other data then, we need to make by custom our own report properties within ASPEN. Therefore, we will have all desired information generated directly from ASPEN which is more efficient compared to calculation by a secondary program such as Excel. For this purpose, we can click on *Data Browser* which has the following functions, Mario (2011)"

- To display forms and sheets and manipulate objects,

- To view multiple forms and sheets without returning to the Data menu, for example, when checking (state the object of checking),
- To input the properties of process parameters,
- To edit the sheets that define the input for the flow-sheet simulation,
- To check the status and contents of a simulation run,
- To evaluate what results are available (Mario, 2011)".

For more detail information about how to use ASPEN Plus™, like kinetic tutorial, is easily accessible in many sources.

3.2.2 Selection of Base Method Thermodynamic Models

Several property methods are available in ASPEN Plus™. They are a group of formula used to develop all physical properties which have a specific formula to calculate a given property, for examples density, vapor pressure and enthalpy. Hence, it is necessary for us to select an appropriate method.

According to Mario (2011), thermodynamic property calculations performed by ASPEN Plus is related to phase equilibrium. The basic theory of phase equilibrium of a system is when the fugacity in the liquid phase is the same as fugacity in the vapor phase (Walas, 1985; Van Ness, 2005). They explained that the direction of a component in a liquid mixture to release, or vaporize, is measured by term fugacity. In fact, the composition of the vapor in the mixture, above the liquid, has more possibility to liberate from the liquid phase. Equation 3.1 shows the relationship between the fugacity of a pure component f_i^o and the fugacity coefficients (ϕ_i^o):

$$f_i^o = \phi_i^o P \quad (3.1)$$

Where, the fugacity is equal to the pressure in the ideal gas due to $\phi_i^o = 1$. Furthermore, Equation 3.2 and 3.3 show relationship between fugacity of component i in the mixture:

$$f_i^v = y_i f_{i,v}^o \text{ for the vapor and,} \quad (3.2)$$

$$f_i^L = x_i f_{i,L}^o \text{ for the liquid} \quad (3.3)$$

(where x and y are mole fractions in the liquid and vapor phases, respectively).

By rearrange Equations 3.1, 3.2 and 3.3 then we can have relationship between fugacity and mol fraction in vapor and liquid phase as $f_i^v = \phi_{i,v} y_i P$ and $f_i^L = \phi_{i,L} x_i P$. Where, at equilibrium state both fugacities should be equal (Walas, 1985; Van Ness, 1995).

Regarding a process which has two-phase state, fugacities is very important to be determined (Walas, 1985; Van Ness, 1995). Fortunately, ASPEN Plus™, can derive those property by Equations of state (EOS) methods, and activity coefficient models methods (Mario, 2011). Cubic and virial equation of state are some of the common equation of state in Aspen. An example of another type of state is Steam Tables. In many literature describes that the simplest EOS is the ideal gas law (PV = nRT), where P is operating pressure (absolute), V is total volume of the molecule gas in the system, n = total mass of the molecule gas, T is operating temperature and R = ideal

gas constant. In ideal gas law there are no interactions between molecular due to molecules is assumed have no size. Coefficient of activity, $a_i = \frac{f_i}{f_i^o}$, the ratio of the fugacity of a component in the mixture to its fugacity in some standard state, represents the deviation of the mixture from ideality (as defined by the ideal solution). If the value of a_i is higher than unity then the mixture is meaning more non-ideal (Walas, 1985; Van Ness, 1995). Generally, when the mixture has the activity coefficient greater than unity then the fugacity will higher than ideal. As mentioned earlier, since the fugacity is a measurement of tendency molecules to vaporize then they increase their average distance in an ideal solution. Hence, repulsion between unlike molecules occurs when activity coefficients greater than unity. The separation between liquid-liquid happens when the repulsion among the molecules is strong. This is another mechanism that decreases close contact between unlike molecules. It is less common than that earlier mentioned.

Table 3.1: EOS and Activity Coefficient Models in comparison (Mario et al., 2011)

EOS Models	Activity Coefficient Models
Have limitation to represent non-ideal liquids	Highly strong for non-ideal liquids
Consistent in critical region	Suitable in medium region
Able to represent both the vapor and liquid phases	Able to represent the liquid phase only. Therefore, the gas phase must still be described by an EOS model
Parameters extrapolate well with temperature	Binary parameters are stronly dependent on temperature

Examples of EOS models, provide by ASPEN Plus™, to determine properties for example: Sanchez-Lacombe (for polymers), Peng Robinson, Redlich-Kwong-Soave, and, Redlich-Kwong while activity coefficient models include: UNIFAC, UNIQUAC, , Electrolyte NRTL , Van Laar, Scatchard Hildebrand, Flory Huggins, NRTL, and Wilson. Mario et al. (2011) have described some of the guidelines to select one of model. The two said models are compared in Table 3.1 above.

Furthermore, the following search tree can help us when there is no information which model suitable for selected system as depicted in Figure 3.4.

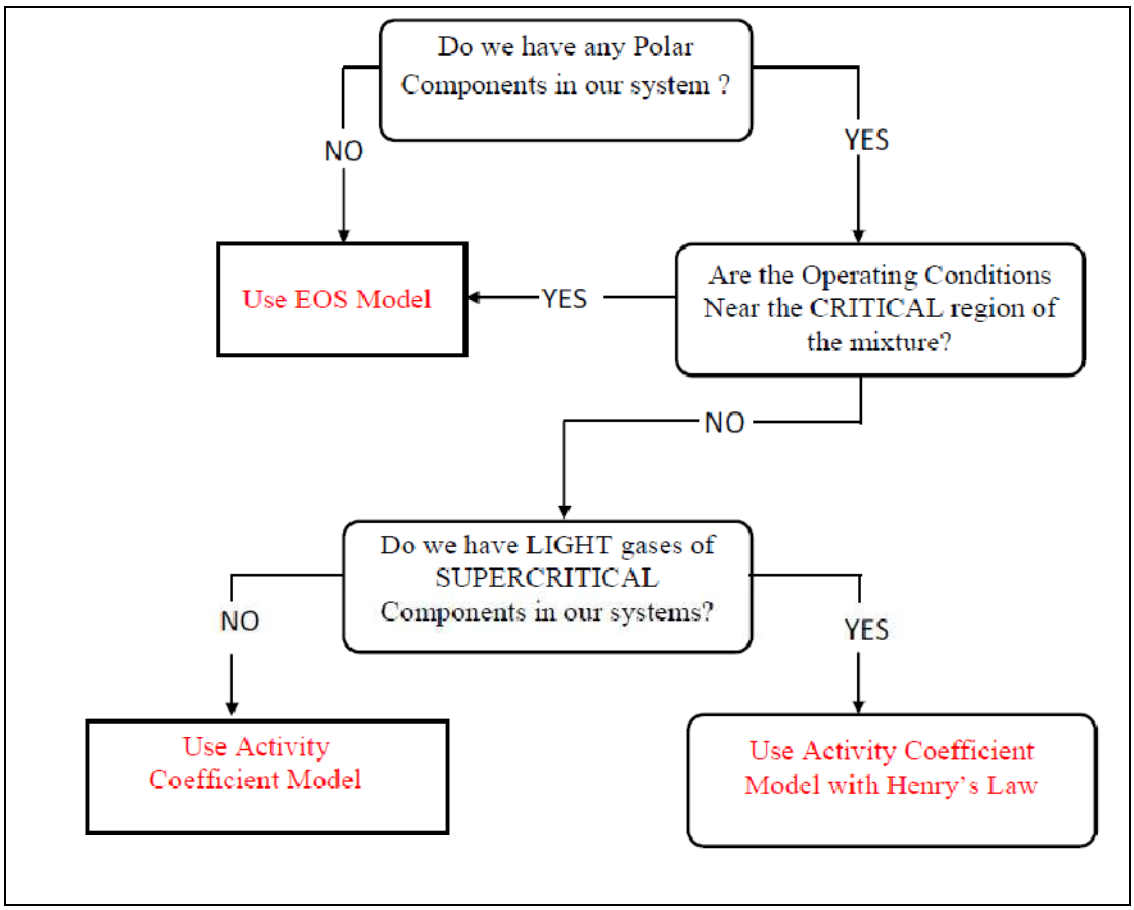


Figure 3.4: Search Tree for the selecting of Thermodynamic Model (Mario et al., 2011)

Based on a briefly description how to use Aspen Plus, an instructional tutorial, , developed by Matthew (2010); Mario (2011), we derived a process flow chart of simulation activities for this work as illustrated in Figure 3.5 while process flow sheet is illustrated in Figure 3.6 below

3.3. Process Simulation of Synthesis of Epichlorohydrin

As discussed in Chapter 2, the synthesis of epichlorohydrin was conducted via two steps process. The first step was hydrochlorination process in which glycerol reacted with hydrochloric acid to dichloropropanol and the second step was a reaction between dichloropropanol and base solution (sodium hydroxide) to produce epichlorohydrin. The simulation of both steps process will be examined in the following sections:

3.3.1 Process Simulation of Hydrochlorination Reaction

As can be seen in Figure 2.18, the hydrochlorination reaction between glycerol and hydrochloric acid involved four distinct, reversible and irreversible, parallel reactions (Tesser et al., 2007). As a intermediate product of the whole process is 1-monochloropropanol, which comprises α-monochloropropanol and very small amount of β-monochloropropanol, then progressively only α-monochloropropanol will convert to final product, 1,3-dichloropropanol and its isomer 1,2-dichloropropanol. Tesser et al. (2007) had conducted kinetics study on

hydrochlorination reaction. The experimental was performed in the presence of carboxylic acid as the catalyst at the temperature range 80-120^{o}C.

The gaseous hydrogen chloride was used as chlorination agent fed continuously with fixed flow rate 24 g/min, glycerol as a reactant was loaded at 200 g, and catalyst concentration were kept constant at 8 percent by mol. Their results in terms of kinetics parameters can be seen in Table 2.6 and 2.7. Based on those result, we run series simulation in order to investigate several parameters affecting the process such as reactant mol ratio of hydrogen chloride to glycerol and the concentration of catalyst. According to Kastanek et al. (1995) the mentioned parameters have marked effects on the reaction selectivity to the hydrochlorination reaction but the extent of the effect has not been reported. In order to validate our simulation, we also analyzed effect of temperature on the process which had been done by Tesser et al. (2007) then our simulation result will be compared to their experimental data.

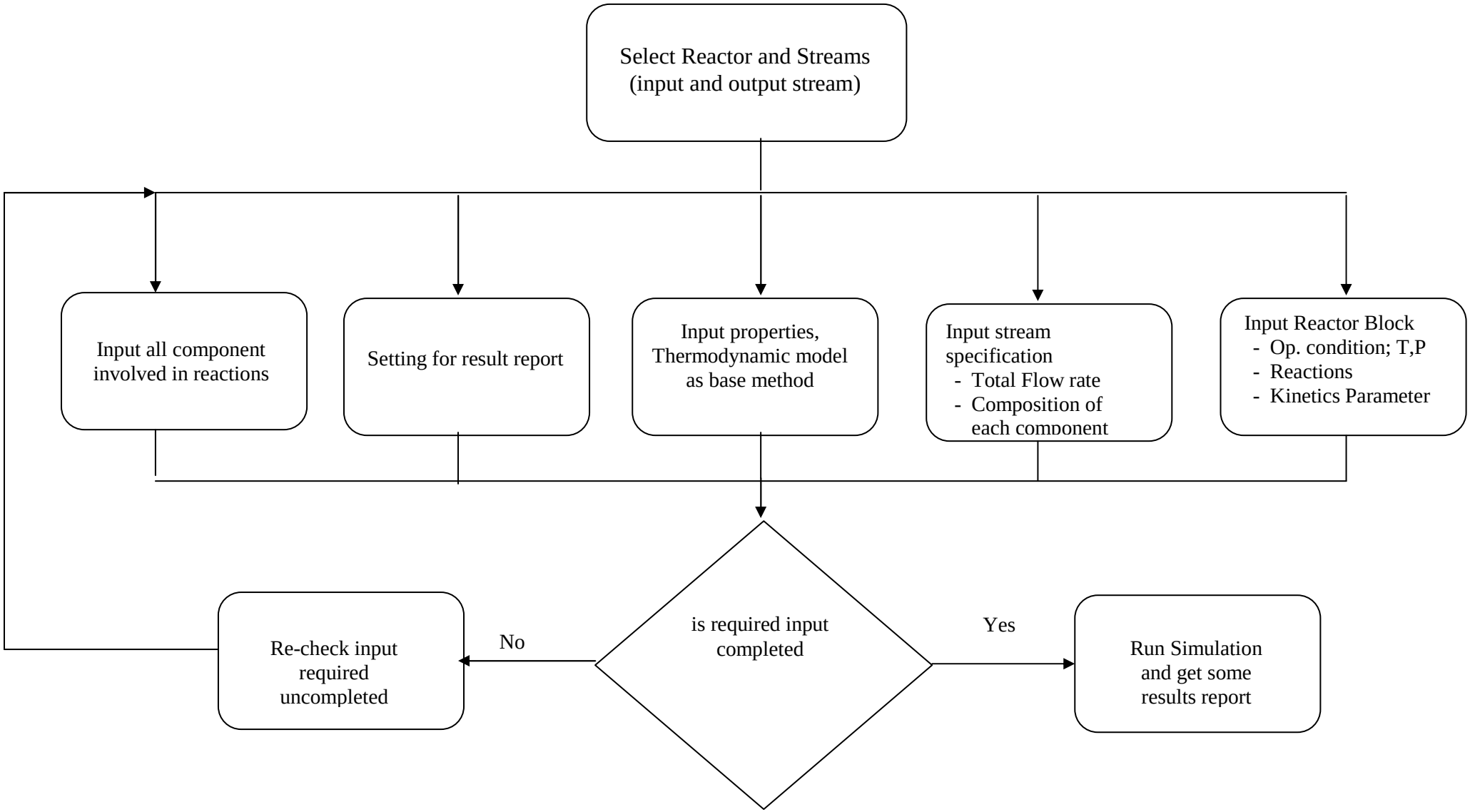


Figure 3.5: Process flow chart of simulation activity

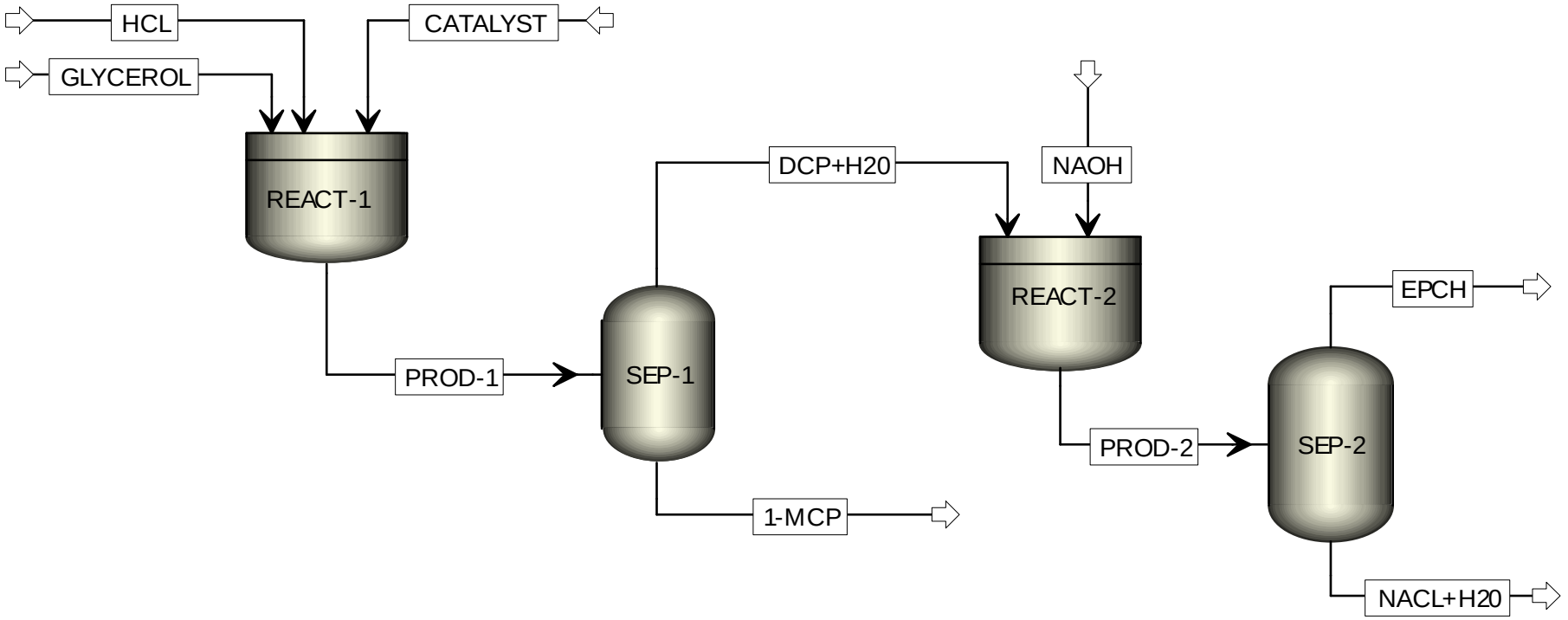


Figure 3.6 Process Flow Diagram for Synthesis of Epichlorohydrin from Glycerol

This simulation study mainly generated a product distribution curve for the hydrochlorination process. The simulated products distribution was then verified against the experimental result obtained by Tesser et al. (2007). Consequently, the ASPEN Plus^{TM} was used to simulate the reaction carried out in a semi-batch stirred tank reactor, by considering the effects of operating temperature, flow rate of chlorinating agent and catalyst concentration on reaction selectivity and yield for 1,3-dichloropropanol. The reactor block utilized in the simulation was RBatch which is suitable for a semi-batch reactor process (Matthew et al., 2004). The results obtained from the simulation study were used to test the performance quickly of the synthesis as a whole. The process simulation activity can minimize experimental efforts and explore the flexibility of process. Finally, the data obtained by simulation can also be used to models the process quantitatively and to predict the process performance strongly.

3.3.1.1 Modeling Approach for Hydrochlorination Process

Tesser et al. (2007) have reported that the overall reaction involve for preparing 1,3-dichloropropanol, starting from glycerol and gaseous hydrochloric acid, as shown in Figure 2.18 and Equation 2.7 (Chapter 2). This reaction started from chlorination of glycerol, which at first 1 hour mostly formed α-monochlorohydrin, a little quantity of β-monochlorohydrin eventually present, and water. According to the reaction mechanism as depicted in Figure 2,17, then a second chlorination of only α-monochlorohydrin will occur from which the desired product, 1,3-dichloropropanol was mostly obtained with a trace amounts of 1,2-dichloropropanol. Based on the

mechanism, therefore Tesser et al. (2007) broken down Equation 2.7 into four different reactions as shown in Figure 2.18. The kinetic parameters were reaction rate constant, k, equilibrium constant, K and activation energy, Ea, and the values for each reaction were tabulated in Tables 2.7 and 2.8. All these value were required in set-up design of simulation.

Table 3.2 shows the reactor characteristics, feed materials, and kinetic parameters used in the ASPEN Plus^{TM} simulation. In this work, parameters such as operating temperature, flow rate of hydrogen chloride and catalyst concentration based on moles of glycerol loaded into the reactor were varied as presented in Table 3.2. The simulation analyzed the effects of the parameters mentioned above on the selectivity and yield of reaction. The following equations were used for selectivity and yield calculations (Felder, 2004):

$$\text{selectivity for } 1,3-\text{D}CP = \frac{\text{moles of } 1,3-DCP \text{ produced}}{\text{moles of glycerol reacted}} \tag{3.4}$$

$$\text{Yield for } 1,3-\text{D}CP = \frac{\text{moles of } \alpha,\gamma-\text{D}CP \text{ produced}}{\text{moles of glycerol fed}} \tag{3.5}$$

Table 3.2 Required Parameters used in the Simulation of Hydrochlorination Process

Parameter	Information
Reactor Block	RBatch
Base Method	Wilson
Input Variable	
Temperature (^{o}C)	80. 90, 100, 110, 120
Pressure (bar)	atmospheric
Chemical reactions	Glycerol + HCl → α-$C_3H_7ClO_2$ + H_2O Glycerol + HCl → β-$C_3H_7ClO_2$ + H_2O Glycerol + HCl → α,γ-C_3H_6ClO + H_2O Glycerol + HCl → α,β-C_3H_6ClO + H_2O
Kinetics data	
k_1, k_2, k_3, k_4 (T = 80 ^{o}C)	7667; 450; 714; 8
k_1, k_2, k_3, k_4 (T = 90 ^{o}C)	11704; 764; 109; 13
k_1, k_2, k_3, k_4 (T = 100 ^{o}C)	13274; 1089; 1784; 26
k_1, k_2, k_3, k_4 (T = 110 ^{o}C)	19 433; 465; 12383; 32
k_1, k_2, k_3, k_4 (T = 120 ^{o}C)	27411; 2215; 2179; 31
*E*a (kJ mol^{-1})	35.2; 44.3; 34.9; 42.1
Ln A	20.9; 21.3; 18.6; 16.5
Feed of Reactor	
HCL flow rate (g/min)	4, 8, 12, 16, 20, 24
Concentration of malonic acid catalyst (mol %)	2,4,6,8,10

3.3.1.2 Hydrochlorination Simulation and Results Validation

As mentioned earlier, in this simulation section we have examined several parameters which affect the hydrochlorination process. Once the simulation was completed, the simulator generated the report containing product distribution profiles for each of the parameters that we set, such as temperature, reactant molar ratio, and catalyst concentration. The simulated results can be presented in the form of product distribution curve to illustrate the progress of chlorination reaction between glycerol

and gaseous hydrochloric acid at 110^{o}C as depicted in Figure 3.7. The complete simulation data at 80^{o}C to 120^{o}C can be found in Appendix B1.

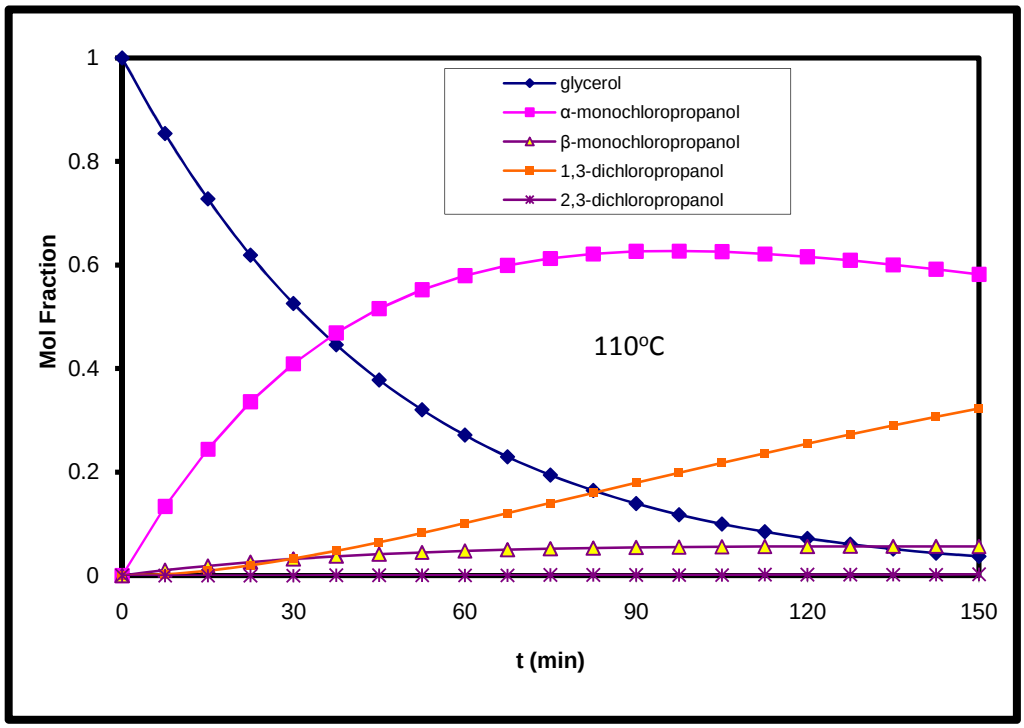


Figure 3.7 Plot of Simulated curves, products composition versus time. Glycerol loaded: 200g; HCL flow rate: 24g/min; Catalyst concentration: 8%; temperature: 110^{o}C.

Figure 3.8 shows that the simulated curves compare well with the experimental observation by Tesser et al. (2007). We can see here also that the amount of α-monochloropropanol is always higher than to those of *β*-monochloropropanol which confirmed the mechanism proposed by Tesser et al. (2007). Furthermore, after 15 minutes of reaction, α-monochlorohydrin had undergone a second chlorination as indicated by the formation of the desired product, 1,3-dichloropropanol. Regarding *β*-monochlorohydrin, even though it increased slightly during the reaction, however, at longer reaction times, when glycerol was almost completely reacted, the concentration of *β*-monochlorohydrin remained nearly constant.

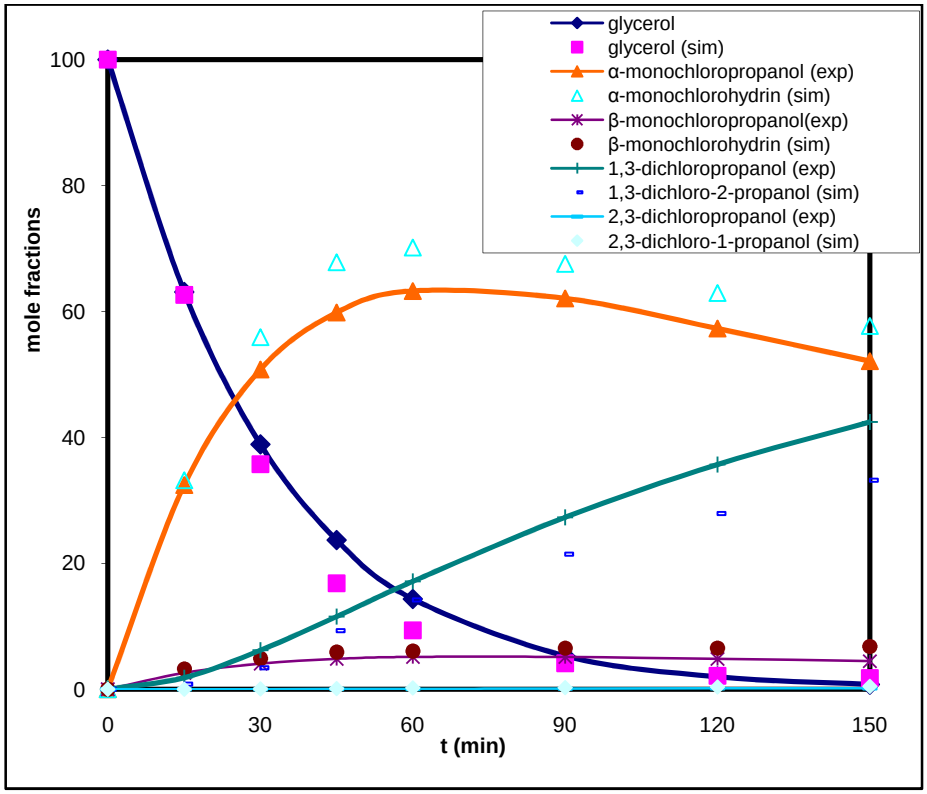


Figure 3.8: Plot of products composition versus time. Comparison between simulation and experimental data by Tesser et al. (2007). Glycerol loaded: 200g; HCL flow rate: 24g/min; Catalyst concentration: 8%; reaction temperature: 110^{o}C.

The effects of temperature on glycerol conversion and reaction selectivity are presented in Figure 3.9 and 3.10. These results also compared well with experimental data. Thus, it can be concluded that the simulation using ASPEN Plus can indeed be used in our study to guide us in the experimental analysis of the hydrochlorination reaction.

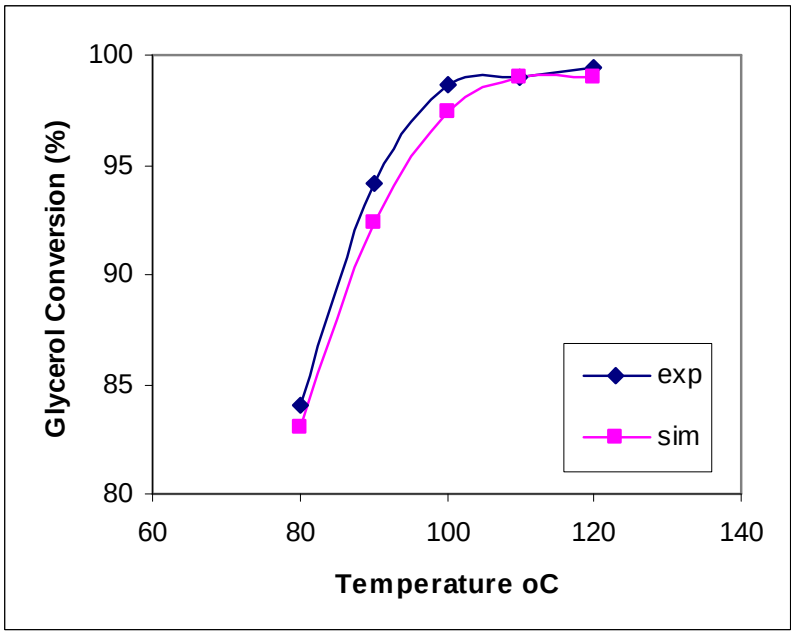


Figure 3.9: The effect of temperature on glycerol conversion. Glycerol loading: 200g; HCl flow rate: 24 g/min; Catalyst concentration: 8%; time: 2.5 h.

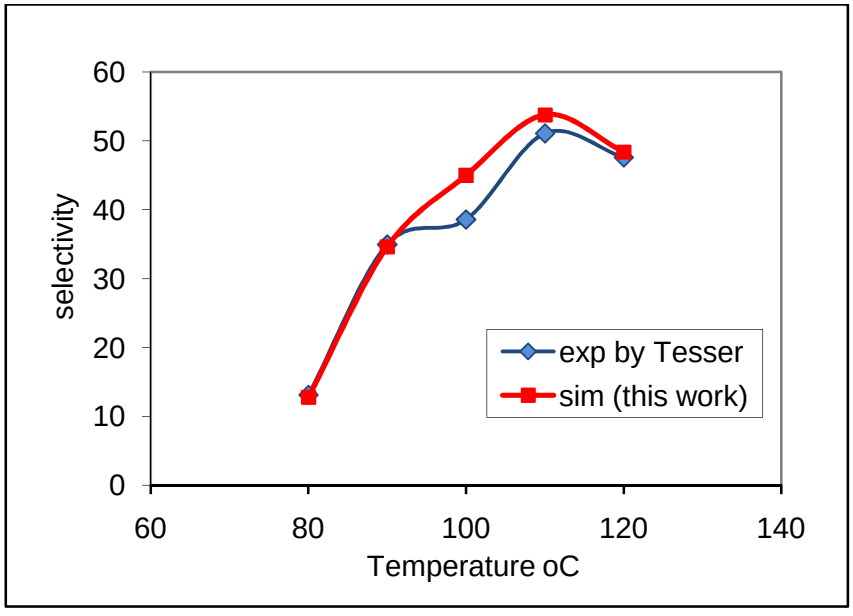


Figure 3.10: The effect of temperature on reaction selectivity. Glycerol loading: 200g; HCl flow rate: 24 g/min; Catalyst concentration: 8%; time: 2.5 h.

In addition, several simulation runs had also been carried out in order to investigate the effects of HCl flow rate and catalyst concentration on the characteristics of

process for 1,3-dichloropropanol preparation which were not observed by Tesser et al. Can be seen here that the selectivity and yield of 1,3-dichloropropanol decreased with the hydrogen chloride flow rate ranged from 4 to 24 g/min as shown in Figure 3.11. It is in a good agreement compared qualitatively to data from the literature. Rose (1981) reported that the gas feed rate to the stirred tank should not exceed the flood point of the impeller in order to avoid the spinning of agitator in a bubble of the gas that have influenced on the reaction. On the contrary, catalyst concentration did not have significant effect on the selectivity and yield for 1,3-dichloropropanol preparation as depicted in Figure 3.12.

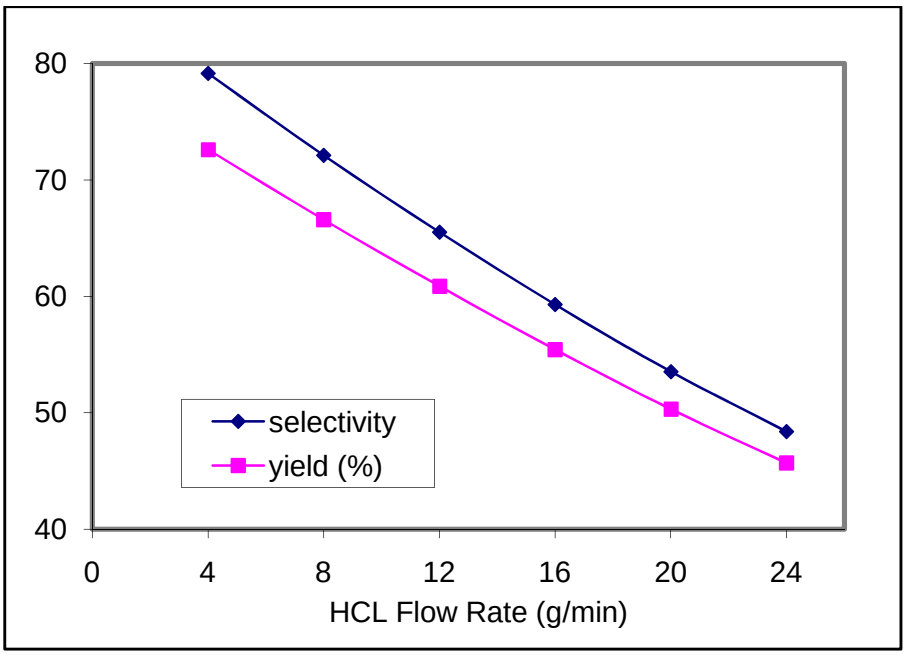


Figure 3.11: The effect of HCl flow rate on selectivity and yield predicted by the simulation. Glycerol loaded: 200g; Catalyst concentration: 8%; temperature: 110^{o}C; reaction time: 2.5 h.

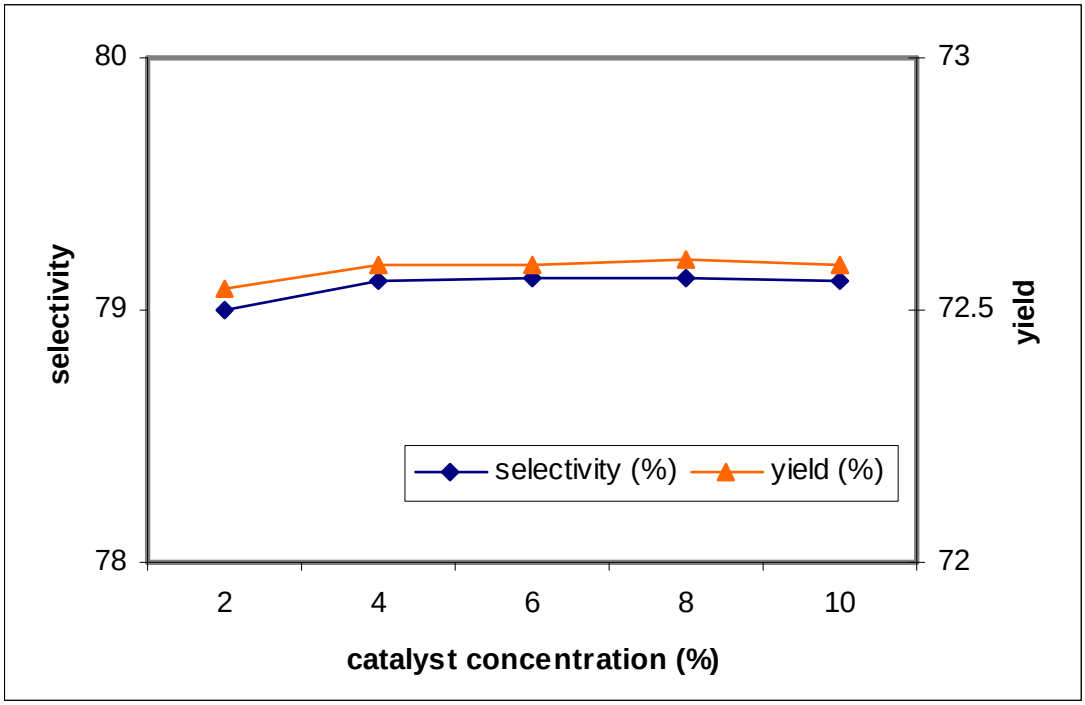


Figure 3.12: The effect of catalyst concentration on selectivity and yield predicted by the simulation. Glycerol loaded: 200g; HCL flow rate: 4 g/min; reaction temperature: 110^{o}C; reaction time: 2.5 h

3.3.2 Simulation of Dehydrochlorination Process

Carra et al. (1979) had conducted dehydrochlorination process where dichloropropanol reacts with aqueous base solution containing an excess of $Ca(OH)_2$ to produce epichlorohydrin. Their work focused on the determination of kinetic parameters such as activation energy (E_a) and pre-exponential factor (A). The reaction was performed at temperature range 295 to 333 K without the presence of catalyst inside a batch stirred tank reactor. In this study, this study used their kinetics parameters to examine process parameters affecting the reaction such as reactant mol ratio of dichloropropanol to base solution and temperature. According to Carra et al.

(1979) the mentioned parameters affects the reaction conversion and the yield of product during the dehydrochlorination reaction but the extent of the effect has not been published.

This simulation study focused mainly on the products distribution profiles during the course of reaction process. In order to validate the simulation results, the data were then compared with the experimental results obtained by Carra et al. (1979). The selected model for the reaction carried out in a batch stirred tank reactor, considered the effects of both percent excess of base solution, and reaction temperature on the reaction conversion and product yield of epichlorohydrin. The reactor block utilized in the simulation was RBatch which is suitable for a batch reactor process (Matthew et al., 2004)

3.3.2.1 Modeling Approach for Dehydrochlorination Process

Preparation of epichlorohydrin, starting from 1,3-dichloropropanol and base solution, is shown in Figure 2.10 (Chapter 2). When the reaction takes place at temperatures above 85^{o}C, a competing reaction, where the product epichlorohydrin is converted to mono-chloropropanol and glycerol, will eventually occur as shown in Figure 2.11 (Chapter 2) (Carra et al., 1979; Ma et al., 2007). The kinetic parameters that are the values of pre-exponential factor, A and activation energy, Ea are tabulated in Table 3.3 as below:

Table 3.3 Kinetic Parameters by Carra et al. (1979)

Reagents	A, s^{-1}	E_a, kJ/mole
1,3-dichloropropanol	10^7	49.21
1,2-dichloropropanol	$6{,}4 \times 10^8$	71.33

The reactor characteristics and feed materials as required input in the ASPEN Plus™ simulation is shown in Table 3.4. In this simulation, both parameters, reaction temperature and reactant mol ratio, were varied as presented in Table 3.4.

Table 3.4: Required Parameters used in the Simulation of dehydrochlorination Process

Parameter	**Information**
Reactor Block	RBatch
Base Method	Wilson
Input Variable	
Temperature (^oC)	20 to 60
Pressure (bar)	1.05
Chemical reactions	Figure 2.10
Kinetics data	
A, s^{-1}	10^7
E_a, kJ/mole	49.21
Feed of Reactor	
Reactan mol ratio (DCP to NaOH))	1:1; 1:1.5; 1:2.3; 1:4; 1: 9

The simulation analyzed the effects of the above mentioned parameters on the conversion of dichloropropanol and the yield of epichlorohydrin. The conversion and yield are calculated by using Equation 3.6 and 3.7 as the following (Felder, 2004):

$$\text{Conversion of } DCP = \frac{\text{moles of } DCP \text{ original} - \text{moles of DCP at certain time}}{\text{moles of DCP original}} \quad (3.6)$$

$$\text{Yield of } Epichlorohydrin = \frac{\text{moles of } Epichlorohydrin \text{ produced}}{\text{moles of DCP original}} \quad (3.7)$$

3.3.2.2 Dehydrochlorination Simulation Results and Validation

As explained above, in this simulation study, we investigated the effects of several parameters on the dehydrochlorination process. The simulator provides an exhaustive report, as long as all required inputs have been completed, consisting of inlet parameters, such as temperature and reactant molar ratio. As a result, we can generate the simulated distribution curves for both reaction conversion and product yield during the dehydchlorination reaction. The reaction was between dichloropropanol and sodium hydroxide solution at various temperatures, 20^{o}C (293 K) to 60^{o}C (333 K), as depicted in Figure 3.13, 3.14, 3.15 and 3.16 respectively. The complete simulation data for each temperature can be found in Appendix B2.

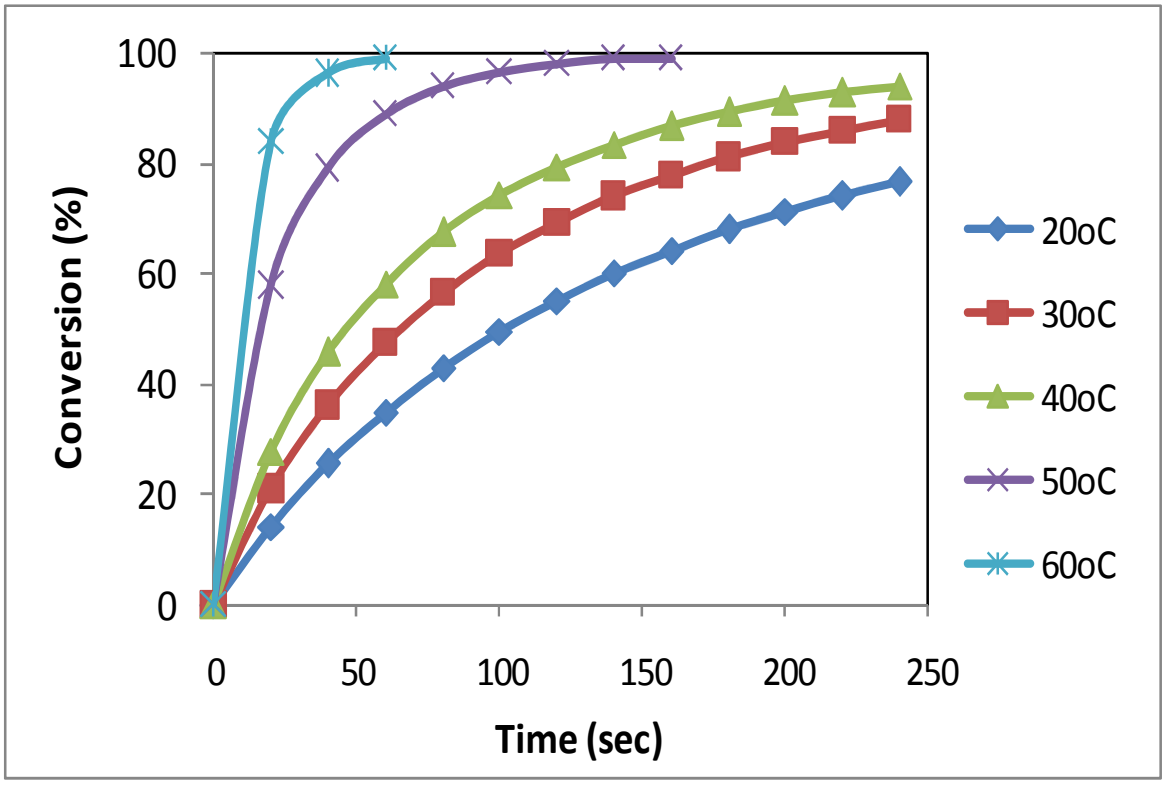


Figure 3.13: Plot of simulated data, conversion of DCP versus time for dehydrochlorination reaction at various temperatures; at reactant molar ratio: 1:1 for 4 minutes

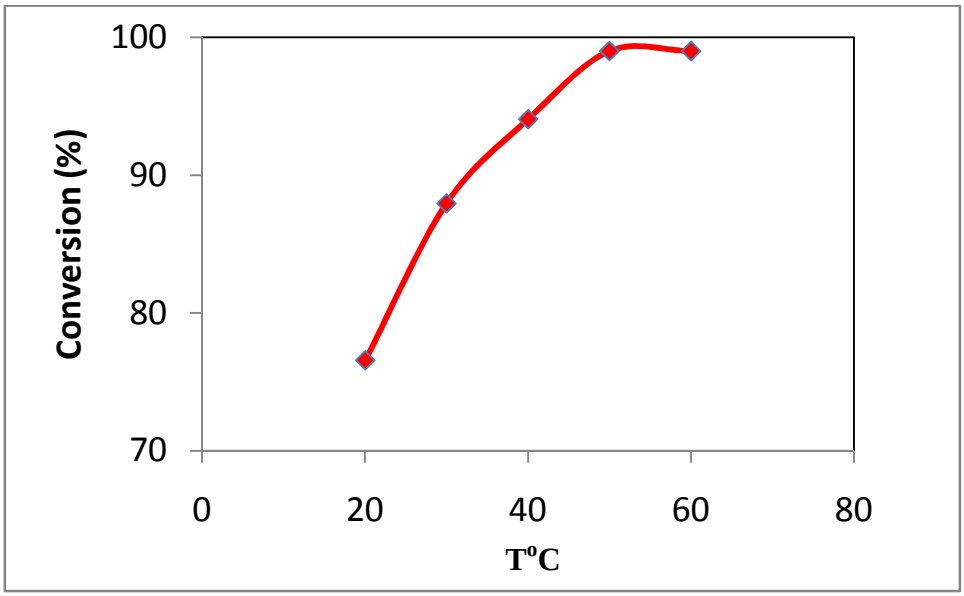


Figure 3.14: Plot of simulated data, conversion versus temperatures; at molar ratio: 1:1.

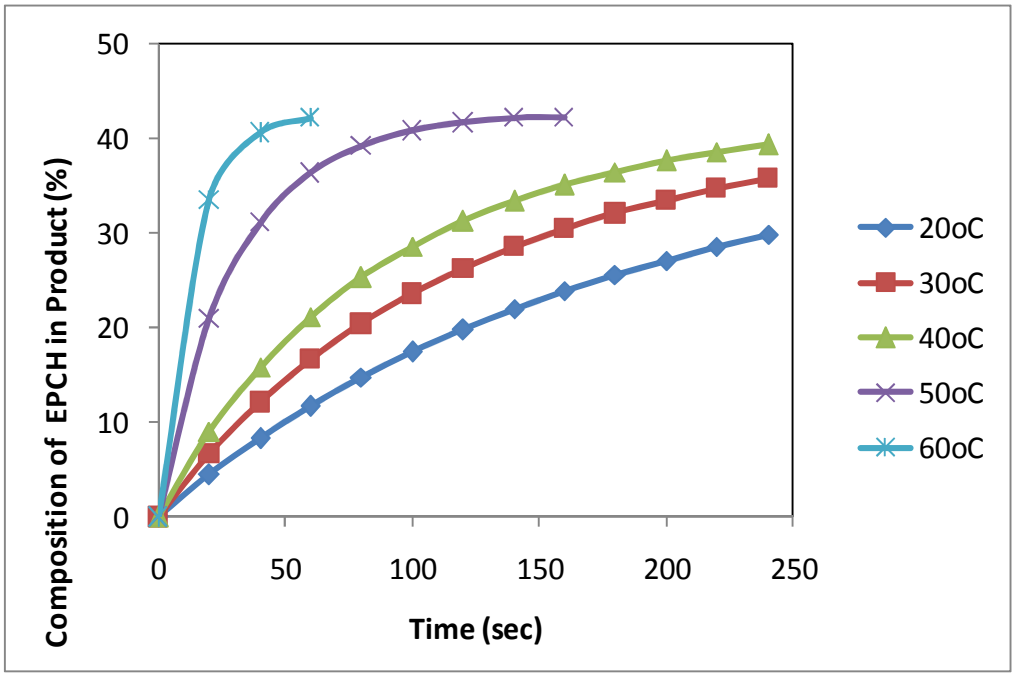


Figure 3.15: Plot of simulated data of composition EPCH versus time for dehydrochlorination reaction at various temperatures; molar ratio: 1:1 for 4 minutes.

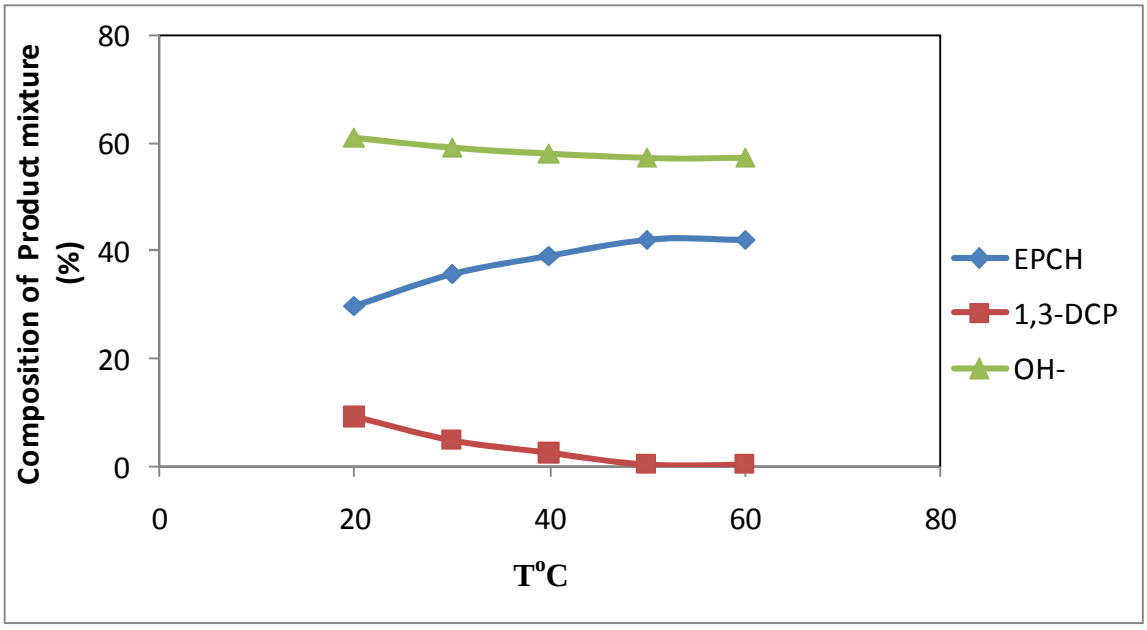


Figure 3.16: Plot of simulated data of composition in product mixture vs temperatures; at molar ratio: 1:1 for 4 minutes.

In order to validate the simulation results they were then compared to the experimental data, found by Carra et al. (1979), in terms of reaction conversion, as depicted in Figure 2.9 (Chapter 2). These two figures illustrate that the simulation results from ASPEN Plus compare well with the experimental data. Figure 3.14 also shows simulation result for yield of epichlorohydrin in product mixture at various reaction times while Figure 3.15 shows effect of different temperature on the product compositions. It can be seen that the reaction is influenced significantly by the operating temperature. Carra et al. (1979), Ma et al. (2008) suggested that the reaction temperature should be lower than 70^{o}C (343 K). This is to prevent a side hydrolysis reaction which can lower the yield of epichlorohydrin.

According to Carra et al. (1979), reactant molar ratio between dichloropropanol and base solution affects the dehydrochlorination process. However, their experimental study did not include this effect on the yield of epichlorohydrin. In order to investigate the effect of the said parameter on the conversion and composition of epichlorohydrin in the product mixture, we also conducted several simulations as depicted in Figure 3.16, 3.17, 3.18 and 3.19.

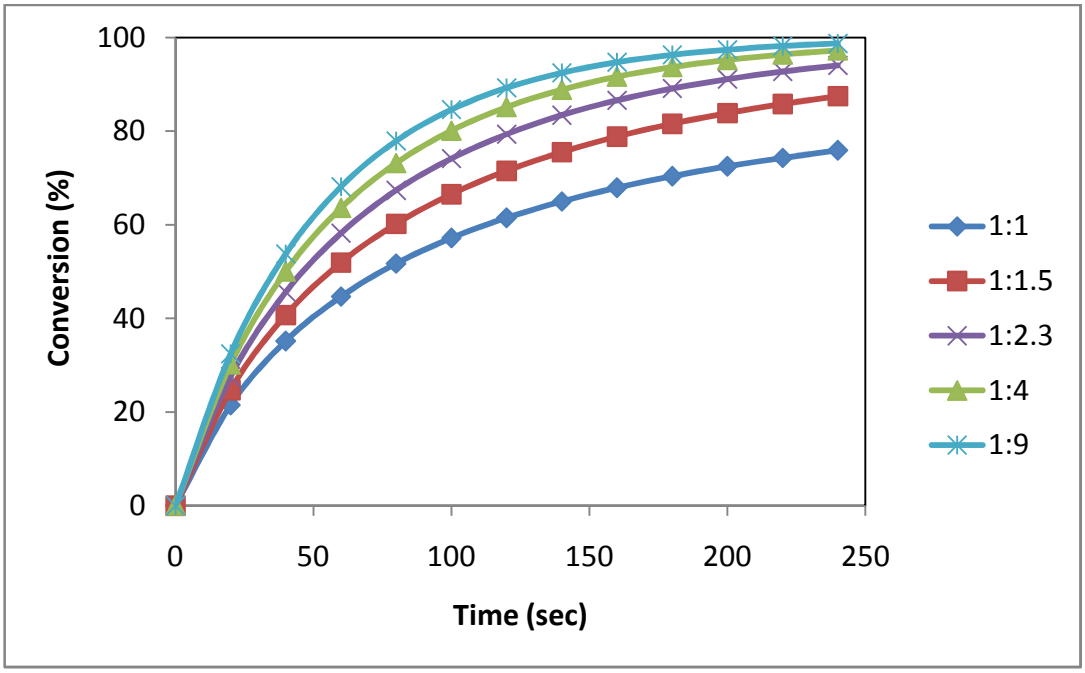


Figure 3.17: Plot trend of conversion vs time for the dehydrochlorination reaction at various reactant molar ratio; at 60^{o}C (333 K)

Figures 3.17 and 3.18 show that the conversion is significantly influenced by increasing molar ratio until ratio of 1:6 after which the conversions remain constant. The use of high amount of NaOH (high ratio) will lead to the decrease in the product yield due to the hydrolysis of epichlorohydrin in the presence of excess water as depicted in Figure 3.19 and 3.20. This side reaction had resulted in the formation of monochloropropanol and glycerol as shown in Figure 2.11 and shown in Figure 3.19.

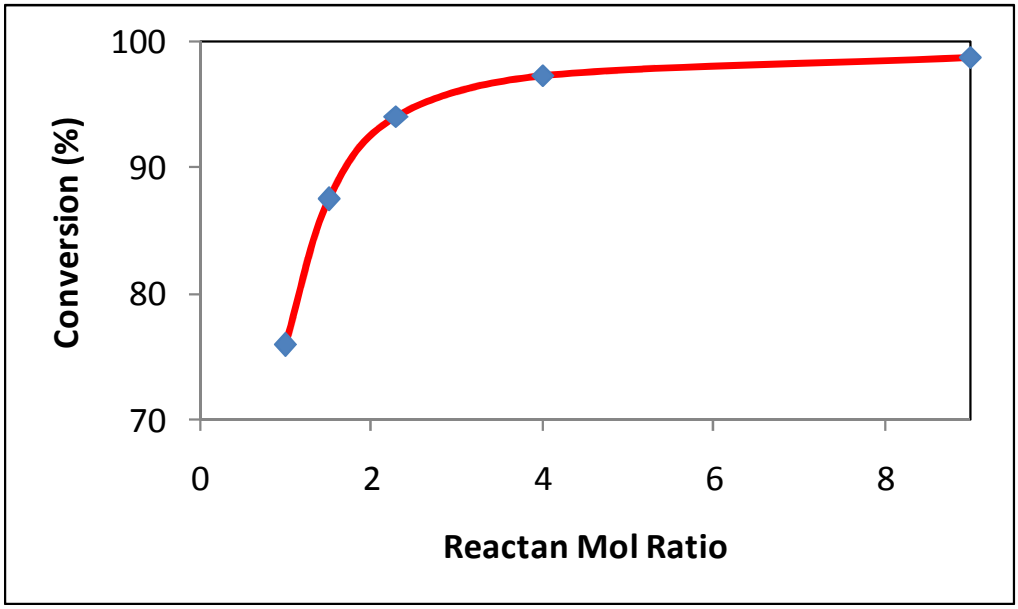


Figure 3.18: Plot effect of mol ratio on conversion of 1,3-DCP at 60°C (333 K)

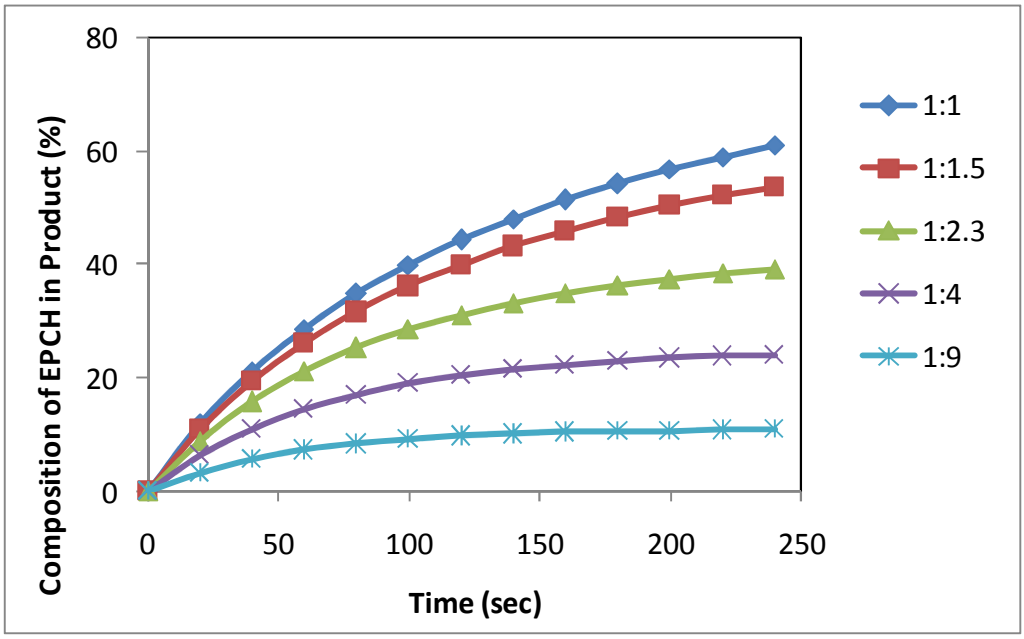


Figure 3.19: Plot trend of composition EPCH in product mixture vs time for dehydrochlorination reaction at various reactant molar ratio, at 60°C (333 K)

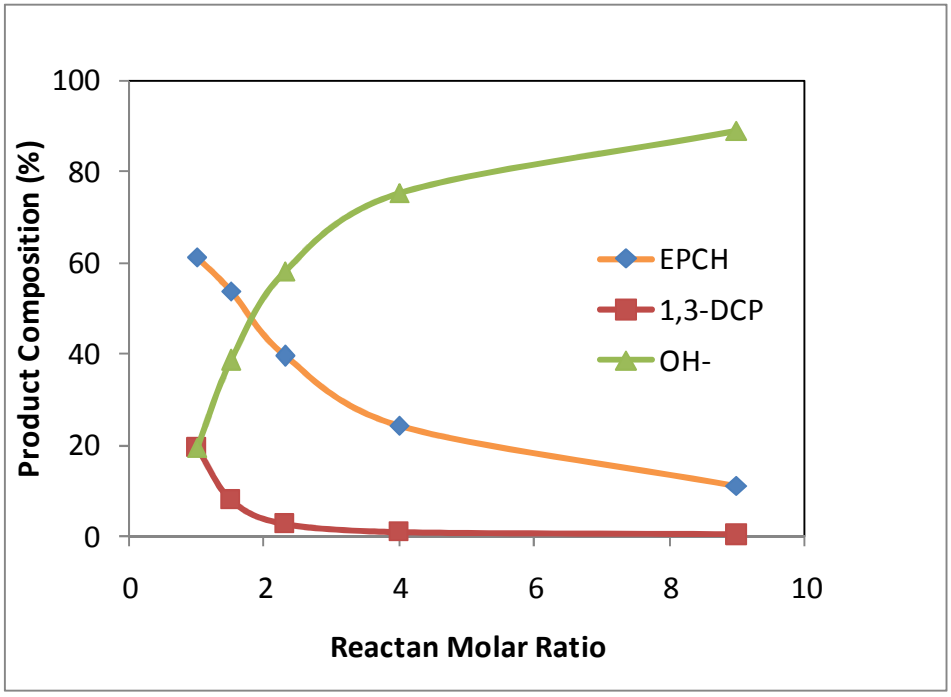


Figure 3.20: Plot effect of molar ratio on composition of product mixture at 60^{o}C (333 K) for 4 minutes

3.4. Conclusions

In this chapter, simulation studies using the ASPEN Plus^{TM} simulation software were conducted on both reactions involved in the two-steps process to produce epichlorohydrin namely synthesis of glycerol to 1,3-dichloropropanol, and synthesis of 1,3-dichloropropanol to form epichlorohydrin. The results from simulation studies shed insights of the performances of these reactions in terms of conversion, selectivity and yield. The synthesis of 1,3-dichloropropanol occurred through hydrochlorination process, in a semi batch stirred tank reactor (SBSTR) , while the synthesis of epichlorohydrin took place via dehydrochlorination reaction,

in a batch stirred tank reactor (BSTR). The results from the simulation were used to predict the performance of SBSTR and BSTR in terms of conversion, selectivity and yield. For the hydrochlorination process, the optimum temperature and molar ratio glycerol:HCl were found at 110^{o}C and 1:16 respectively. Moreover, the investigation on the effect of catalyst (HCL) revealed that catalyst concentration had shown marginal effect on product yield. On the contrary, lower HCl flow rate improved the hydrochlorination process on both the selectivity and yield of 1,3-dichloropropanol. For the dehydrochlorination process, effect of reactant molar ratio showed that excessive use of base solution can lower the yield of product significantly due to the competing hydrolysis reaction. The optimum temperature and molar ratio 1,3-DCP:NaOH were found at 60^{o}C (333 K) and 1:6 respectively. The findings from these simulation results will be useful for our subsequent experimental work, in chapter 4, to develop the technology to convert crude glycerol to 1,3-dichloropropanol and in chapter 5, to convert 1,3-DCP to epichlorohydrin..

CHAPTER 4

SYNTHESIS OF 1,3-DICHLOROPROPANOL FROM GLYCEROL AND MURIATIC ACID (HCl 37%)

4.1. Introduction

As mentioned in the previous chapter, the conventional method to prepare dichloropropanol involves two-steps process, the first process is the preparation of allyl chloride by reacting propylene and chlorine at high operating temperature followed by chlorination of allyl chloride to produce dichloropropanol (Nagato, 1987). Then, the second reaction is the formation of epichlorohydrin by adding the base solution to the dichloropropanol as shown in Figure 4.1. However, the said process is not economically viable because the method utilizes propylene, a high cost non-renewable feedstock.

Glycerol, which is the byproduct from the process for making biodiesel, is considered to be a potential low cost renewable feedstock. A process for the conversion of glycerol to a mixture of dichloropropanol compounds, 1,3-dichloropropanol and 1,2-dichloropropanol, is known as hydrochlorination as shown in Figure 4.2 (Kruper et al., 2008). The said reaction can be carried out in the presence of gaseous hydrogen chloride, in large excess, and a carboxylic acid catalyst (Tesser et al., 2007; Krafft et al., 2007; and Kruper et al., 2008). Both compounds 1,3- dichloropropanol and 1,2-dichloropropanol can then be converted to epichlorohydrin by treatment with caustic soda (Kruper et al., 2008). Carboxylic

acid catalysts mentioned earlier may include acetic acid, malonic acid, succinic acid, propionic acid, citric acid, levulinic acid, trichloroacetic acid, loaded in the range of 8 to 10 percent by mole (Tesser et al., 2007; Krafft et al., 2007).

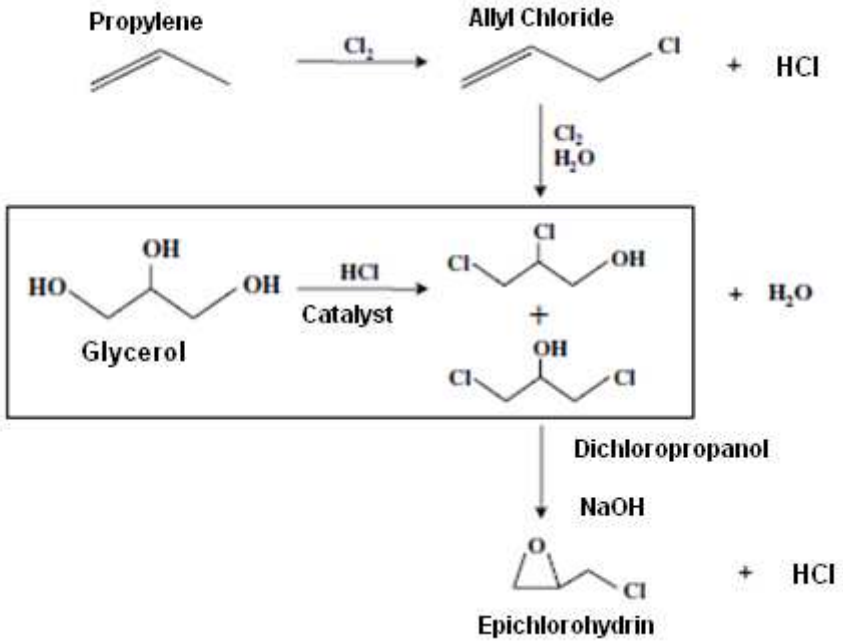


Figure 4.1: Preparation of epichlorohydrin via allyl chloride and via Dichloropropanol (Lee et al., 2008)

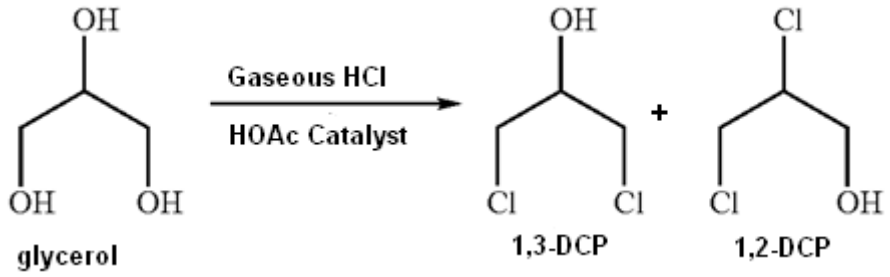


Figure 4.2 Glycerol to Dichloropropanol (Krupper et al., 2008)

The use of large excess amount of anhydrous hydrogen chloride may not be economically viable (Krafft et al., 2007). According to the above process route, for hydrochlorination of glycerol, aqueous hydrogen chloride of 28 to 37 percent by weight can also be used as a chlorinating agent under atmospheric condition. The reaction can be carried out in either batch or continuous mode by vigorously stirring within temperature range of 100 to 120^{o}C. However, other hydrochlorination studies to produce dichloropropanol were not developed around aqueous hydrogen chloride as a chlorination agent.

The main objective of this study is to develop a process for the synthesis of 1,3-dichloropropanol through hydrochlorination glycerol and aqueous hydrogen chloride in the presence of carboxylic acid. The carboxylic acid as the catalyst will be selected among several different carboxylic acid by considering several operating parameters affecting the process. The aqueous hydrogen chloride selected was muriatic acid (hydrogen chloride, 37 % w/wt). Our experimental data will be compared to experimental data reported by Tesser et al. (2007).

To develop the optimum synthesis method, the effects of various operating conditions on the chemical hydrochlorination of glycerol and aqueous hydrogen chloride must be studied. Firstly, our experimental work focused on the performances of catalysts containing carboxylic acid groups with a lower volatility with respect to acetic acid, such as propionic acid, malonic acid and lactic acid. After identifying the best catalyst for the synthesis, the experiments were then directed towards investigating the effects of operating parameters such as reactant

mol ratio and temperature of reaction on the reaction yields. These reactions were conducted under atmospheric condition, and temperature range of 80 to 120^{o}C using malonic acid as the catalyst, based on its performances during the screening.

4.2. Materials

Commercially available carboxylic acid catalysts namely acetic acid, propionic acid, lactic acid, and malonic acid, glycerol and muriatic acid were purchased from Merck Chemical Co. While 1,3-dichloropropanol for GC standard calibration was obtained from Sigma Aldrich Co.

Figure 4.3: Experimental setup for hydrochlorination glycerol to 1,3-dichloropropanol

4.3. Experimental Procedures

4.3.1. Synthesis of 1,3-dichloropropanol

The reactions were performed in a 250-ml three-neck flask equipped with a thermometer, a sampling port and a reflux condenser. The set up is shown in Figure 4.3. The condenser was connected to an accumulator. The reactor was immersed in a temperature controlled oil bath and was under constant stirring by the magnetic stirrer. Initially, the reactants comprised of glycerol and aqueous hydrogen chloride solution 37 % w/w (chlorination agent) was loaded into reactor. After the homogeneous solution reached certain temperature (in the range of 80 to 120^{o}C) under vigorous stirring, aqueous hydrogen chloride, chlorination agent, was slowly added to the mixture followed by the catalyst. In this way, the catalyst would be uniformly distributed in the reactor. This would increase the effective surface area provided by the catalyst for the reaction. The reaction in the presence of catalyst was conducted for 3 h. For analysis of reaction products, gas chromatography method was used throughout the experiments.

The screening of the best catalyst was conducted at a molar ratio of glycerol and muriatic acid of 1:16 and 8 percent catalyst by mole. Four types of carboxylic acid, namely propionic acid, malonic acid, lactic acid, and acetic acid, were investigated at 90^{o}C with respect to the acetic acid low volatility (117^{o}C). According to simulation result (Chapter 3), the amount of the catalyst recommended for the reaction was 8 % mole/mole which was calculated based on the molar amount of glycerol supplied. The experiments on the effects of reactant molar ratio ranged from 1:16 to 1:32 were

conducted at temperatures around 120 ± 5^{o}C using the best selected catalyst from the previous screening experiments. After which, the experiments were performed to examine the effect of temperature on conversion of glycerol and selectivity of 1,3-dichloropropanol at temperatures, 80, 90, 100 110, and 120^{o}C.

The effects of reactant mol ratio and operating temperature on both conversion of glycerol and selectivity of 1,3-dichloropropanol were examined by using aforementioned procedure. Equations 4.1 and 4.2 were used to calculate the conversion of glycerol and selectivity of DCP respectively:

$$Conversion\ of\ glycerol\ (\%) = \frac{Moles\ of\ glycerol\ reacted}{Moles\ of\ glycerol\ supplied}\ x\ 100 \qquad (4.1)$$

$$Selectivity\ for\ DCP\ \ (\%) = \frac{Moles\ of\ dichloropropanol\ produced}{Moles\ of\ glycerol\ reacted}\ x\ 100 \qquad (4.2)$$

4.3.2 Removal of unreacted hydrochloric acid, water, and catalyst

When the reaction had completed, the un-reacted hydrogen chloride and water formed from the reaction, and catalyst must be separated from the product mixture. This was carried out by using atmospheric distillation apparatus. The sample was filled into the flask and heated in the constant-temperature oil bath at 110^{o}C. For analysis purposes, the dissolved hydrochloric acid residue and eventually the catalyst, were neutralized by means of calcium carbonate. According to Tesser et al. (2007), about 3 cm^{3} of sample was treated with 0.5 g of the mentioned salt and kept

at 100 °C for 30 min in order to remove the entire water residues. The sample was then filtered with whatman filter paper in order to separate the precipitate formed, and the clarified solution was then analyzed by using gas chromatographic mass spectrometry (GC-MS)

4.3.3 Sampling

Product sampling was carried out at certain interval time to monitor the progress of reaction. About 1 ml of sample was withdrawn from the reaction flask and kept in small vial before sent for analysis using the following gas chromatographic method. The reaction was completed when the amount of glycerol remained constant. This was achieved in approximately three (3) hours of reaction. The samples were put in an ice water bath before analysis in order to stop the reaction.

Quantitative analyses were carried out using GC-MS under the following conditions: column, Capillary HP Wax; stationary phase; length = 25 m; i.d. = 0.25 mm; film thickness = 0.25 µm; Ionization mode; helium as gas carrier; injector temperature = 250 °C; detector temperature = 230 °C; temperature ramp = 1 min at 80 °C; heating rate = 6 °C/min to 150 °C, then 3 °C/min up to 190 °C, then hold for 1 min at finally = 240^{o}C. The sample of the reaction mixture was first diluted with methanol in a volumetric ratio of 1:20. The injected volume of the obtained solution was 1 μL.

4.4. Results and Discussions

4.4.1 Screening of Catalyst

As mentioned earlier, the preparation of DCP from glycerol was carried out in a liquid-phase batch rector (200 ml) using carboxylic acid catalyst. The selection of the best catalyst from carboxylic acid groups is crucial to obtain a good selectivity from the reaction. To observe the performances of the selected carboxylic acid catalysts on the conversion and also selectivity, four experiments were conducted using acetic acid, propionic acid, lactic acid, and malonic acid.

The screening of the catalyst was conducted initially by running the reaction between aqueous hydrogen chloride and glycerol without the presence of catalyst. It was observed that without catalyst there was no conversion of glycerol at all. After that, the experimental runs were directed towards finding the best catalyst among the four selected carboxylic acids of which having a lower volatility than acetic acid (Table 4.1). From the results, we can observe that malonic acid is the best catalyst for the conversion of glycerol to 1,3-dichloropropanol. Malonic acid has relatively lower volatility of which enables the reaction to be conducted at higher temperatures without appreciable loss of catalyst. In general, the conversion of glycerol was almost complete after 3 h using these catalysts. In addition, the selectivity of the reaction was also analyzed based on the concentration of 1,3-dichloropropanol which was at 44 percent by moles using malonic acid catalyst. The maximum selectivity of dichloropropanol obtained in the earlier work was higher 21 percent compared to earlier study by Tesser et al. (2007). On the other hand, the simulation analysis at

Chapter 3 demonstrated that up to 70 percent selectivity of dichloropropanol could be obtained from simulation study using Aspen Plus^{TM}. However, the previous result was obtained using gaseous hydrogen chloride as a chlorination agent instead of liquid. Therefore, in terms of cost, the use of liquid chlorination agent in this study can be a viable method compared to others because the cost of our technology is lower. But this conclusion should be supported by a more comprehensive study.

Table 4.1: Experimental Runs for Catalyst Screening

Catalyst	amount of catalyst (g)	glycerol conversion after 30 min (%)	glycerol conversion after 3 h (%)	Selectivity to 1,3-dichloropropanol at 30 min (%)	Selectivity to 1,3-dichloropropanol at 3 h (%)
AA	15.73	85.28	99.23	6.95	13.95
LA	15.70	56.59	97.83	5.71	11.41
MA	16.19	82.01	99.10	22.17	44.34
PPA	15.84	88.31	96.56	14.48	28.96

products distribution after 3 h of reaction (% by moles)				
Catalyst	Glycerol	1-MCP	1,3-DCP	1,2-DCP
AA	0.36	73.75	22.80	3.08
LA	0.90	73.31	21.55	4.24
MA	0.66	66.94	31.30	1.11
PPA	0.87	67.61	29.44	2.08

Others experimental condition: T= 90^{o}C, glycerol loaded = 12.6 g, aqueous HCl solution loaded = 78.9 g, catalysts concentration = 8 percent by moles. AA: Acetic acid; LA : Lactic acid; MA : Malonic acid; PPA : Propionic acid

The results for glycerol conversion after 30 min of reaction and conversion after 3 h, and selectivity toward the desired product 1,3-dichlopropanol are shown in the Table 4.1. The best catalyst should have the character of high activity and high selectivity and, low volatility in order to ensure minimum losses. The product distribution profiles obtained after 3 h of reaction for all the screened catalysts are also shown in Table 4.1.

In this reaction carboxylic acid containing carboxyl group acts as electrophile, thus the strongest acid shall be the most effective (Clayden, 2000). As can be seen in Table 4.1 the trend of findings indicate that the Brönsted acid sites of malonic acid [$CH_2(COOH)_2$)] catalyst is favorable to the said reaction. The acidity (pK_a) of those selected catalyst, propionic acid, acetic acid, lactic acid, and malonic acid are 4.8, 4.76, 3.9, and 2.83 respectively. Thus, it is concluded that the acid strength of the carboxyl group significantly influenced the catalytic activity. This conclusion is supported well with the previous study by Lee et al. (2008). They said that increasing acid strength of the catalyst will increase selectivity towards 1,3-DCP. Similarly, acid property of the catalyst plays an important role in the hydrochlorination reaction of glycerol to dichloropropanol (Krafft, 2007; Kruper, 2008).

Moreover, even though the price of malonic acid is 3.5 fold over than the acetic acid the high volatility of acetic acid renders the acid to be not suitable for operation at high temperature. This is evidenced from the results shown in Table 4.1, where though the conversion of glycerol for acetic acid is high (99%), most of the products remained as monochloropropanol (1-MCP). On the contrary, malonic acid can allow

one to perform the reaction at higher temperature without appreciable loss of catalyst, thus high selectivity.

4.4.2 Effect of Reactant Molar Ratio

Under the state of a chemical equilibrium system, based on Le-Chatelier's Principle, one of the methods to shift the reaction towards the forward direction is by using excess amount of either glycerol or hydrogen chloride (Figure 2.14). Hydrogen chloride functions as a nucleophilic for hydrochlorination reaction of glycerol through substitution of nucleophilic S_N2. The said ion attacks the nucleophile onto the glycerol containing electrophilic carbon. Thus, we chose hydrogen chloride as excess reactant. The stoichiometric molar ratio between the glycerol and aqueous hydrogen chloride is 1:2. For catalyst screening, the molar ratio of 1:16 (Glycerol: HCl) was used throughout the experiments to evaluate the effect on both extent of reaction and selectivity. This is to ensure that the reaction was unconstrained by the effect of excess reactant. The investigation on the effects of Glycerol: HCl molar ratio on conversion to 1,3-dichloropropanol was carried out at 120^{o}C and atmospheric condition for 3 hours. The amount of catalyst was maintained at 8 percent by mole in all experiments.

The effects of various molar ratio of glycerol:HCl on product composition are shown in Tables 4.3 to 4.7. The results are summarized in Figure 4.4 which shows that there is no significant effect of increasing molar ratio on the conversion of 1,3-dichloropropanol. Slightly higher percentage of 1,3-dichloropropanol was obtained at mol ratio of 1:20 and 1:24. However, the difference was so small (42.79 % and

43.12%) that no conclusion could be withdrawn from the study. These results are strongly in agreement with the results from Aspen Plus™ on hydrochlorination reaction between glycerol and gaseous hydrogen chloride prior to this experimental work. According to Aspen Plus™ simulation, on both extent of reaction and yield for 1,3-dichloropropanol, the maximum flow rate of gaseous hydrogen chloride was at 4 g/min (molar ratio glycerol:HCl 1:26) which correspond to flow rate range from 2 to 24 g/min. After the maximum point, the effect of those parameters decreased significantly caused by spinning of agitator which will usually happen for gas-liquid reaction at flooding point condition (Rose, 1981).

Table 4.2: Experimental Run with malonic acid at HCl:Glycerol, 1:16

t, min	Glycerol	1-MCP	1,3-DCP	1,2-DCP
0	100	0	0	0
15	78.82383	20.24625	0.91992658	0.009993
30	58.29827	38.01886	3.643298551	0.039578
60	27.33296	59.99316	12.53767613	0.136213
120	4.535865	64.9842	30.15230128	0.327637
180	1.424873	60.28143	37.88204026	0.411659

Other experimental conditions: T = 120^{o}C; glycerol loading = 12.6 g; catalyst concentration 8 percent by moles

Table 4.3: Experimental Run with malonic acid at HCl:Glycerol, 1:20

t, min	Glycerol	1-MCP	1,3-DCP	1,2-DCP
0	100	0	0	0
15	72.39915	26.0214	1.570343455	0.009097
30	49.31057	44.98323	5.673328756	0.032869
60	20.40683	62.58426	16.91092333	0.097982
120	3.079151	61.32888	35.38691197	0.205057
180	0.937568	56.01956	42.79487899	0.247992

Other experimental conditions: T = 120^{o}C; glycerol loading = 12.6 g; catalyst concentration 8 percent by moles

Table 4.4: Experimental Run with malonic acid at HCl:Glycerol, 1:24

t, min	Glycerol	1-MCP	1,3-DCP	1,2-DCP
0	100	0	0	0
15	72.28072	25.97032	1.739960077	0.009
30	49.05091	44.70929	6.207693855	0.032111
60	20.16419	61.71202	18.03051817	0.093271
120	3.067488	60.5044	36.24062448	0.187489
180	0.927215	55.72525	43.12442411	0.223108

Other experimental conditions: T = 120^{o}C; glycerol loading = 12.6 g; catalyst concentration 8 percent by moles

Table 4.5: Experimental Run with malonic acid at HCl:Glycerol, 1:28

t, min	Glycerol	1-MCP	1,3-DCP	1,2-DCP
0	100	0	0	0
15	81.9964	16.82906	1.164415631	0.010119
30	62.69158	32.62958	4.638528652	0.04031
60	30.65665	53.48985	15.71691292	0.136587
120	5.362694	59.80184	34.53532582	0.300145
180	1.619633	57.34563	40.68117832	0.353564

Other experimental conditions: T = 120^{o}C; glycerol loading = 12.6 g; catalyst concentration 8 percent by moles

Table 4.6: Experimental Run with malonic acid at HCl:Glycerol, 1:32

t, min	Glycerol	1-MCP	1,3-DCP	1,2-DCP
0	100	0	0	0
15	81.93396	16.81054	1.245476493	0.010021
30	62.53116	32.52075	4.908587897	0.039496
60	30.50562	53.09582	16.26765917	0.130901
120	5.438429	59.78702	34.49695871	0.277595
180	1.654334	57.34258	40.67576627	0.327316

Other experimental conditions: T = 120^{o}C; glycerol loading = 12.6 g; catalyst concentration 8 percent by moles

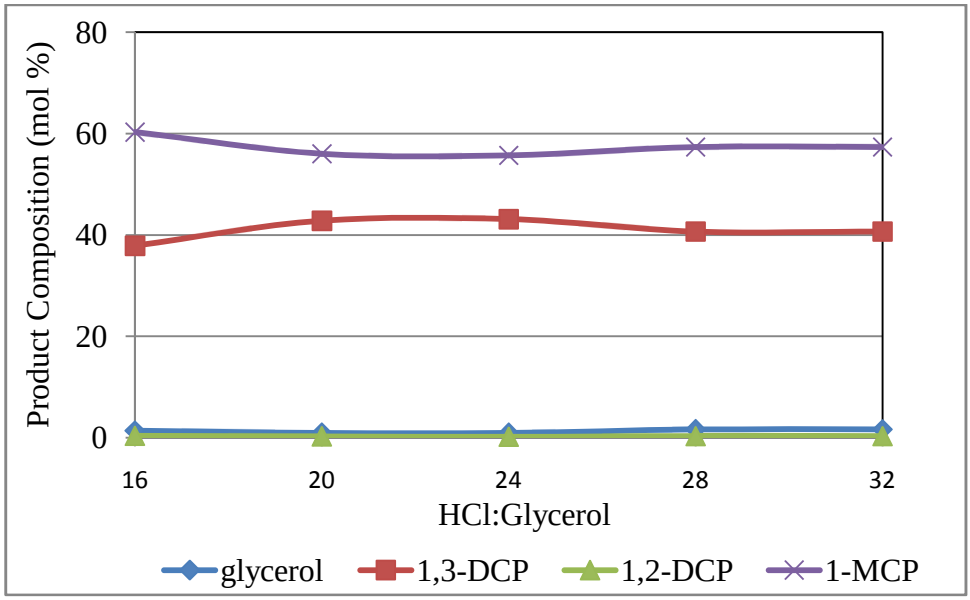


Figure 4.4: Effect of molar ratio on hydrochlorination of glycerol

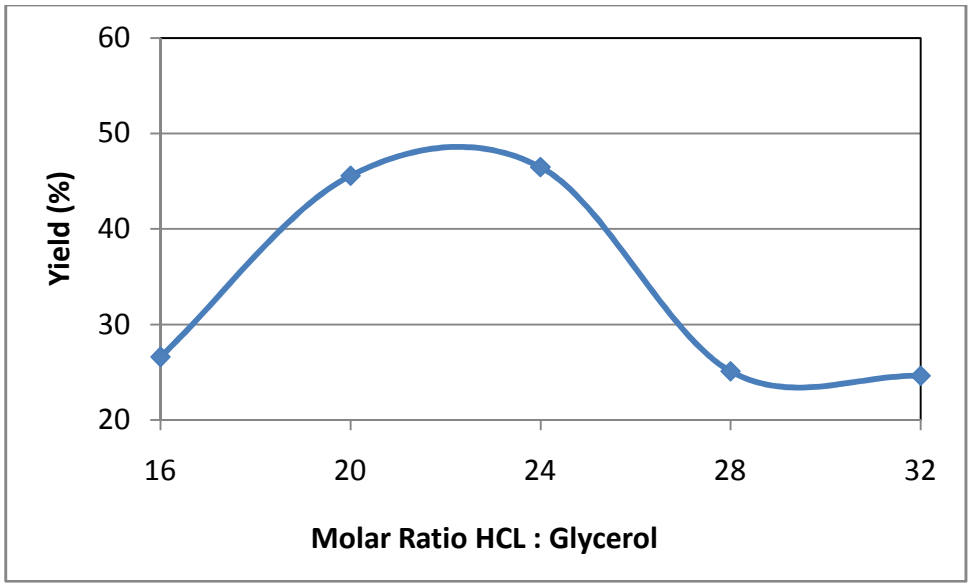


Figure 4.5: Effects of molar ratio on yield of 1,3-dichloropropanol

In contrast, Figure 4.6 shows an interesting result where the yield of 1,3-dichloropropanol increased from 26.6 % to 46.49 % as the molar ratio increased from 1:16 to 1:24. After that point, there is no benefit of using higher ratio. At higher ratio, the reaction slowed down due to the excessive presence of water in the reaction

mixture, due to the use of aqueous hydrochloric acid, and water that is formed as a consequence of the reaction itself (Siano et al., 2006). In addition, failure to remove the excessive water negatively impact on the second nucleophilic substitution S_N2 that involves the attack of chlorine anion on the gamma position (Kubicek et al., 2005). The removal of water from the reaction mixture, preferably by distillation under reduced pressure, in order to shift the reaction towards the forward direction would be considered for the subsequent study.

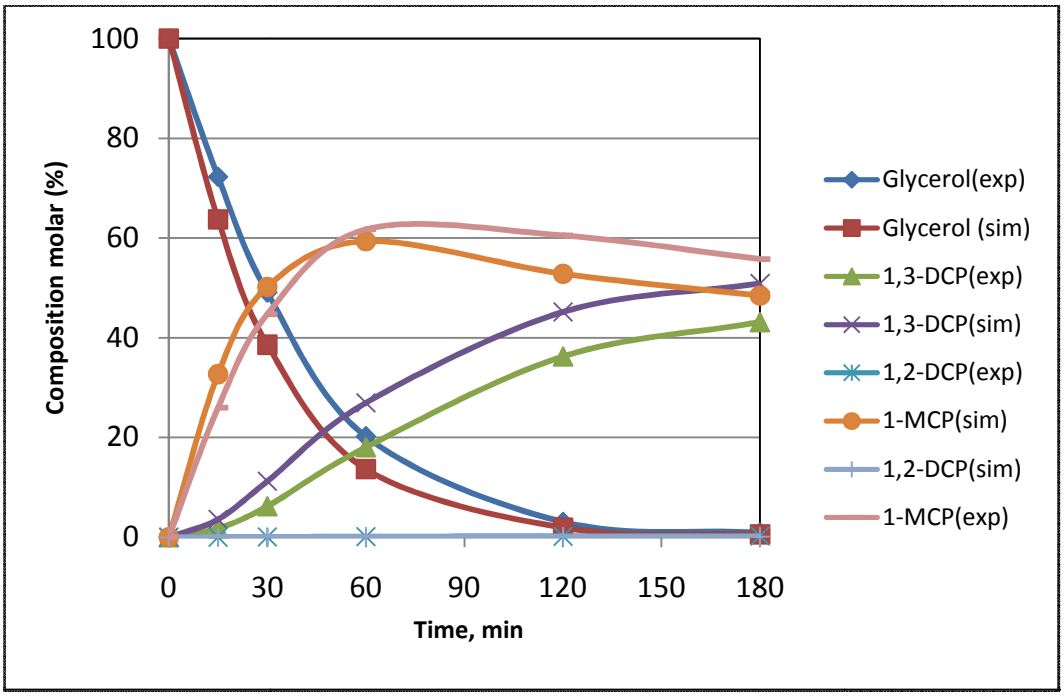


Figure 4.6 Product Distribution: Comparison between Experimental data and simulation study by Yunus (2011)

There is no similar experimental study that considers the effect of molar ratio on the hydrochlorination process. However, simulation study on the hydrochlorination of glycerol to 1,3-dichloropropanol using gaseous hydrogen chloride, has been reported at Chapter 3. These results compared well with their findings as can be seen in Figure 4.4. Thus, it can be concluded that employing a 12-fold excess of hydrogen

chloride, as a hydrochlorination agent, can drive reaction to produce more 1,3-dichloropropanol. It is in line with the Le Chatelier's Principle which stated that more products will be formed by increasing reactant concentration and gradually the reverse rate will also increase because of the new products being formed. Consequently, the concentration of products will continue to rise until the reverse and forward rates equalizes (equilibrium state).

4.4.3 Effect of Temperature

The temperature range selected for this study was between 80 to 120 ^{o}C. The reaction was conducted for 3 hours using 8 percent malonic acid (by mole) as the catalyst and 1:24 molar ratio of glycerol to HCL.

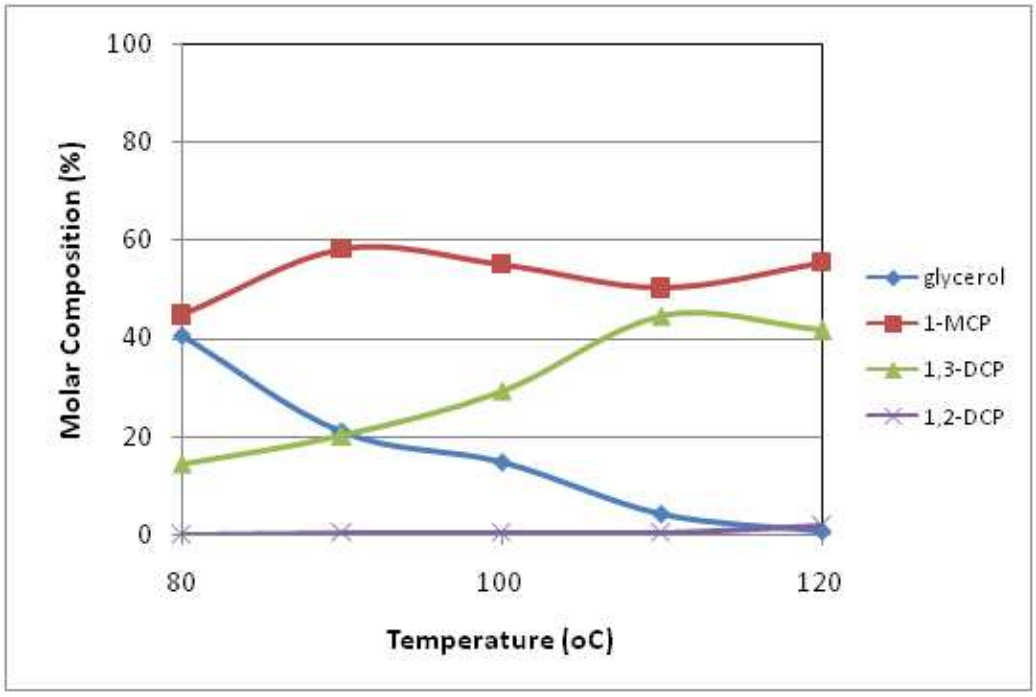


Figure 4.7: Effect of Temperature on Hydrochlorination of Glycerol.

The aim of this study was to observe the effect of temperature on the product composition, conversion of glycerol and yield of 1,3-DCP. The distribution product at five different temperatures on the hydrochlorination of glycerol with muriatic acid is shown in Figure 4.7 while Figure 4.8 and Figure 4.9 show effect of those temperatures on the conversion reaction and the product selectivity respectively.

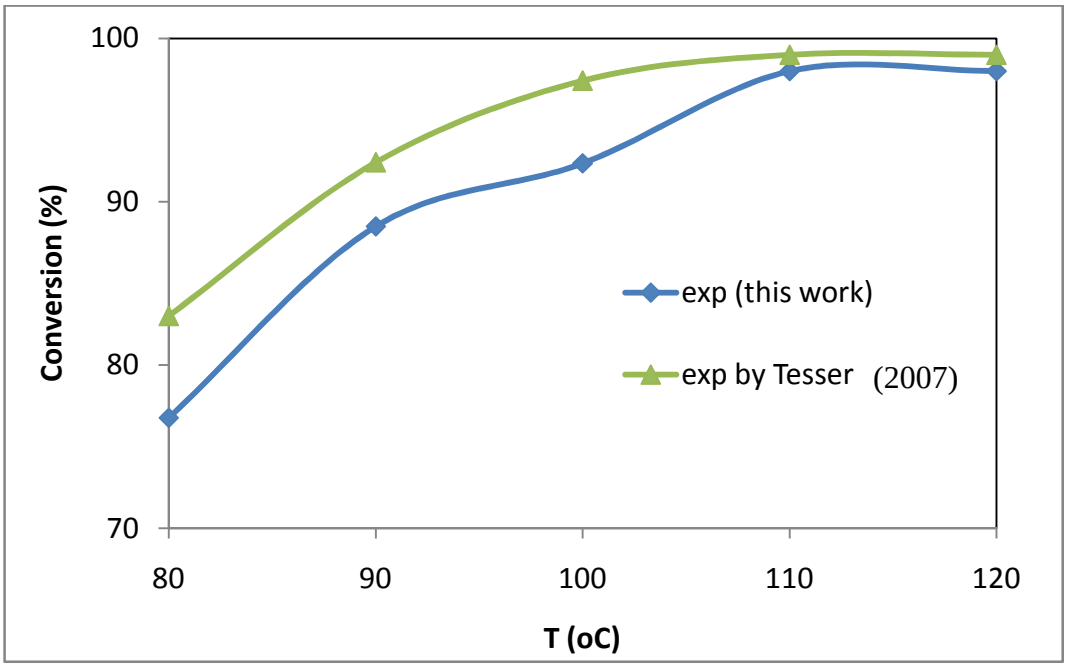


Figure 4.8: Effect of Temperature on Conversion of Glycerol

As predicted by the simulation both conversion of glycerol and yield of 1,3-DCP increases with temperature until it reached the optimum value. Tesser et al. (2007) also reported the same optimum value at 110^{o}C. Above this temperature, the yield of 1,3-DCP had dropped markedly while the yield of 1-MCP had increased and the conversion remained constant. This could be due to the dominance of the reverse reaction as illustrated in Figure 2.18. Those two figures also show similar trend even though the result is slightly lower than those reported in literatures. With some

improvement on the conditions using aqueous hydrogen chloride as a hydroclorination agent, it is believed that this proposed technology can be considered as a viable approach. The use of aqueous HCL (muriatic acid) is cheaper and very much safer compared to gaseous HCL

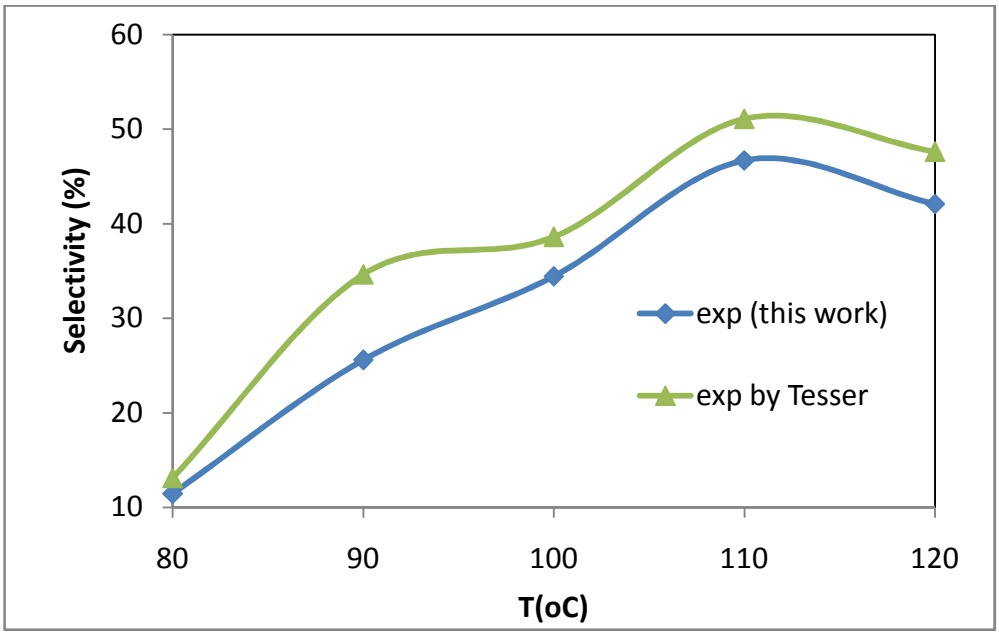


Figure 4.9: Effect of Temperature on Selectivity of 1,3-DCP

4.5. Conclusion

In this chapter, several experimental studies were conducted to synthesize DCP from bio-based glycerol via hydrochlorination process using aqueous hydrochloric acid 37 percent (muriatic acid). Three process parameters were examined namely types of catalyst, effect of mol ratio and effect of temperature. Among the four selected

carboxylic acid catalysts chosen for the screening, the best catalyst in terms of activity and selectivity was malonic acid. Its low volatility ensures minimum losses during the hydrochlorination process. The most favorable molar ratio of HCl : glycerol was at 24:1 while the optimum operating temperature for the reaction was at 110^{o}C. These experimental results, which used muriatic acid (37% aqueous hydrochloric acid) as a chlorination agent for hydrochlorination of glycerol were comparable to the conventional methods using gaseous hydrogen chloride. However, some improvement is still necessary due to the selectivity. In conclusion, the optimal reaction conditions obtained so far are as follows:

- Duration : 3 hours
- Temperature : 110^{o}C
- Catalyst : Malonic Acid (8 percent by mol)
- Molar ratio HCl: Glycerol : 24:1

CHAPTER 5

KINETICS OF DEHYDROCHLORINATION REACTION BETWEEN DICHLOROPROPANOL AND SODIUM HYDROXIDE

5.1. Introduction

Epichlorohydrin, an organochlorine compound and an epoxide, is the main raw material in the production of several synthetic materials, such as epoxy, phenoxy, and polyamide resins, polyether rubber used in car parts, synthetic glycerin, glycidyl ethers, polythiols, elastomers, surface active agent, plasticizers, polyester, products of pharmaceutical, lubricants, oil emulsifiers, and adhesives (Solvay, 2009). In particular, epichlorohydrin can also be used as a homopolymer or copolymer in the preparation of epichlorohydrin rubber. According to Dow (2007), other applications of epichlorohydrin are as a solvent for resins, gums, cellulose, esters, paints, and lacquers; to cure propylene-based rubbers; and in resins with high wet strength for the paper industry. Epichlorohydrin is also largely used as a stabilizer in chlorine-containing substances such as rubber, pesticide formulations, and solvents (Report on Carcinogens, 2011).

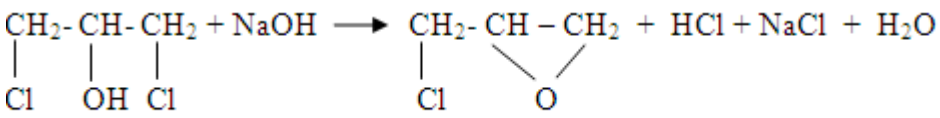
Conventionally (Bijsterbosch et al., 1994), epichlorohydrin is made by chlorohydrination of allyl chloride, which is obtained by high-temperature chlorination of propylene. Unfortunately, the method has some drawbacks such as formation of a large amount of chlorinated by-product and high energy consumption because of high operating temperature. Today, the glycerol is in abundance as by-

product of biodiesel, thus has given an opportunity to synthesize epichlorohydrin from glycerol by adding some basic solution (as discussed in Chapter 4).

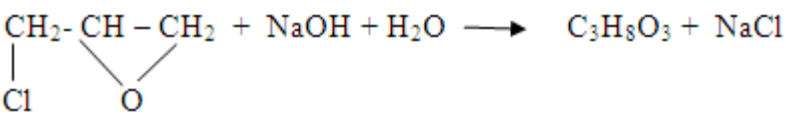
The mentioned process has been being developed by Solvay involving two steps reaction. First step, the direct synthesis of dichloropropanol via a hydrochlorination process involves a reaction between glycerol and hydrochloric acid. The second step is dehydrochlorination process involving a reaction between dichloropropanol obtained from first step with basic solution, generating the final product, epichlorohydrin. Glycerol used in the Solvay process was derived from rapeseed oil which is the raw material for biodiesel production.

This chapter is focus on the second step, the dehydrochlorination reaction between dichloropropanol and sodium hydroxide as a basic solution. A preliminary study using Aspen Plus simulation software had been conducted, in order to investigate some parameters affecting the process such as temperature and reactant molar ratio. From the simulation study reported in Chapter 3, this second reaction is very fast of which it can be completed in about 4 minute which is very close to the experimental result reported by Carra et al. (1979). Based on the result obtained by simulation, we conducted the kinetics study on the dehydrochlorination of dichloropropanol and sodium hydroxide at various temperatures. Before that effect of excess sodium hydroxide on both conversion of dichloropropanol and yields of the product also be investigated. By considering the results obtained by simulation and literatures then the mol ratio of 1:10 (excess of sodium hydroxide solution) was used for examining the kinetics study at different temperature.

Determination of all kinetics parameters for the reactions at Equation 5.1 are needed to design proper reactors for the dehydrochlorination process. However, the kinetics of this process was poorly explained in literatures. Carra et al. (1979) reported dehydrochlorination kinetics using calcium hydroxide and Ma et al. (2008) focused on the kinetics of the side reaction of epichlorohydrin hydrolysis. In preliminary study, a series of simulation on dehydrochlorination reaction dichloropropanol with sodium hydroxide have been done. The simulation, using Aspen Plus, gave some interesting results (as discussed in Chapter 3) for setting the experimental design, temperature range, molar ratio of reactants, and duration of reaction. The simulation data analysis was in good agreement with the values reported by Carra et al. (1979) which used potentiometry and gas chromatography techniques to analyze reaction products. The simulation results were also compared well with the values reported by Ma et al. (2008) where quantitative analyses of reaction product was done using potentiometry technique only.



(5.1)



(5.2)

5.2. Experimental Procedures

The above mentioned reactions were carried out in a three neck flask (500-ml), which was immersed in an oil bath, equipped with a thermometer, a sampling port and a condenser. The condenser was connected to an accumulator. A temperature controlled oil bath was used to control the reactor temperature and the mixture inside the reactor was stirred vigorously by the magnetic stirrer. The reactor was fed with base solution which contained about 0.05 molar of sodium hydroxide then the temperature was increased to the desired temperature. When the operating temperature of the reaction was reached, a known amount of the organic reagent, dichloropropanol, was slowly poured into the reactor containing the base solution. The experimental set up is the same as hydrochlorination process shown in Figure 4.1 (Chapter 4). Analysis of the reaction products was performed using GC-MS. HP-WAX capillary column with a dimension of 25 meter, 0.25 mm and a film thickness of 0.25 μm was used. The prepared gas chromatographic column was able to separate the reaction products: EPCH and 1,3-DCP. In addition, titration method was used to analyze the moles of OH^- during the reaction.

Based on the results obtained from the simulation, the optimal molar ratio of dichloropropanol to basic solution was found at 1:6 in terms of conversion of limiting reactant 1,3-DCP. However, in terms of product yield, epichlorohydrin, optimal mol ratio was found to be at a stoichiometric molar ratio. Excessive presence of solution sodium hydroxide, particularly at both high temperature (above 70^oC) and longer reaction time, can lower yield of product epichlorohydrin due to competing

reaction of hydrolysis of epichlorohydrin to glycerol (Ma *et.al*, 2007; Carra et al., 1979). Ma et al. (2008) used a stoichiometric mol ratio between 1.3-DCP and NaOH while Carra et al. (1979) used molar ratio 1,3-DCP : $Ca(OH)_2$ at 1:10 .

The simulation study confirmed that conducting the reaction above 70^{o}C (343 K) accelerated hydrolysis reaction of epichlorohydrin to form glycerol, thus should be avoided. This finding is in good agreement with the one reported by Ma et al. (2008). They said that above 70^{o}C, the hydrolysis reaction will take place of which would lower the yield of epichlorohydrin. In their kinetics study, Ma et al. (2008) used stoichiometric molar ratio of dichloropropanol to sodium hydroxide and the rate of reaction was concluded as a second order. While, Carra et al. (1979) used calcium hydroxide in excess, and the rate of reaction for dehydrochlorination for 1,3-DCP was regarded as *pseudo-first* order.

In this work, since excess of$[OH^-]$ also be applied, then effect of $[OH^-]$ on the rate of reaction can be ignored as shown in Equation 2.31. Since dehydrochlorination reaction is an exothermic reaction, then reaction system must be provided by the necessary cooling system in order to maintain the isothermal condition. This is also to ensure the dominance of dehydrochlorination reaction instead of hydrolysis reaction.

The five different temperatures was applied namely 50, 60, 70, and 80^{o}C to investigate the effect of temperature on the reaction rate constants. Samples were taken at certain time intervals for analysis. Each sample was collected in a small vial,

capped and kept in an ice water bath. This was done to prevent the backward hydrolysis reaction of epichlorohydrin to glycerol, before GC analysis. Samples were analyzed for 1,3-dichloropropanol, 1,2-dichloropropanol, and epichlorohydrin by gas chromatography. Carra et al. (1979) and Zhang et al. (2012) also used Gas Chromatography Mass Spectroscopy (GC-MS) method to monitor rate of the reaction.

5.3 Effects of Operating Parameters on Dehydrochlorination

Following the Le'Chatelier principle, one of the methods to promote forward reaction (Equation 5.1) is by using amount of one of the reactants in excess. Since sodium hydroxide is relatively cheaper compared to organic compound dichloropropanol, the reaction was subjected to excess base solution. The stoichiometric molar ratio between the dichloropropanol and sodium hydroxide is 1:1. However, in the kinetics study, molar ratio of 1:9 was used throughout the experiments. This is to ensure that the rate of reaction was not influenced by concentration of hydroxide. The effects of molar ratio dichloropropanol: NaOH on the conversion to epichlorohydrin was conducted at 60^{o}C.

5.3.1 Effect of Molar Ratio

The effect of molar ratio DCP: NaOH on conversion (moles of DCP consumed over moles of DCP fed) is shown in Figure 5.1 and 5.2.

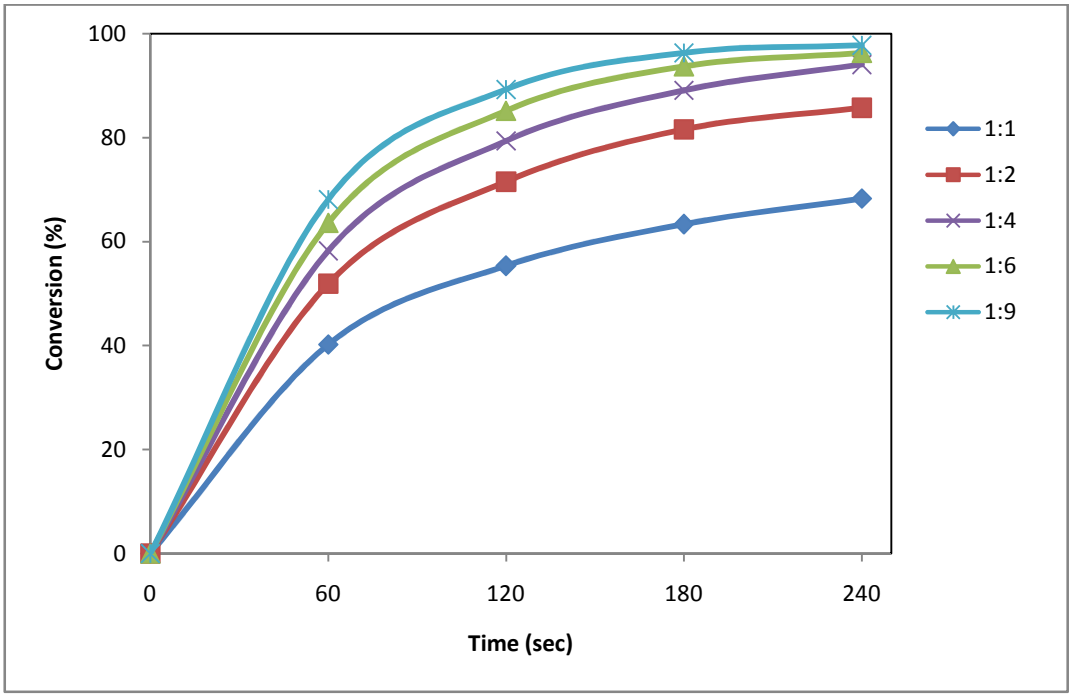


Figure 5.1: Conversion vs. time for the dehydrochlorination reaction of 1,3-DCP at different molar ratios

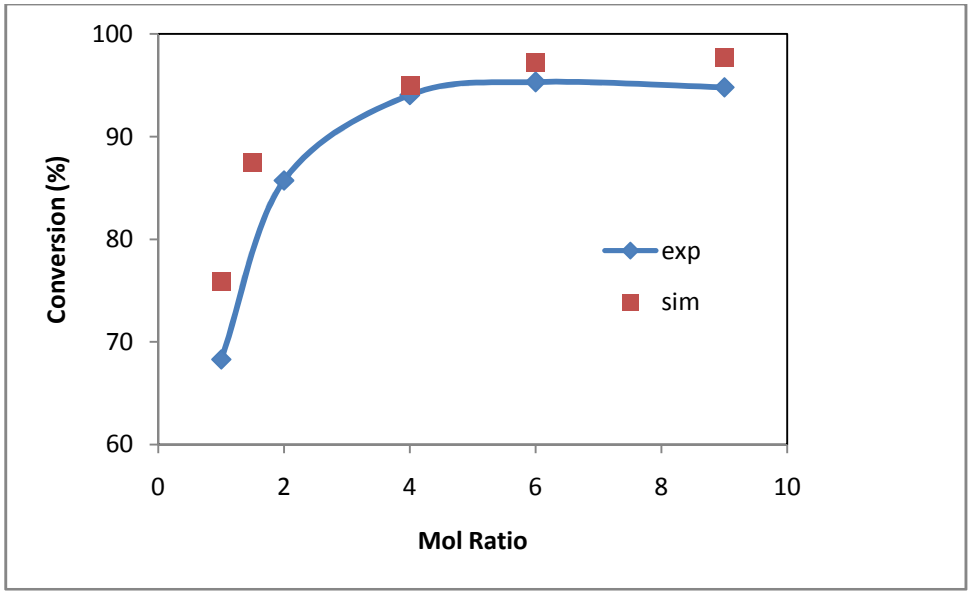


Figure 5.2: Effect of mol ratio on Conversion of 1,3-DCP:Comparison between experimental and simulation using Aspen Plus

These two figures show that increasing molar ratio DCP: NaOH from stoichiometric to 1:5 can improve the conversion of the reaction. After that there is no benefit of increasing molar ratio where conversion nearly remained constant due to the fact that the reaction equilibrium has been reached. This result compared well with the simulation analysis using Aspen Plus as can be seen in Figure 5.2.

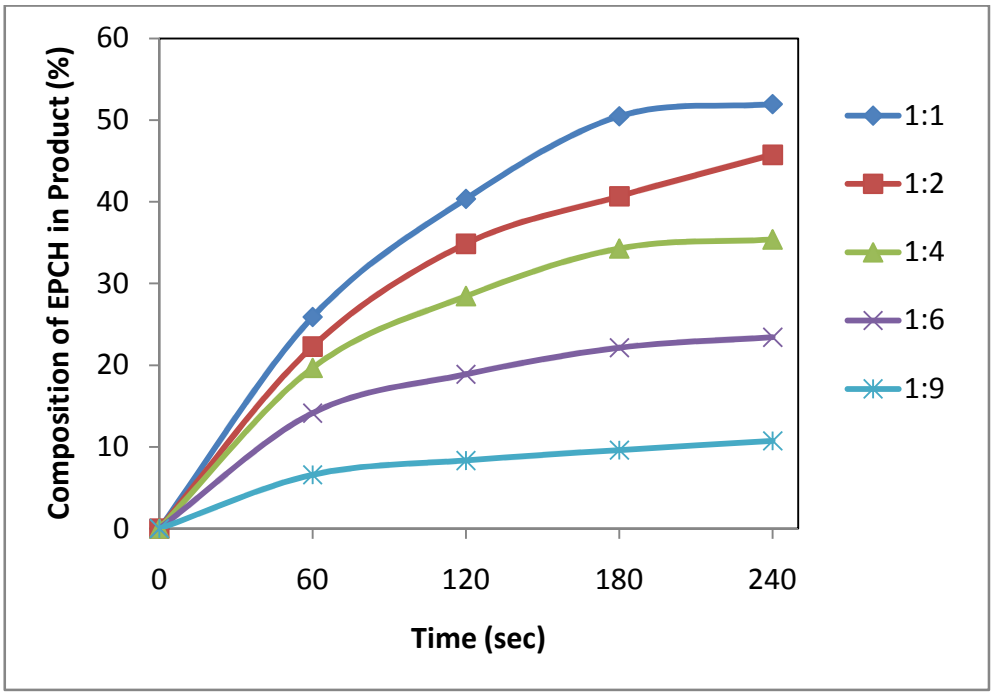


Figure 5.3: Yield of EPCH vs. time for the dehydrochlorination reaction of 1,3-DCP at different molar ratios

In contrast, the effect of molar ratio on epichlorohydrin composition is shown in Figure 5.3. It clearly shows that the excessive use of base solution in the dehydrochlorination reaction accelerates the hydrolysis of epichlorohydrin, thus lower the yield of epichlorohydrin significantly. This is evidenced in the GC chromatogram (Figure 5.4) showing the formation of glycerol from hydrolysis reaction at higher ratio 1:6 compared to 1:1. Nonetheless, the experimental results compared with the simulation results using Aspen Plus as depicted in Figure 5.5

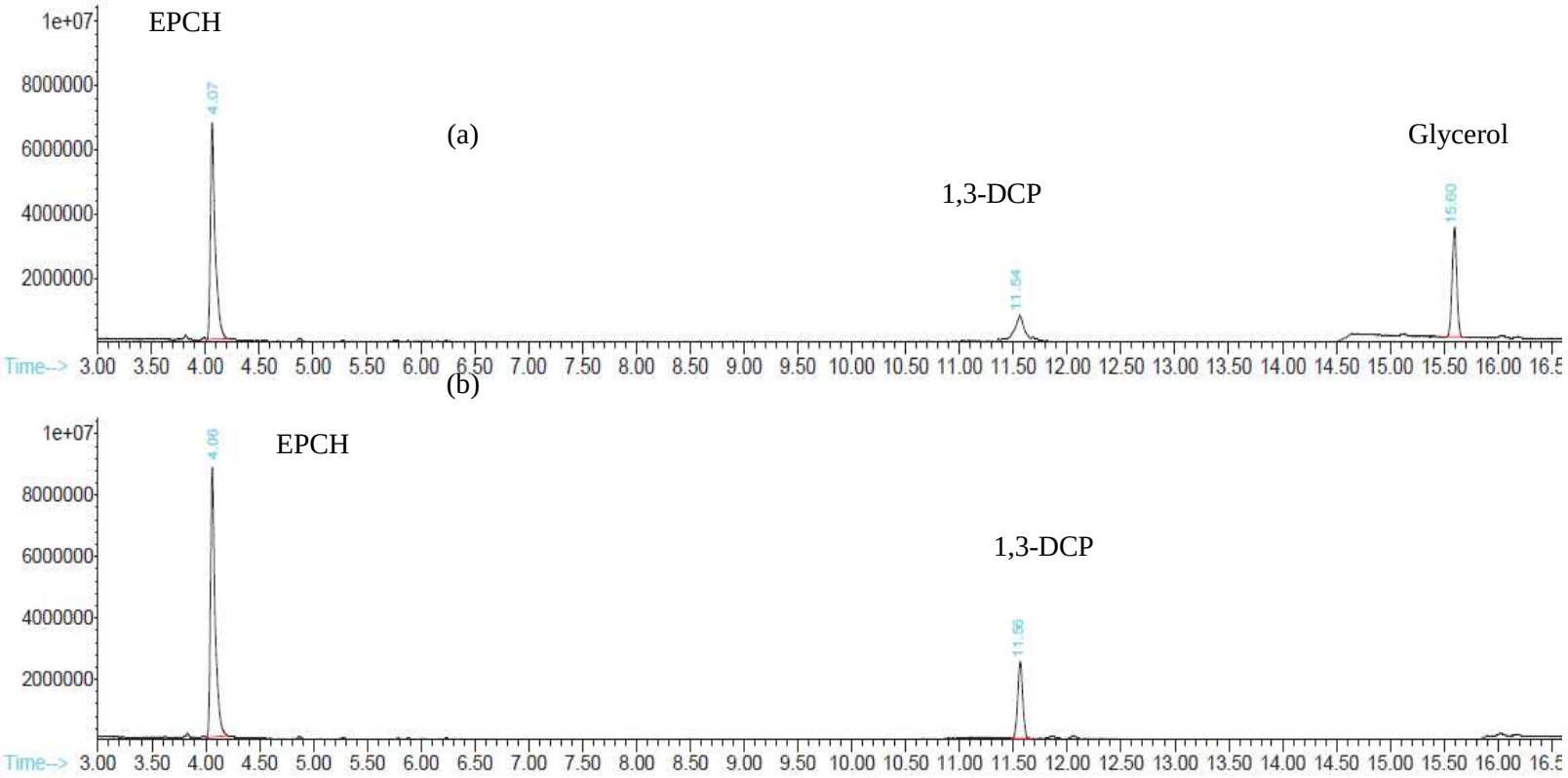


Figure 5.4: GC Chromatogram (a) molar ratio 1:5 (b) ratio molar 1:1

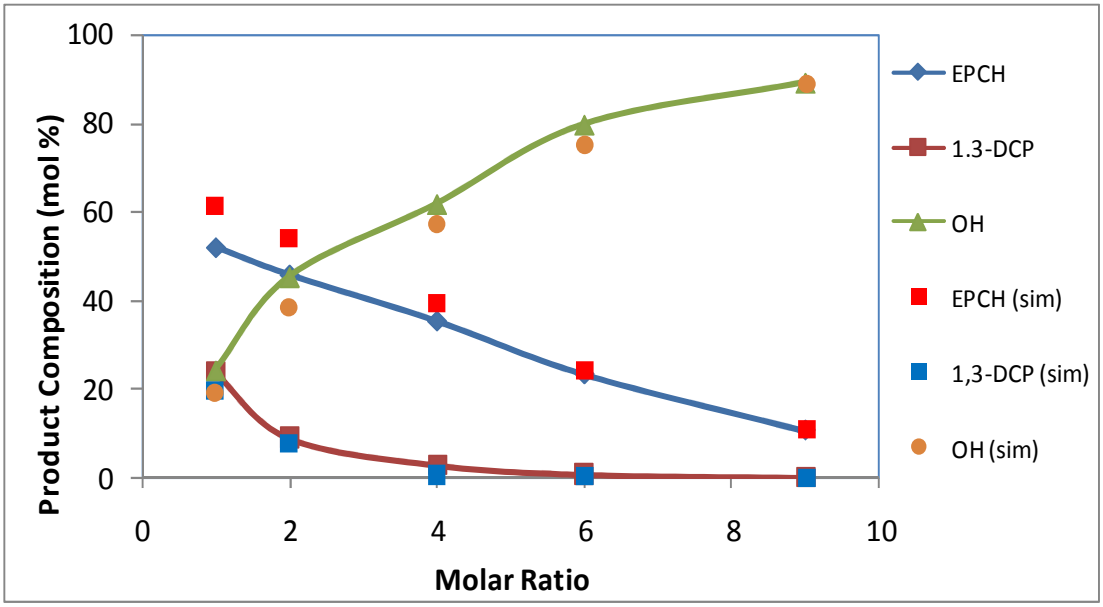


Figure 5.5: Effect of mol ratio on Product composition: Comparison between Experimental data and simulation using Aspen Plus

5.3.2 Effect of Temperature

The effect of temperature on the conversion of 1,3-DCP within the range 50 – 80^{o}C as a function of time is given in Figure 5.6. Under the operating conditions employed in this study, can be seen that the reaction rate was further improved as temperature was slowly raised to 70^{o}C. Carra et al. (1979) found optimal temperature of 60^{o}C at 0.5 bar pressure while Ma et al. (2008) did not find any effect of temperature on the reaction. However, Figure 5.6 clearly shows that there is no marked improvement on conversion by increasing the temperature after 70^{o}C. It seems the occurrence of hydrolysis reaction of epichlorohydrin to glycerol may have taken place at temperature above 80^{o}C.

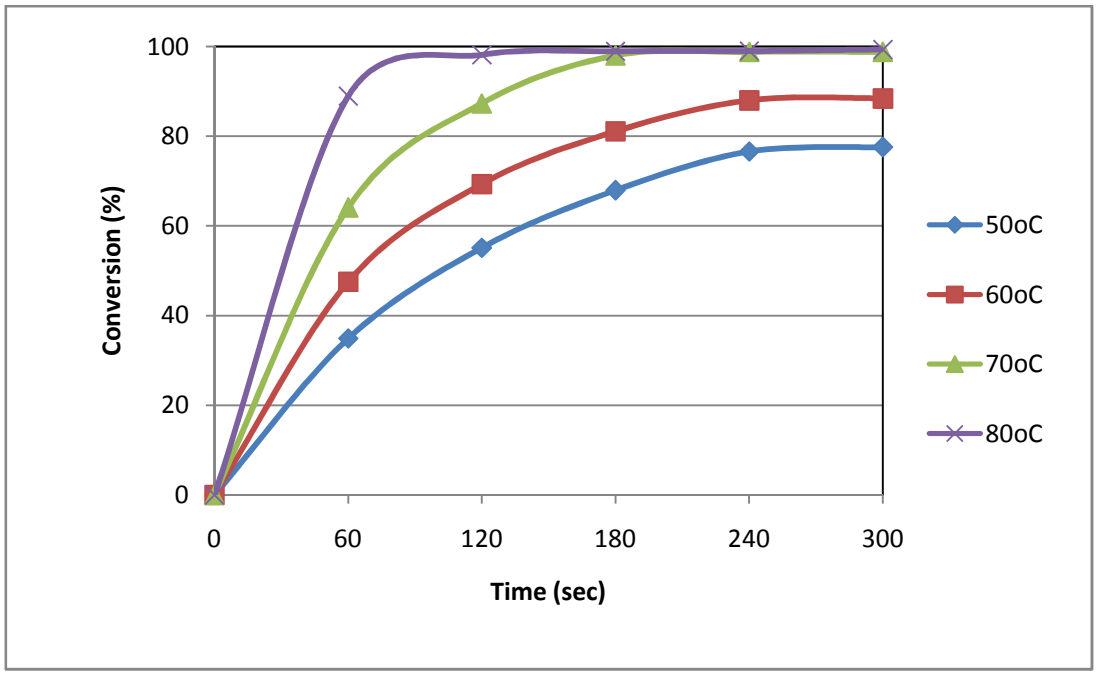


Figure 5.6: Conversion vs. time for the dehydrochlorination reaction of 1,3-DCP at different temperatures

According to Carra et al. (1979) when the temperature was above 80^{o}C and longer reaction time, the hydrolysis reaction rate was enhanced which can lower yield of epichlorohydrin. Similar conclusion was also made by Ma et al. (2007) that at the maximum temperature, the reaction was constrained by the competitive hydrolysis reaction. Therefore, a suitable operating temperature and short contact time should be considered in order to reduce the probability of hydrolysis reaction. Carra et al. (1979) reported 98 percent total conversion to dichloropropanol at 0.5 bar and 60^{o}C. This study also compared well with our own simulation results as shown in Figure 5.7.

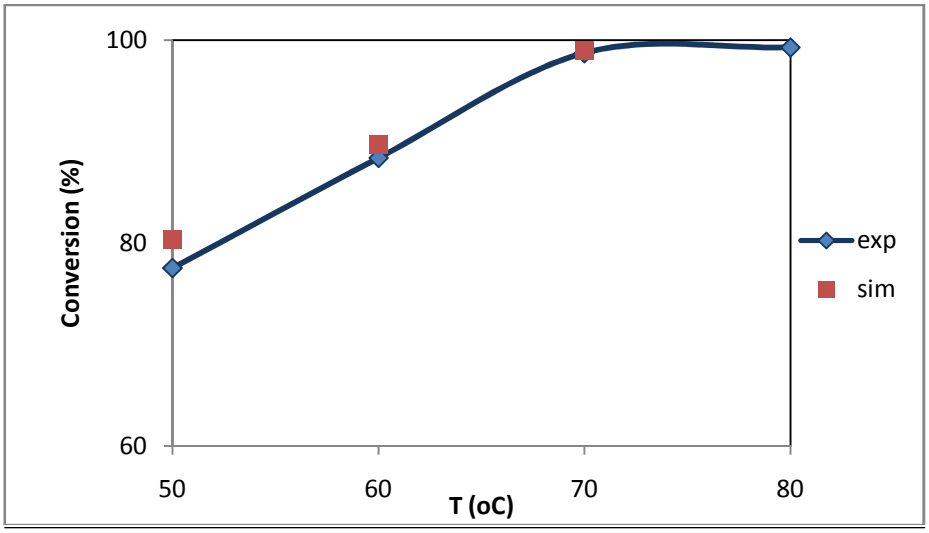


Figure 5.7: Effect of Temperature on Conversion of 1,3-DCP: Comparison between experimental and simulation using Aspen Plus

Furthermore, Figure 5.8 and 5.9 illustrate the influence of temperature on the yield of epichlorohydrin in the product mixture. Again, it exhibits similar behavior as the conversion described above. The said figures show that the yield of epichlorohydrin is relatively low at 50^{o}C where it tends to be higher by increasing the temperature up to 70^{o}C.

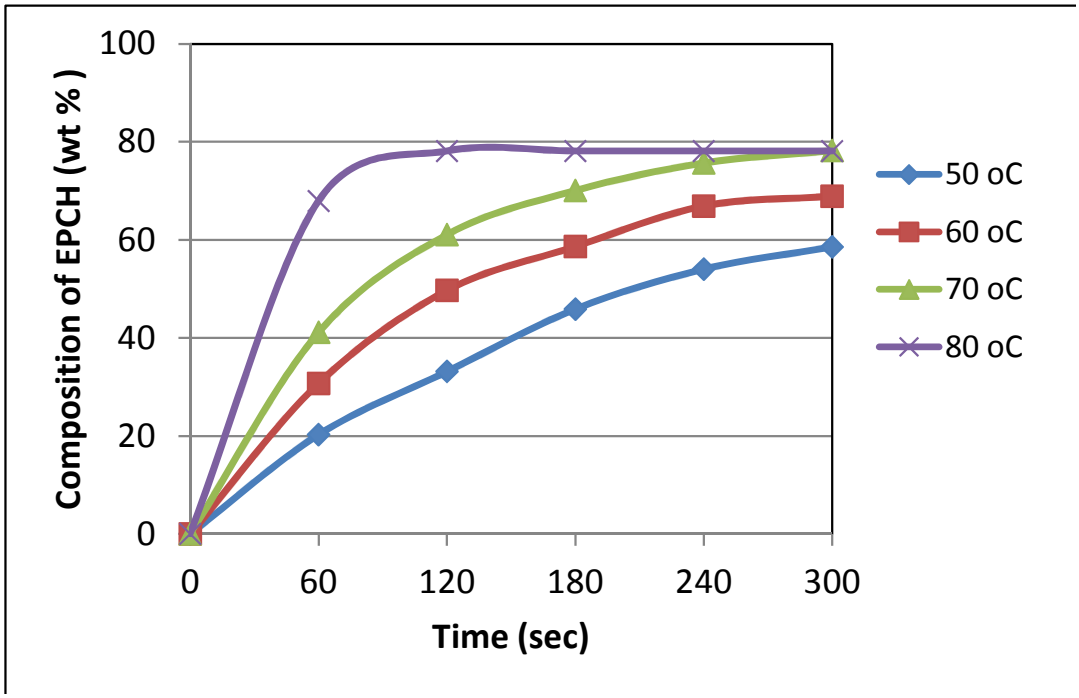


Figure 5.8: Effect of temperature and time on composition of epichlorohydrin

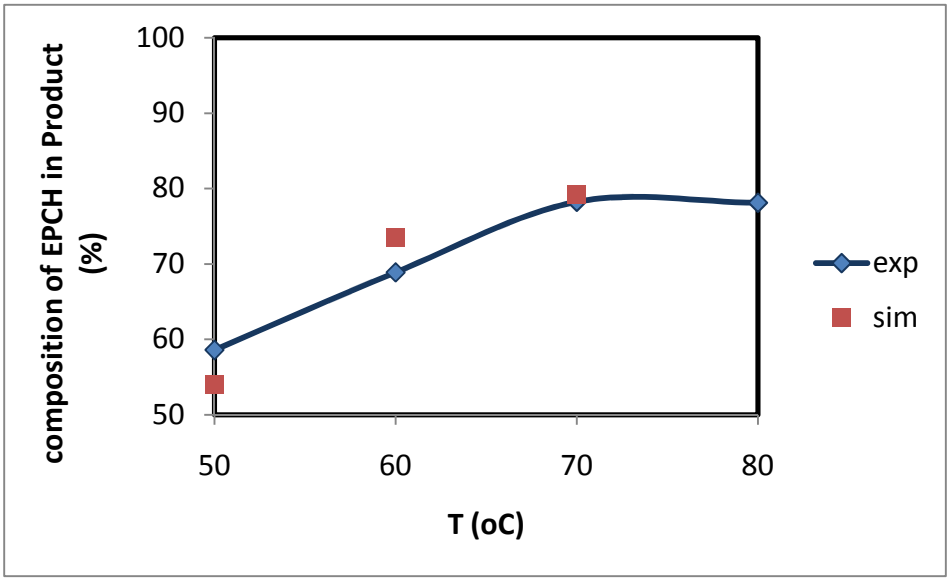


Figure 5.9: Effect of Temperature on Composition of EPCH: Comparison between experimental and simulation using Aspen Plus

However at 80^{o}C the yield of EPCH remained constant after 2 minutes of reaction as shown in the above figure. This indicates that the reaction has reached the

equilibrium and increasing the temperature could only promote the hydrolysis reaction of epichlorohydrin to glycerol. The insights into the occurrence of this hydrolysis reaction would be further exemplified in the forthcoming kinetics study. The peak in the GC chromatogram confirmed the appearance of glycerol by the hydrolysis described above as shown in Figure 5.5. Nonetheless, these results were in good agreement with our own simulation data using Aspen Plus as can be seen in Figure 5.9.

5.4. Reaction Kinetics

5.4.1. Model Development

Kinetics of dehydrochlorination reaction was studied in the presence of sodium hydroxide solution at various concentrations. According to Carra et al. (1979), Ma et al., (2007), and Zhang et al. (2012) dehydrochlorination of DCP in aqueous basic solution is a fast reaction (Equation 5.1). However, the competing hydrolysis reaction may be occur, as can be seen in Equation 5.2, especially when the operating temperature is higher than 80^{o}C, presence of excessive base solution and longer reaction time (Carra et al., 1979; Ma et al., 2008). In this study, the experiments were designed to determine the kinetics parameters such as reaction rate constants and activation energies for the reactions shown in Scheme 5.1. According to Ma et al. (2008), dehydrochlorination of dichloropropanol with sodium hydroxide is a second order irreversible reaction then the rate Equation of the reaction can be written as follows:

$$-r_{epy} = -\frac{d[DCP\}}{dt} = k[DCP]^{\propto}[OH^{-}]^{\beta} \quad (5.3)$$

where [DCP] and [OH^-] are concentration of DCP and OH^-, respectively.

According to Ma et al. (2007), the epichlorohydrin formation, the ring closures, happen according to the mechanism of an internal nucleophilic substitution (SN_2) prior to the base catalyzed dissociation equilibrium. It was modeled by the Williamson reaction (Carra et al., 1979), and was similar to the reaction occurred between propylene chlorohydrins and caustic soda, as explained by Patai (1967). The mechanism of the reaction can be represented by Figure 5.10. Ma et al. (2007) reported that protonation of the hydroxyl results in a better C-O-H-O-C group where this step is slow and reversible thus is considered as the rate determining step. The lone pairs on the oxygen make it a Lewis base.

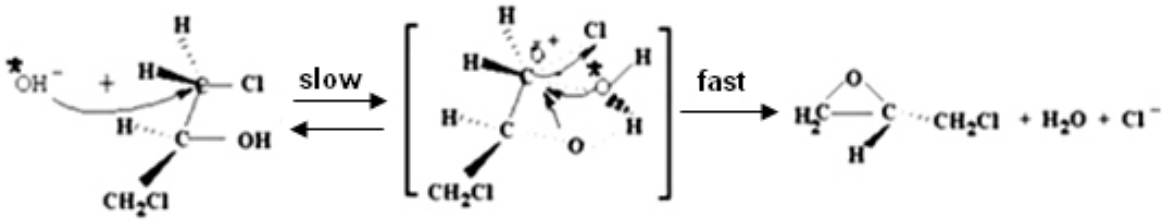


Figure 5.10 Mechanism of reaction dehydrochlorination (Ma et al., 2007)

Simultaneously formation of C-O-C bond and cleavage of the C-Cl bond may loss of the good leaving group, a neutral molecule of water. The reaction rate equation in this case is as the following (Ma et al., 2007):

$$r = k\ x\ K_e\ x\ [OH^-][R] \quad (5.4)$$

Where k is the kinetic rate constant and K_e is the equilibrium constant for the formation of the intermediate ion [R] is the reagent concentration. Ma et al. (2007) observed that this equilibrium constant strongly influenced the reaction and therefore influenced by the enthalpy change for the intermediate ion formation.

In this study, 2,3-DCP was not be considered which is the isomer of 1,3-DCP because pure 1,3-DCP (99.9%) was used in the reaction. Moreover, based on observation studied by Ma et al. (2007), the reactivity of 1,3-DCP is much higher than the reactivity of its isomer 2,3-DCP due to the inductive effects and space effect (Figure 5.11). In the structure molecule, both halogenoalkyls in 1,3-DCP increased the chlorine mobility or the negative charge on the oxygen, and the hydroxyl could attack 1-C and 3-C. However, only one halogenoalkyl in 2,3-DCP could increase the negative charge on the oxygen, and the hydroxyl could only attack 2-C. at the same time. According to Salaun (2000), it is difficult for the hydroxyl group to attack 2-C in 2,3-DCP due to the steric hindrance (Ma et al., 2007), which does not exist in 1,3-DCP.

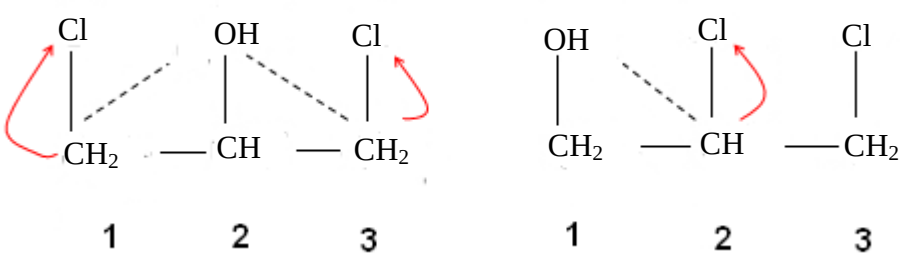


Figure 5.11 Space effect (Ma et al., 2007)

In order to determine kinetic parameters, in this study the initial concentration of OH^- was 10 times of initial concentration of DCP, so $[OH^-]$ is zero order, then the rate law can be written as:

$$-r_{epy} = -\frac{d[DCP\}}{dt} = k[DCP]^{\propto} \quad (5.5)$$

A simple analysis, based on the observation that the time for half-transformation is independent of the initial concentration of the reagents, revealed that our experimental data could be described by a pseudo-first-order kinetic model. As a consequence the rate law can be written as Equation 5.6

$$-r_{epy} = -\frac{d[DCP\}}{dt} = k[DCP] \quad (5.6)$$

In a similar study, Carra et al. (1979) reported, they also used excess of base solution where based on their observation the mass of hydroxyl ion decreased very slowly after the initial stage, justifying the employment of first order kinetics as an effective model in describing our experimental data.

5.4.2. Determination of Reaction Rate Constant

Determination of rate constant highly depends on the order of the reaction. Using the experimental data, the correct order would be determined by which function of rate equation best fit the linear requirement. The rate constants are estimated from the slope of the linear plot once the order is established. The rate of formation

epichlorohydrin can be described by the first order rate equation given in Equation 5.5. The integration form of Equation 5.5 is follow:

$$\ln [DCP]_o - \ln [DCP] = kt \quad (5.7)$$

As shown in Figure 5.12, a straight line plot supports our hypothesis that the dehydrochlorination of DCP and sodium hydroxide follows the first order irreversible kinetics. A temperature reaction maximum at 80^{o}C and reaction time control has completely hindered competing hydrolysis reaction.

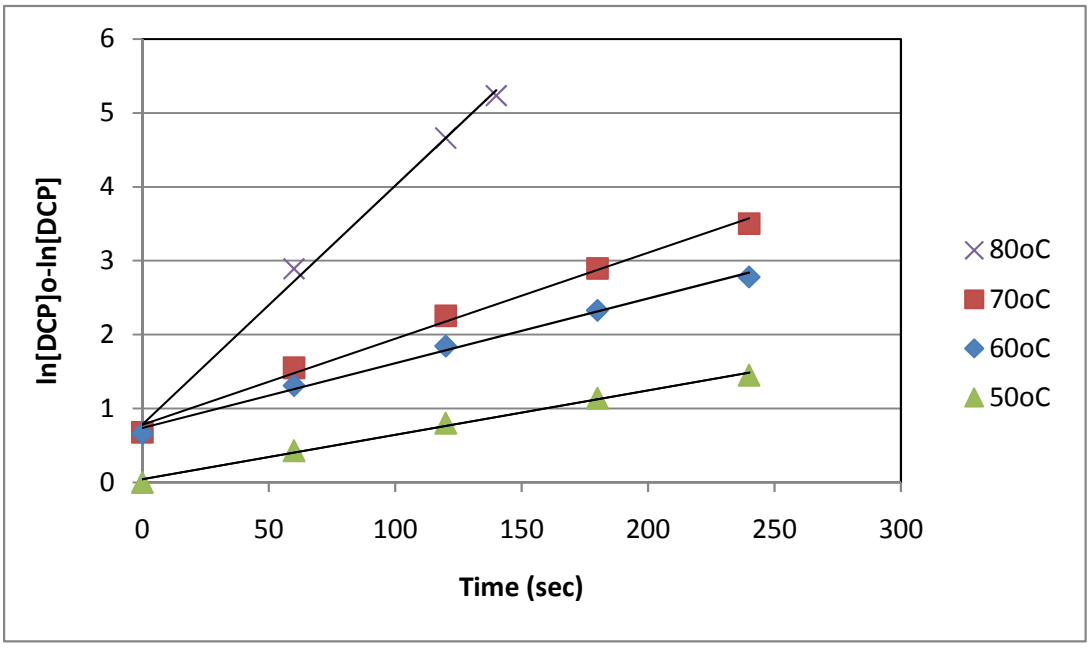


Figure 5.12: First-order kinetic model for dehydrochlorination of 1,3-DCP and NaOH

The value of k at various temperatures were obtained from the slopes of these lines and tabulated in Table 5.1. Compared to the earlier reports on the kinetics of similar reaction using calcium hydroxide by Carra et al. (1979), this study provides information closer to the kinetics parameter. However, it is important to note that Carra et al. (1979) used calcium hydroxide in their study as opposed to sodium hydroxide used herein.

Table 5.1: Rate constant, k for reaction between 1,3-DCP and NaOH

Temperature (^oC)	k (1^{st}Order) sec^{-1}	k (1^{st}Order) sec^{-1} by Carra et al. (1,3-DCP and $Ca(OH)_2$)
50	0.0056	0.0024
60	0.008	0.0038
70	0.012	0.0066
80	0.021	0.0117

Linear regression analysis of the data at 50 – 80^oC for epichlorohydrin synthesis gave correlation coefficient of 0.996, 0.994, 0.994, and 0.995. Figure 5.13 shows the exponential-like variation of the kinetic constants with temperature of dehydrochlorination reaction. It can be concluded that said reaction obeys the general rule of reaction kinetics.

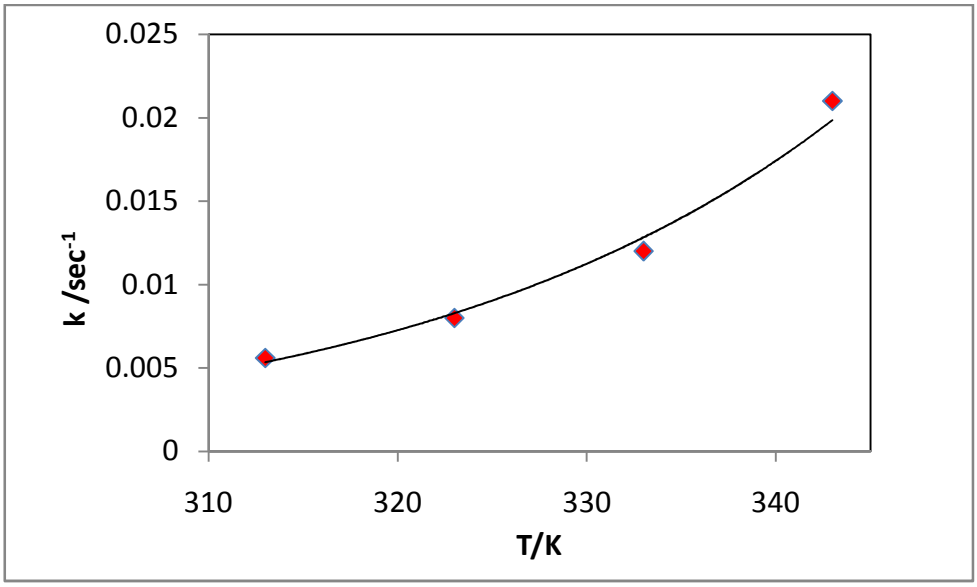


Figure 5.13: Variation of the kinetic constant with the temperature

5.4.3. The pre-exponential factor and Activation Energy

The dependency of rate constant, k, on temperature follows the Arrhenius Equation:

$$lnk = lnA - \frac{Ea}{RT} \tag{5.8}$$

Where A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature expressed in K. From the slope of a plot of ln(k) versus 1/T then the activation energy can be estimated. The pre-exponential factor A was determined from the y-intercept. The values of k at different temperature compared to the values reported by Carra *et al.* (1979) are tabulated in Table 5.1 and the plot of ln (k) versus 1/T is shown in Figure 5.14.

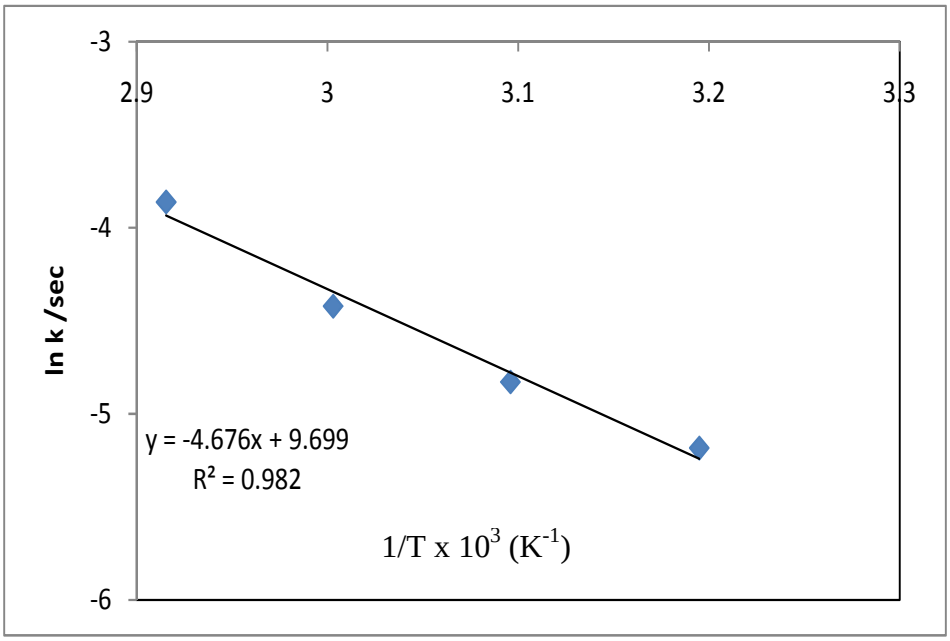


Figure 5.14: Plot of ln (k) versus 1/T for the dehydrochlorination reaction

The fitting parameters from this linear plot gives R^2=0.982 giving the activation energy Ea at 38.85 kJ/mol and the pre-exponential factor A at 1.62 x 10^7 sec^{-1}. Carra et al. (1979) reported the activation energy for the reaction involved in the dehydrochlorination of dichloropropanol with $Ca(OH)_2$ of A and E_a at 10^7 sec^{-1} and 49.14 kJ/mol.

Activation energy, E_a, can be thought of as the height of the potential barrier (sometimes called the energy barrier). A chemical reaction can be performed when an appreciable number of molecules with energy equal to or greater than the activation energy for a chemical reaction to proceed. Otherwise lower activation energy makes rate of reaction faster. In addition, for a catalytic chemical reaction, the catalyst does not change the energies of the original reactants or products instead it

reduces the activation energy value. The Arrehenius equation, $= Ae^{\frac{-Ea}{RT}}$, shows that k value will higher when the activation energy is lower therefore the rate of reaction proceed faster. In this study, since the activation energy was slightly lower compared to the value reported by Carra et al. (1979), the reaction is faster as evidenced by the shorter reaction time for completion. The reaction was 1 minute faster than of Carra.

Once the value of E_a and A at the temperature range have been determined, then formulation of equation for the rate of dehydrochlorination reaction can be estimated. The reaction rate in the presence of caustic soda within the selected temperature range can be expressed as follows:

$$r = 7.65\ x\ 10^{16} e^{-9.25/RT}[DCP] \quad (5.9)$$

5.5. Conclusions

Kinetics of dehydrochlorination of dichloropropanol (DCP) to epichlorohydrin (EPCH) using sodium hydroxide was investigated. The effect of temperatures (50 to 80^{o}C) on such reaction was observed where the optimum value was found at 70^{o}C as opposed to 60^{o}C given by Aspen Plus simulation. Effect of molar ratio 1,3-DCP:NaOH also was investigated where the best molar ratio in terms of conversion of DCP and yield of EPCH were found at 1:6. For the kinetic study sodium hydroxide was used in large excess (1:9), where the reaction rate is found to follow

pseudo first order with respect to dichloropropanol concentration. The activation energy of the reaction was 38.85 kJ/mol and the pre-exponential factor A was 1.62 x 10^7/sec. Compared to the earlier reports on the kinetics of this reaction which used calcium hydroxide, this study provides information much closer to the kinetics parameter. As mentioned above, the conversion rate was nearly constant after 2 minute. Therefore, low contact time is one of the important factors in the design of dehydrochlorination reactor, failing which could promote the hydrolysis of EPCH, thus lower the final product yield. Selection of the optimal operating conditions for the synthesis of epichlorohydrin from DCP is also imperative.

CHAPTER 6

CONCLUSIONS AND RECOMENDATIONS

6.1. Conclusions

The main objective of this research was to develop a simple technology to convert glycerol by-product from biodiesel production to epichlorohydrin. The whole process comprised of two steps. The first step was hydrochlorination process where glycerol reacted with hydrogen chloride to form dichloropropanol (DCP) in the presence of carboxylic acid catalyst. Hydrogen chloride acted as a hydroclorination agent in either gaseous or aqueous phase. The next step was dehydrochlorination process where the dichloropropanol obtained from the previous step reacted with the base solution, such as sodium hydroxide, calcium hydroxide, and the like, to form epichlorohydrin.

A series of simulation work was conducted on both the 1,3-dichloropropanol preparation, and the epichlorohydrin preparation using the ASPEN Plus^{TM} simulation software. The synthesis of 1,3-dichloropropanol took place via hydrochlorination process, in a semi batch stirred tank reactor (SBSTR) while, the synthesis of epichlorohydrin via dehydrochlorination reaction, was simulated using a batch stirred tank reactor (BSTR). The results of simulation were used to predict the performance of SBSTR and BSTR in terms of conversion, selectivity and product yield. For the hydrochlorination process, the effects of both HCl flow rate and catalyst concentration were investigated. While lower HCl flow rate was found to improve

the hydrochlorination process based on both selectivity and yield of 1,3-dichloropropanol, the catalyst concentration did not have significant effect on the process. For the dehydrochlorination process, effect of reactant molar ratio indicated that the excessive use of base solution can lower the yield of product significantly. The findings from these simulation results were used to facilitate the experimental work, as reported in chapter 4 and in chapter 5. The main aim was to develop the technology to convert crude glycerol to 1,3-dichloropropanol and to develop kinetic of dehydrochlorination process to convert 1,3-DCP to epichlorohydrin..

In this study a series of experimental works were conducted to synthesize DCP from glycerol via hydrochlorination process using aqueous hydrochloric acid (muriatic acid - 37 %). Three process parameters were examined namely types of catalyst, mol ratio and temperature. Among the four selected carboxylic acid catalysts chosen for the screening, the best catalyst in terms of activity and selectivity was malonic acid. Beside that its low volatility ensures minimum losses during the hydrochlorination process. The most favorable molar ratio of HCl : glycerol was at 24:1 while the optimum operating temperature for the reaction was at 110^{o}C. These experimental results, which used muriatic acid (37% aqueous hydrochloric acid) as a chlorination agent for hydrochlorination of glycerol, are comparable with other methods which used gaseous hydrogen chloride. However, some improvement is still necessary due to selectivity. In conclusion, the optimal reaction conditions so far are as follows:

- Duration : 3 hours
- Temperature : 110^{o}C
- Catalyst : Malonic Acid (8 percent by mol)
- Molar ratio HCl : Glycerol 24:1

The kinetics of dehydrochlorination of dichloropropanol and sodium hydroxide to epichlorohydrin was investigated. The effect of temperatures (50 to 80^{o}C) on such reaction was observed. The reaction rate was found to be pseudo first order with respect to dichloropropanol concentration. The activation energy of the rate constant was 9.25 kcal/mol, the pre-exponential factor A was 1.62 x 10^{7} sec^{-1}, and reaction rate constant were 0.0056; 0.008; 0.012; 0.021 for 40, 50, 60, and 70^{o}C respectively Compared to the earlier reports on the kinetics of similar reaction using calcium hydroxide, this study provides information much closer to the kinetics parameter. As observed from the experimental study, the rate of reaction was nearly constant after 2 minute of reaction. Since the reaction is very fast, choosing the optimal operating conditions for the process of synthesis of epichlorohydrin from DCP is important to prevent the occurrence of a side reaction. One of the common side reactions is the hydrolysis of epichlorohydrin to form glycerol.

6.2. Recommendations for Future Work

The current work has focused on the synthesis of epichlorohydrin via dichloropropanol instead of allyl chloride. Dichloropropanol has been successful synthesized by reacting glycerol with aqueous hydrogen chloride in the presence of malonic acid as the catalyst. After that, the final product epichlorohydrin would be obtained by adding some sodium hydroxide solution into dichloropropanol. In this study, we found that the yield and selectivity of hydrochlorination of glycerol to dichloropropanol were lower compared to other approaches due to the failure to

remove water from the reaction mixture. However it could be improved by choosing the optimum operating pressure.

For future work, it is recommended that the following areas to be explored:

1. As mentioned before that the yield and selectivity of hydrochlorination of glycerol to dichloropropanol were lower compared to other approaches due to the failure to remove water from the reaction mixture thus investigation effect of different vacuum pressure on the performance of hydrochlorination would be an interesting topic.
2. Study on the possibility of running an in-situ process in which both hydrochlorination and dehydrochlorination take place simultaneously in a single reactor. This is, in-situ technology, maybe give an advantage such as lower equipment investment due to use single reactor instead of two series reactor. However, it is recommended that the simulation would have been done prior to the experimental work.
3. Scale-up study of the hydrochlorination process should also be considered in order to investigate how far deviation of parameters between small and pilot scale production.

REFERENCES

ABG. (2008). *www.abginc.com.* Retrieved 2009, from http://www.asaimsea.com/Glycerin Market Analysis

Azhari. (2010). Continuous Production of Jatropha Curcas Biodiesel Using Oscillatory Flow Reactor. Malaysia: Universiti Putra Malaysia.

Barnwal, M., & Sharma. (2005). Prospects of Biodiesel Production from Vegetable oils in India Alternate Hydro Energy Centre. *Renewable & Sustain Energy Review* , 9 (4): 363 - 378.

Bhatnagar, M. (1996). Epoxy Resin. In *The Polymeric Materials Encyclopedia.* Bombay: India.

Bijsterbosch, J. W., Das, A., & Kerkhof, F. J. (1994). Clean Technology in the production of Epichlorohydrin. *Journal Cleaner Product* , 2 (3-4): 181-184.

Biodiesel Technotes. (2006). Retrieved 2012, from biodiesel@uidaho.edu: http://web.cals.uidaho.edu/biodiesel/files/2012/11/Technote06.pdf

Bruce M, B., John R, B., Robert M, C., Susanne M, C., Phil D, G., Jeffrey G, H., et al. (2008). Glycerin as a Renewable Feedstock for Epichlorohydrin Production (The GTE Process). *Clean Journal* , 36 (8) 657-661.

Carine, B., Sandrine, A., Xavier, C., Carole, M. J., Jean, L. U., & Stephane, E. G. (2006). Minimization of Glycerol Production during the High-Performance Fed-Batch Ethanolic Fermentation Process in Saccharomyces cerevisiae, Using a Metabolic Model as a Prediction Tool. *Applied Environmental Microbiology* , 72 (3): 2134-2140.

Carra, S., Santacesaria, M., Morbidelli, M., Schwarz, P., & Divo, C. (1979). Synthesis of Epichlorohydrin by Elimination of Hydrogen Chloride from Chlorohydrins, Kinetic Aspect of the Process. *Industrial Engineering Chemical Process Design Development* , 18 (3): 424-427.

Clark, C. (2005). Polyepichlorohydrin Elastomer. *Zeon Chemicals L.P* , 800: 735 - 3388.

Clarke, H., & Hartman, W. (1941). Organic Synthesis Preparation. *Organic Syntheses* , 1:233.

Clayden, J., Nick, G., Stuart, W., & Peter, W. (2000). *Organic Chemistry* . New York: Wiley and Sons.

Compagno, C., Bosehi, F., & Ranzi, B. (1996). Glycerol Production in Triose Phosphate Isomerase Deficient Mutant of Sacharomyces Cerevisiae. *Biotechnology Progress* , 12: 591-595.

Dow. (2007). Epichlorohydrin:. *Product Stewardship Manual Handling and Storage* .

Dow. (2007). Glycerine to Epichlorohydrin and Liquid Epoxy Resin Projects by Choosing Shanghai Site. Innovative Technology Provides Significant Environment & Cost Advantages.

Fogler, S. H. (1992). *Elements of Chemical REactions Engineering* . Prentice Hall.

Fogler, S. H., Nihat, M., & Gurmen. (2002). Aspen Plus : Workshop for Reaction Engineering and Design . The University of Michigan Department of Chemical Engineering Ann Arbor, MI.

Froment, G. F., & Kenneth B, B. (1979). *Chemical Reactor Analysis and Design* . New York: John Wiley & Sons.

Giri, A. (1996). Genetic Toxicology of Epichlorohydrin (A Review). Calcuta: Indian Institute of Chemical Biology 4 Raja S.C. Mullick Road Jadalpur.

HSBD. (2009). Hazardous Substances Data Bank . National Library of Medicine.

HSBD. (1997). Hazardous Substances Data Bank. Denver Co: Tomes Micromededex, Incorporation.

Huntress, E. (1948). *Organic Chlorine Compounds.* New York: Wiley Academic Press.

IARC. (1999). Epichlorohydrin in Evaluation of Carcinogenic Risk of Chemical to Humans. France: International Agency for Research on Cancer.

IARC. (1987). Epichlorohydrin in Overall Evaluation of Carcinogenicity. France: International Agency For Research on Cancer.

ICIS. (2012). *www.icis.com.* Retrieved November 26, 2012, from http://www.icis.com/epoxy-resin-methodology

Kastanek, F., Zahradnik, J., Kratochvil, J., & Cermak, J. (1993). *Chemical Reactor for GAs-Liquid System.* New York: Crezh Republic.

Krafft, P., Franck, C., Andolenko, D., & Veyrac, R. (2007). *Patent No. WO2007/054505A2.*

Krafft, P., Patrick, G., Benoit, G., & Sara, C. (2007). *Patent No. 2007/0112224A1*.

Kruper, J., William, J., Tina, A., Bruce, M. B., John, B., Robert M, C., et al. (2008). *Patent No. 2008/0015369A1*.

Kubicek, P., Sladek, P., & Buricova, I. (2005). *Patent No. WO2005/021476A1*.

Lee, H., & Neville, K. (1967). *Handbook of Epoxy Resin.* New York: McGraw Hill.

Ma, L., Zhu, J., Yuan, X., & Yue, Q. (2007). Synthesis of Epichlorohydrin from Dichloropropanol: Kinetic Aspects of the Process . *Chemical Engineering Research and Design* , 85 (A12):1580-1585.

Maneely, T. (2006). Glycerin Production and Utilization. Biodiesel One-Day Course From Field to Fuel Coeur d'Alene, Idaho.

Mario, R. E. (2011). Introduction to Aspen Plus Simulation. Chemical Engineering Department Auburn University.

Matthew, B., & Rene, O. (2004). ASPEN PLUS 12.1: Instructional Tutorials. Department of Chemical Engineering University of Washington.

Michael J, H., Andrew J, M., Winnie C, Y., & Thomas A, F. (2006). A Process Model to Estimate Biodiesel Production Costs. *Bioresource technology* , 97:671-678.

Michael, H. J., Andrew, M. J., Winnie, Y. C., & Thomas, Y. A. (2006). A Process Model to Estimate Biodiesel Production Costs. *Bioresource Technology* , 671-678.

Michael, M. (2005). Business Glycerin Surplus: Plants are Closing and new uses for the Chemical are being found. 84(6):7.

Myszkowski, J., & Zielinski, A. (1964). Chlorohydroxylation of Butene-1. *Chemistry and Industry* , 91:654.

Nagato, N., Mori, H., Maki, R., & Ishioka, R. (1987). *Patent No. 4,634,784.*

Newswire, P. (2006). Biodiesel boom wreaks havoc on Glycerin Market.

Nexant. (2006). Epichlorohydrin Process Route.

Octave, L. (1999). *Chemical Reaction Engineering.* New York: Wiley and Sons.

Osamu, H. (1990). Curing Agents for Epoxy Resin. Three Bond Technical News.

Report on Carcinogens. (2011). National Toxicology Program, Department of Health and Human Services.

Report, C. (2003). *Epichlorohydrin: Chemical Product Trends.* Sri Consulting.

Rose, L. (1981). *Chemical Reactor Design in Practice.* New York: Amsterdam.

Salaun, J. (2000). Small Ring Compounds in Organic Synthesis . Berlin Germany: Springer-Verlag.

Sang, H. L., Dong, r. P., Heesoo, K., Joohyung, L., Ji, C. J., Sung, Y. W., et al. (2008). Direct Preparation of Dichloropropanol from Glycerol using Heteropolyacid (HPA) catalysis: A Catalyst screen Study. *Elsevier, Catalysis Communications* , 9:1920-1923.

Saul, p. (1967). *The Chemistry of Functional Groups.* New York: Interscience: Wiley and Sons.

Schreck, D., Kruper, W., Varjian, R., Jones, M., Campbell, R., Kearn, K., et al. (2006). *Patent No. WO 020234A1.*

Siano, D., Santacesario, E., Fiandra, V., Tesser, R., Di Nuzzi, G., Serio, D. M., et al. (2006). *Patent No. WO 111810A2.*

Smith, J. (1981). *Chemical Engineering Kinetics.* Singapore: McGraw Hill International.

Smith, J., & Van Ness, H. (2005). *Introduction to Chemical Engineering Thermodynamics.* New York: McGraw Hill.

Solvay. (2009). *Chemical technology.Com.* Retrieved may 2009, from http://www.chemical technology.com/solvay-plant

Solvay. (2009). *Chemical-Technology.Com.* Retrieved January 2009, from http://www.chemicals-technology.com/Epichlorohydrin Plant in Thailand

Solvay. (2002). EPichlorohydrin Properties. Solvay Chemical Inc.

Solvay. (2007). *www.solvay.com.* Retrieved April 4, 2009, from http://www.solvay.com/Epicerol Process Receives French Award

Tesser, R., Santacesario, E., Serio, D. M., Nuzzi, D. G., & Fiandra. (2007). Kinetic of Glycerol Chlorination with Hydrochloric Acid: A New Route to 1,3-Dichlorohydrin. *Industrial Engineering Research* , 46:6456-6465.

Thompson, J., & He, B. (2006). Characterization of Crude Glycerol from Biodiesel Production from Multiple Feedstocks. *Applied Engineering Agriculture* , 22(2): 261-265.

Walas, S. (1985). *Measurement of the Thermodynamic Properties of Multiple Phases in Chemical engineering.* Boston: Butterworth.

Wang, Z.-X., Jian, Z., Huiying, F., & Bernard, P. (2001). Glycerol Production by Microbial Fermentation: A Review. *Biotechnology Advances* , 19:201-223.

WHO. (1984). Environmrntal Health Criteria 33. Geneva: International Programe on Chemical Safety.

Wilson, & Charles, E. (1996). Cargill Biodiesel Fuel Earns BQ-9000 Designation. National Petroleum News 98 (12):12.

Yohei, M. (2011). *Patent No. WO2011135785 A1*.

Zhang, J., Lu, Y., Jin, Q., Wang, K., & Luo, G. (2012). Determination of Kinetic Parameters of Dehydrochlorination of Dichloropropanol in a Microreactor. *Chemical Engineering Journal* , 203: 142-147.

Zheng, Y., Chen, X., & Shen, Y. (2008). Commodity Chemicals Derived from Glycerol an Important Biorefinery Feedstock. *Chemical review* , 108:5253-5277.

Appendix A

Calculation Method

A1. Rate Constant (k)

General form of equation for calculating the rate constant (k) of first order is as below:

$$\ln [DCP]_o - \ln [DCP] = kt \quad \text{(A.1)}$$

where $[DCP]_o$ and $[DCP]$are the initial concentration of reactants and concentration of reactant at certain temperature during the reaction respectively.

Example: calculation k value at 50^{o}C. The data for $[DCP]_o$ and $\ln[DCP]$ at certain interval time can be seen in Table A1 as below

Table A1: Data for 50^{o}C

Time (s)	[DCP]o	ln [DCP]o	[DCP]	ln[DCP]	ln [DCP]o-ln[DCP]
0	0.519516	-0.65486	0.519516	-0.65486	0
60			0.33827	-1.08391	0.429054
120			0.233434	-1.45486	0.799998
180			0.16673	-1.79138	1.136519
240			0.121776	-2.10557	1.450715

By plotting $\ln [DCP]_o - \ln[DCP]$ versus t we will have k value as a slope of the linear line , y = 0.056x + 0.041 then k value = 0.056

Analogy with the above method, we can calculate k value for another temperature. All data for 60, 70 and 80^{o}C are shown in Table A2, A3, and A4 respectively.

Table A2: Data for 50^{o}C

Time (s)	[DCP]o	ln [DCP]o	[DCP]	ln[DCP]	ln [DCP]o-ln[DCP]
0	0.514113	-0.66531	0.514113	-0.66531	0.665313158
60			0.269676	-1.31054	1.310535226
120			0.15783	-1.84623	1.84623441
180			0.097426	-2.32866	2.328659539
240			0.061941	-2.78157	2.781572501

Table A3: Data for 70^{o}C

Time (s)	[DCP]o	ln [DCP]o	[DCP]	ln[DCP]	ln [DCP]o-ln[DCP]
0	0.507464	-0.67833	0.507464	-0.67833	0.678329727
60			0.212034	-1.55101	1.551006922
120			0.104719	-2.25648	2.25647776
180			0.055317	-2.89467	2.894672056
240			0.030196	-3.50005	3.50005255

Table A4: Data for 80^{o}C

	[DCP]o	ln [DCP]o	[DCP]	ln[DCP]	ln [DCP]o-ln[DCP]
0	0.5023	-0.68856	0.5023	-0.68856	0.688557731
60			0.055599	-2.88959	2.889590785
120			0.009482	-4.65835	4.658350497
140			0.005344	-5.23178	5.231780682

All values of the rate constant are tabulated in Table A.5 as below

Table A.5: Rate constant, k for reaction between 1,3-DCP and NaOH

Temperature (^{o}C)	k (1stOrder) sec^{-1}
50	0.0056
60	0.008
70	0.012
80	0.021

A2. Energy Activation (E_a)

Arrhenius equation,$lnk = lnA - \frac{Ea}{RT}$, where A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature expressed in K. From the slope of a plot of ln(k) versus 1/T x 10^3 we can estimate the activation energy. The pre-exponential factor A was determined from the y-intercept. Data for k at various temperatures are shown in Tale A6 as below:

Table A.6

t	T	k
50	313	0.0056
60	323	0.008
70	333	0.012
80	343	0.021

Y = -4676 X + 9.699; then $E^a/R = 4676$, substitute R = 8.314 then we have

E^a = 38.54 kJ/mol = 9.25 kcal/mol.

While ln A = 9.699, then exponential factor, A = 1.62 x 10^7/sec

Appendix B

Simulation Raw Data

B.1. Hydrochlorination

B.1.1 Effect of Temperature

Temperature 80^{o}C

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.918967	0	0.090294	0	0	0	0	0
450	0.864738	0.0984435	9.03E-02	0.010651	0.000306	2.18E-06	0.061215	0.003611
900	0.813681	0.19797921	9.03E-02	0.020763	0.001186	8.44E-06	0.11834	0.00701
1350	0.765625	0.29855046	9.03E-02	0.030362	0.002602	1.85E-05	0.171598	0.01021
1800	0.720411	0.40010322	0.090294	0.039477	0.004523	3.22E-05	0.2212	0.013221
2250	0.677868	0.50258064	0.090294	0.048135	0.006911	4.92E-05	0.267369	0.016054
2700	0.637852	0.60593369	0.090294	0.05636	0.009737	6.93E-05	0.310297	0.018719
3150	0.600208	0.71011052	0.090294	0.064179	0.012968	9.23E-05	0.350185	0.021225
3600	0.564791	0.81506209	0.090294	0.071614	0.016573	0.000118	0.387225	0.023584
4050	0.531465	0.92074302	0.090294	0.078689	0.020526	0.000146	0.421595	0.025803
4500	0.500105	1.02711087	0.090294	0.085425	0.024799	0.000177	0.453459	0.027892
4950	0.470594	1.13412663	0.090294	0.09184	0.029369	0.000209	0.48297	0.029857
5400	0.442826	1.24175381	0.090294	0.097954	0.034214	0.000244	0.51027	0.031706
5850	0.416695	1.34995764	0.090294	0.103782	0.039311	0.00028	0.535494	0.033447
6300	0.392109	1.45870597	0.090294	0.109342	0.044642	0.000318	0.558767	0.035084
6750	0.368973	1.5679678	0.090294	0.114648	0.050187	0.000357	0.580209	0.036625
7200	0.347204	1.67771439	0.090294	0.119714	0.05593	0.000398	0.599932	0.038075
7650	0.326719	1.78791836	0.090294	0.124554	0.061853	0.00044	0.618042	0.039439
8100	0.307445	1.89855407	0.090294	0.129181	0.067942	0.000484	0.634639	0.040723
8550	0.289308	2.00959736	0.090294	0.133607	0.074181	0.000528	0.649815	0.041931
9000	0.272242	2.12102542	0.090294	0.137842	0.080558	0.000574	0.663659	0.043068
9450	0.256183	2.23281693	0.090294	0.141898	0.087059	0.00062	0.676253	0.044138
9900	0.241071	2.34495146	0.090294	0.145784	0.093672	0.000667	0.687676	0.045145
10350	0.226852	2.45741044	0.090294	0.14951	0.100388	0.000715	0.697999	0.046092
10800	0.213472	2.57017565	0.090294	0.153085	0.107194	0.000763	0.707294	0.046984
11250	0.200882	2.68323029	0.090294	0.156517	0.114081	0.000812	0.715623	0.047823
11700	0.189035	2.79655903	0.090294	0.159813	0.12104	0.000862	0.723046	0.048612

Temperature 90^{o}C

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC Kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.229742	0	0.022574	0	0	0	0	0
450	0.209234	0.111848	2.26E-02	0.004028	0.000115	2.46E-06	0.02301	0.001504
900	0.190553	0.224357	2.26E-02	0.007729	0.000442	9.47E-06	0.043776	0.002875
1350	0.173545	0.337474	2.26E-02	0.01113	0.000962	2.06E-05	0.062488	0.004123
1800	0.158057	0.451143	0.022574	0.014259	0.001653	3.54E-05	0.079336	0.005259
2250	0.143953	0.565315	0.022574	0.017138	0.002498	5.35E-05	0.094491	0.006294
2700	0.131107	0.679945	0.022574	0.019791	0.00348	7.45E-05	0.108107	0.007236
3150	0.119409	0.794995	0.022574	0.022237	0.004585	9.82E-05	0.120323	0.008094
3600	0.108756	0.910427	0.022574	0.024494	0.005798	0.000124	0.131266	0.008876
4050	0.099054	1.026208	0.022574	0.026579	0.007108	0.000152	0.141052	0.009588
4500	0.090219	1.142307	0.022574	0.028506	0.008504	0.000182	0.149787	0.010237
4950	0.082173	1.258697	0.022574	0.03029	0.009975	0.000214	0.157567	0.010827
5400	0.074845	1.375352	0.022574	0.031943	0.011512	0.000247	0.164479	0.011365
5850	0.068171	1.492249	0.022574	0.033476	0.013108	0.000281	0.170603	0.011855
6300	0.062093	1.609368	0.022574	0.0349	0.014754	0.000316	0.176011	0.012301
6750	0.056558	1.726688	0.022574	0.036224	0.016444	0.000352	0.180769	0.012707
7200	0.051517	1.844194	0.022574	0.037456	0.018171	0.000389	0.184938	0.013077
7650	0.046926	1.961868	0.022574	0.038605	0.019931	0.000427	0.188571	0.013414
8100	0.042744	2.079697	0.022574	0.039678	0.021717	0.000465	0.191719	0.013722
8550	0.038936	2.197667	0.022574	0.040681	0.023526	0.000504	0.194427	0.014001
9000	0.035468	2.315766	0.022574	0.04162	0.025354	0.000543	0.196735	0.014256
9450	0.032309	2.433983	0.022574	0.042501	0.027196	0.000582	0.198682	0.014488
9900	0.029432	2.552309	0.022574	0.043328	0.02905	0.000622	0.200301	0.014699
10350	0.026812	2.670735	0.022574	0.044106	0.030911	0.000662	0.201623	0.014892
10800	0.024426	2.789251	0.022574	0.044839	0.032778	0.000702	0.202678	0.015067

Temperature 100^{o}C

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC Kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.339844	0	0.033392	0	0	0	0	0
450	0.305171	0.166186	3.34E-02	0.006826	0.000303	4.38E-06	0.038188	0.003167
900	0.274043	0.333617	3.34E-02	0.013036	0.001156	1.67E-05	0.071967	0.00601
1350	0.246098	0.502172	3.34E-02	0.018691	0.002488	3.60E-05	0.101798	0.008562
1800	0.22101	0.671739	0.033392	0.023846	0.004233	6.13E-05	0.128101	0.010853
2250	0.198487	0.84222	0.033392	0.028549	0.006335	9.17E-05	0.151251	0.012911
2700	0.178266	1.013524	0.033392	0.032846	0.008742	0.000127	0.171582	0.014758
3150	0.160111	1.185571	0.033392	0.036776	0.011409	0.000165	0.189396	0.016417
3600	0.143811	1.35829	0.033392	0.040373	0.014297	0.000207	0.204961	0.017906
4050	0.129175	1.531614	0.033392	0.043672	0.01737	0.000252	0.218519	0.019243
4500	0.116034	1.705487	0.033392	0.046699	0.020596	0.000298	0.230287	0.020444
4950	0.104235	1.879854	0.033392	0.049482	0.023947	0.000347	0.240457	0.021522

5400	0.09364	2.054669	0.033392	0.052044	0.0274	0.000397	0.249204	0.02249
5850	0.084126	2.22989	0.033392	0.054406	0.030931	0.000448	0.256685	0.02336
6300	0.075582	2.405478	0.033392	0.056586	0.034521	0.0005	0.263037	0.024141
6750	0.06791	2.581399	0.033392	0.058601	0.038155	0.000553	0.268386	0.024842
7200	0.061019	2.757621	0.033392	0.060468	0.041815	0.000606	0.272844	0.025472
7650	0.054832	2.934118	0.033392	0.062199	0.04549	0.000659	0.27651	0.026038
8100	0.049275	3.110863	0.033392	0.063807	0.049167	0.000712	0.279475	0.026546
8550	0.044284	3.287835	0.033392	0.065303	0.052836	0.000765	0.281818	0.027003
9000	0.046353	3.468297	0.033392	0.065075	0.05408	0.000783	0.27639	0.028866
9450	0.035776	3.642379	0.033392	0.067999	0.060117	0.000871	0.284921	0.027781
9900	0.032161	3.819916	0.033392	0.069216	0.063714	0.000923	0.285803	0.028112
10350	0.028913	3.99761	0.033392	0.070355	0.067273	0.000974	0.286309	0.028409
10800	0.025996	4.175446	0.033392	0.071425	0.07079	0.001025	0.286487	0.028677
11250	0.023375	4.353413	0.033392	0.072429	0.07426	0.001076	0.286375	0.028917
11700	0.02102	4.5315	0.033392	0.073374	0.07768	0.001125	0.286013	0.029132
12150	0.018904	4.709697	0.033392	0.074265	0.081046	0.001174	0.285432	0.029326
12600	0.017003	4.887996	0.033392	0.075106	0.084356	0.001222	0.284662	0.0295

Temperature 110^{o}C

Time sec	GLYCEROL Time kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.229742	0	0.022574	0	0	0	0	0
450	0.196417	0.166694	2.26E-02	0.006575	0.000394	5.29E-06	0.036853	0.002804
900	0.167933	0.335103	2.26E-02	0.012302	0.001488	2.00E-05	0.067695	0.005202
1350	0.143584	0.504984	2.26E-02	0.017301	0.003161	4.24E-05	0.093417	0.007251
1800	0.122769	0.676127	0.022574	0.021678	0.005313	7.13E-05	0.11478	0.009003
2250	0.104976	0.848354	0.022574	0.025518	0.007856	1.05E-04	0.13243	0.010501
2700	0.089764	1.021512	0.022574	0.028899	0.010718	0.000144	0.146923	0.011782
3150	0.076758	1.195469	0.022574	0.031885	0.013836	0.000186	0.15873	0.012878
3600	0.065639	1.370116	0.022574	0.03453	0.017159	0.00023	0.168254	0.013814
4050	0.056133	1.545355	0.022574	0.036882	0.020641	0.000277	0.175839	0.014615
4500	0.048006	1.721105	0.022574	0.038982	0.024245	0.000325	0.181779	0.0153
4950	0.041058	1.897296	0.022574	0.040864	0.027939	0.000375	0.186325	0.015885
5400	0.035118	2.073868	0.022574	0.042558	0.031696	0.000426	0.189691	0.016386
5850	0.030039	2.250769	0.022574	0.044089	0.035494	0.000477	0.19206	0.016814
6300	0.025697	2.427956	0.022574	0.045479	0.039314	0.000528	0.193588	0.017181
6750	0.021984	2.60539	0.022574	0.046747	0.043139	0.000579	0.194408	0.017494
7200	0.018809	2.783039	0.022574	0.047908	0.046957	0.00063	0.194635	0.017762
7650	0.016095	2.960876	0.022574	0.048977	0.050757	0.000682	0.194363	0.017991
8100	0.013774	3.138877	0.022574	0.049965	0.054529	0.000732	0.193677	0.018188
8550	0.011789	3.317021	0.022574	0.050882	0.058265	0.000782	0.192647	0.018356
9000	0.010092	3.495291	0.022574	0.051737	0.061959	0.000832	0.191331	0.018499
9450	0.008641	3.673671	0.022574	0.052537	0.065607	0.000881	0.189782	0.018622
9900	0.0074	3.852149	0.022574	0.053289	0.069204	0.000929	0.188043	0.018728
10350	0.006338	4.030714	0.022574	0.053998	0.072746	0.000977	0.18615	0.018818
10800	0.00543	4.209356	0.022574	0.054669	0.076232	0.001024	0.184135	0.018895
11250	0.004653	4.388067	0.022574	0.055306	0.079659	0.00107	0.182025	0.018961

Temperature 120^{o}C

Time sec	GLYCEROL Time kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.223333	0	0.021944	0	0	0	0	0
450	0.178919	0.16237	2.19E-02	0.008711	0.000156	6.77E-06	0.049246	0.003924
900	0.143398	0.328187	2.19E-02	0.015719	0.000566	2.46E-05	0.088376	0.007063
1350	0.114978	0.49676	2.19E-02	0.021365	0.001159	5.04E-05	0.119445	0.009575
1800	0.092235	0.667543	0.021944	0.025919	0.00188	8.17E-05	0.144089	0.011585
2250	0.074029	0.840098	0.021944	0.029598	0.002686	0.00011669	0.16361	0.013195
2700	0.059451	1.014073	0.021944	0.032574	0.003544	0.00015397	0.179052	0.014484
3150	0.047774	1.189189	0.021944	0.034988	0.004428	0.0001924	0.191244	0.015517
3600	0.038417	1.365222	0.021944	0.036948	0.005319	0.00023111	0.200851	0.016345
4050	0.030917	1.541993	0.021944	0.038543	0.006201	0.00026944	0.2084	0.017009
4500	0.024903	1.719358	0.021944	0.039846	0.007063	0.00030692	0.214314	0.017542
4950	0.020079	1.897202	0.021944	0.040911	0.007897	0.00034315	0.218932	0.017969
5400	0.016207	2.075433	0.021944	0.041785	0.008697	0.00037789	0.222521	0.018312
5850	0.013099	2.253978	0.021944	0.042504	0.009457	0.00041094	0.225296	0.018588
6300	0.0106	2.432777	0.021944	0.043097	0.010176	0.00044218	0.22743	0.01881
6750	0.008591	2.611782	0.021944	0.043589	0.010852	0.00047156	0.229059	0.018989
7200	0.006974	2.790955	0.021944	0.043997	0.011485	0.00049905	0.23029	0.019132
7650	0.005671	2.970266	0.021944	0.044338	0.012074	0.00052467	0.231211	0.019248
8100	0.004621	3.149688	0.021944	0.044623	0.012622	0.00054847	0.231888	0.019342
8550	0.003774	3.329203	0.021944	0.044863	0.013129	0.00057051	0.232376	0.019417
9000	0.003089	3.508794	0.021944	0.045065	0.013598	0.00059089	0.232717	0.019479
9450	0.002534	3.688447	0.021944	0.045237	0.014031	0.00060969	0.232946	0.019528

B.2 Effect of Molar Ratio

2:1

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.223333	0	2.19E-02	0	0	0.00E+00	0	0
450	0.178886	0.003806	2.19E-02	0.008718	0.00016	6.94E-06	0.049279	0.003927
900	0.143297	0.011038	2.19E-02	0.015743	0.000594	2.58E-05	0.088463	0.007072
1350	0.114796	0.021013	0.021944	0.021413	0.001245	5.41E-05	0.119571	0.009591
1800	0.091967	0.033183	0.021944	0.025998	0.002065	8.97E-05	0.144221	0.011609
2250	0.073683	0.047113	0.021944	0.029714	0.003018	0.000131	0.163698	0.013226
2700	0.059041	0.062455	0.021944	0.032732	0.004073	0.000177	0.179034	0.014521
3150	0.047315	0.078928	0.021944	0.035191	0.005206	0.000226	0.191058	0.015559
3600	0.037923	0.096308	0.021944	0.037202	0.006399	0.000278	0.200432	0.01639
4050	0.030402	0.114416	0.021944	0.038853	0.007636	0.000332	0.207687	0.017057
4500	0.024378	0.133106	0.021944	0.040217	0.008905	0.000387	0.213248	0.017591
4950	0.019553	0.152265	0.021944	0.041349	0.010198	0.000443	0.217456	0.018019
5400	0.015688	0.171799	0.021944	0.042296	0.011505	0.0005	0.220582	0.018362

5850	0.012592	0.191635	0.021944	0.043093	0.012821	0.000557	0.222846	0.018638
6300	0.010112	0.211714	0.021944	0.043771	0.014142	0.000615	0.224421	0.018859
6750	0.008125	0.231987	0.021944	0.044352	0.015464	0.000672	0.225447	0.019036
7200	0.006532	0.252418	0.021944	0.044856	0.016782	0.00073	0.226036	0.019179
7650	0.005256	0.272975	0.021944	0.045297	0.018096	0.000787	0.226278	0.019294
8100	0.004234	0.293634	0.021944	0.045687	0.019404	0.000844	0.226244	0.019386
8550	0.003414	0.314377	0.021944	0.046037	0.020703	0.0009	0.225992	0.01946
9000	0.002756	0.335186	0.021944	0.046354	0.021993	0.000956	0.225568	0.01952
9445.802	0.002233	0.355855	0.021944	0.046641	0.023261	0.001011	0.225013	0.019568
9455.805	0.002231	0.693892	0.021944	0.046491	0.022228	0.000966	0.22594	0.019567

4:1

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.223333	0	2.19E-02	0	0	0.00E+00	0	0
450	0.178879	0.007103	2.19E-02	0.008719	0.000159	6.92E-06	0.049287	0.003928
900	0.143287	0.017635	2.19E-02	0.015745	0.000593	2.58E-05	0.088474	0.007073
1350	0.114789	0.030911	0.021944	0.021414	0.001242	5.40E-05	0.119581	0.009592
1800	0.091966	0.046384	0.021944	0.025998	0.00206	8.95E-05	0.144226	0.011609
2250	0.073685	0.063616	0.021944	0.029712	0.003009	0.000131	0.163703	0.013226
2700	0.059045	0.082261	0.021944	0.032729	0.004059	0.000176	0.179041	0.014521
3150	0.04732	0.102036	0.021944	0.035187	0.005187	0.000225	0.191069	0.015559
3600	0.037929	0.122718	0.021944	0.037197	0.006373	0.000277	0.200449	0.01639
4050	0.030407	0.144128	0.021944	0.038847	0.007601	0.00033	0.207712	0.017056
4500	0.024383	0.166121	0.021944	0.040209	0.008861	0.000385	0.213282	0.01759
4950	0.019558	0.188583	0.021944	0.04134	0.010143	0.000441	0.2175	0.018019
5400	0.015693	0.211421	0.021944	0.042285	0.011438	0.000497	0.220637	0.018362
5850	0.012596	0.23456	0.021944	0.043081	0.012742	0.000554	0.222912	0.018637
6300	0.010115	0.257943	0.021944	0.043756	0.014049	0.000611	0.2245	0.018859
6750	0.008127	0.28152	0.021944	0.044336	0.015355	0.000668	0.225541	0.019036
7200	0.006534	0.305255	0.021944	0.044837	0.016658	0.000724	0.226146	0.019179
7650	0.005257	0.329117	0.021944	0.045276	0.017955	0.000781	0.226404	0.019293
8100	0.004234	0.353082	0.021944	0.045664	0.019244	0.000837	0.226387	0.019386
8550	0.003414	0.377129	0.021944	0.046011	0.020524	0.000892	0.226152	0.01946
9000	0.002756	0.401244	0.021944	0.046325	0.021794	0.000948	0.225747	0.01952
9445.416	0.002233	0.425168	0.021944	0.046609	0.023039	0.001002	0.225212	0.019568
9455.805	0.002231	0.693892	0.021944	0.046491	0.022228	0.000966	0.22594	0.019567

8:1

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.223333	0	2.19E-02	0	0	0.00E+00	0	0
450	0.178881	0.019855	2.19E-02	0.008719	0.000159	6.91E-06	0.049285	0.003928
900	0.143296	0.043139	2.19E-02	0.015743	0.00059	2.57E-05	0.088467	0.007072
1350	0.114803	0.069169	0.021944	0.02141	0.001235	5.36E-05	0.119572	0.00959
1800	0.091988	0.097397	0.021944	0.025991	0.002044	8.88E-05	0.144217	0.011607
2250	0.073714	0.127387	0.021944	0.029702	0.002979	0.000129	0.163698	0.013223
2700	0.059078	0.158788	0.021944	0.032716	0.004012	0.000174	0.179047	0.014518
3150	0.047356	0.191321	0.021944	0.03517	0.005117	0.000222	0.191091	0.015555
3600	0.037966	0.224762	0.021944	0.037176	0.006276	0.000273	0.200494	0.016386
4050	0.030445	0.258931	0.021944	0.038821	0.007474	0.000325	0.207784	0.017053
4500	0.02442	0.293684	0.021944	0.040178	0.008698	0.000378	0.213388	0.017587
4950	0.019593	0.328907	0.021944	0.041304	0.009939	0.000432	0.217643	0.018015
5400	0.015725	0.364507	0.021944	0.042242	0.01119	0.000486	0.220824	0.018359
5850	0.012625	0.40041	0.021944	0.043032	0.012444	0.000541	0.223147	0.018634
6300	0.010141	0.436556	0.021944	0.0437	0.013697	0.000595	0.224787	0.018856
6750	0.00815	0.4729	0.021944	0.044272	0.014946	0.00065	0.225882	0.019033
7200	0.006554	0.509402	0.021944	0.044765	0.016187	0.000704	0.226545	0.019176
7650	0.005275	0.546032	0.021944	0.045194	0.017418	0.000757	0.226865	0.019291
8100	0.004249	0.582767	0.021944	0.045573	0.018637	0.00081	0.226914	0.019384
8550	0.003426	0.619585	0.021944	0.045909	0.019843	0.000863	0.226748	0.019458
9000	0.002767	0.656472	0.021944	0.046212	0.021036	0.000915	0.226413	0.019518
9450	0.002237	0.693416	0.021944	0.046487	0.022213	0.000966	0.225947	0.019566
9455.805	0.002231	0.693892	0.021944	0.046491	0.022228	0.000966	0.22594	0.019567

16:1

Time sec	GLYCEROL Time Kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.223333	0	0.021944	0	0	0	0	0
450	0.178906	0.102365	2.19E-02	0.008714	0.000157	6.83E-06	0.049259	0.003925
900	0.143357	0.208168	2.19E-02	0.015728	0.000576	2.50E-05	0.088411	0.007067
1350	0.114908	0.316723	2.19E-02	0.021383	0.00119	5.17E-05	0.119496	0.009581
1800	0.092132	0.427483	0.021944	0.025949	0.001946	8.46E-05	0.144144	0.011595
2250	0.073893	0.540009	0.021944	0.029642	0.002804	0.000122	0.163655	0.013207
2700	0.059286	0.653953	0.021944	0.032634	0.003732	0.000162	0.179066	0.014499
3150	0.047586	0.769034	0.021944	0.035065	0.004705	0.000204	0.191205	0.015534
3600	0.038212	0.885028	0.021944	0.037044	0.005703	0.000248	0.200734	0.016364
4050	0.0307	1.001757	0.021944	0.03866	0.006711	0.000292	0.208184	0.017029
4500	0.02468	1.119076	0.021944	0.039985	0.007717	0.000335	0.213978	0.017562
4950	0.019852	1.236872	0.021944	0.041074	0.008712	0.000379	0.218454	0.01799
5400	0.015979	1.35505	0.021944	0.041974	0.009689	0.000421	0.221886	0.018334
5850	0.012871	1.473538	0.021944	0.042721	0.010642	0.000462	0.224488	0.01861
6300	0.010375	1.592277	0.021944	0.043344	0.011569	0.000503	0.226433	0.018832
6750	0.008371	1.711219	0.021944	0.043867	0.012465	0.000542	0.227858	0.01901

7200	0.00676	1.830326	0.021944	0.044308	0.01333	0.000579	0.228875	0.019154
7650	0.005465	1.949569	0.021944	0.044682	0.014161	0.000615	0.229571	0.01927
8100	0.004423	2.068921	0.021944	0.045002	0.014958	0.00065	0.230015	0.019363
8550	0.003585	2.188364	0.021944	0.045278	0.015721	0.000683	0.230264	0.019438
9000	0.002909	2.307882	0.021944	0.045516	0.016449	0.000715	0.230363	0.019499
9450	0.002365	2.427461	0.021944	0.045724	0.017144	0.000745	0.230346	0.019548
9575.62	0.002233	2.460852	0.021944	0.045777	0.017331	0.000753	0.230325	0.01956

24:1

Time sec	GLYCEROL Time kg	HCl kg	MALONIC kg	WATER kg	1,3-D-01 kg	2,3-D-01 kg	1-MCP kg	2-BCP kg
0	0.223333	0	0.021944	0	0	0	0	0
450	0.178919	0.16237	2.19E-02	0.008711	0.000156	6.77E-06	0.049246	0.003924
900	0.143398	0.328187	2.19E-02	0.015719	0.000566	2.46E-05	0.088376	0.007063
1350	0.114978	0.49676	2.19E-02	0.021365	0.001159	5.04E-05	0.119445	0.009575
1800	0.092235	0.667543	0.021944	0.025919	0.00188	8.17E-05	0.144089	0.011585
2250	0.074029	0.840098	0.021944	0.029598	0.002686	0.000117	0.16361	0.013195
2700	0.059451	1.014073	0.021944	0.032574	0.003544	0.000154	0.179052	0.014484
3150	0.047774	1.189189	0.021944	0.034988	0.004428	0.000192	0.191244	0.015517
3600	0.038417	1.365222	0.021944	0.036948	0.005319	0.000231	0.200851	0.016345
4050	0.030917	1.541993	0.021944	0.038543	0.006201	0.000269	0.2084	0.017009
4500	0.024903	1.719358	0.021944	0.039846	0.007063	0.000307	0.214314	0.017542
4950	0.020079	1.897202	0.021944	0.040911	0.007897	0.000343	0.218932	0.017969
5400	0.016207	2.075433	0.021944	0.041785	0.008697	0.000378	0.222521	0.018312
5850	0.013099	2.253978	0.021944	0.042504	0.009457	0.000411	0.225296	0.018588
6300	0.0106	2.432777	0.021944	0.043097	0.010176	0.000442	0.22743	0.01881
6750	0.008591	2.611782	0.021944	0.043589	0.010852	0.000472	0.229059	0.018989
7200	0.006974	2.790955	0.021944	0.043997	0.011485	0.000499	0.23029	0.019132
7650	0.005671	2.970266	0.021944	0.044338	0.012074	0.000525	0.231211	0.019248
8100	0.004621	3.149688	0.021944	0.044623	0.012622	0.000548	0.231888	0.019342
8550	0.003774	3.329203	0.021944	0.044863	0.013129	0.000571	0.232376	0.019417
9000	0.003089	3.508794	0.021944	0.045065	0.013598	0.000591	0.232717	0.019479
9450	0.002534	3.688447	0.021944	0.045237	0.014031	0.00061	0.232946	0.019528
9735.735	0.002238	3.802548	0.021944	0.045332	0.014288	0.000621	0.233045	0.019555

B.2. Dehydrochlorination

B.2.1 Effect of Temperature

296 K

Time sec	1,3-DCP Time kg	WATER kg	OH- kg	EPCH kg
0	0.017422	0	0.00536	0
20	0.014967	0.000343	0.005036	0.001761
40	0.01298	0.00062	0.004775	0.003186
60	0.011344	0.000849	0.004559	0.00436
80	0.009975	0.00104	0.004378	0.005342
100	0.008817	0.001202	0.004226	0.006172
120	0.007828	0.00134	0.004095	0.006882
140	0.006976	0.001459	0.003983	0.007493
160	0.006237	0.001562	0.003885	0.008023
180	0.005591	0.001652	0.0038	0.008486
200	0.005025	0.001731	0.003726	0.008893
220	0.004526	0.001801	0.00366	0.009251
240	0.004084	0.001863	0.003601	0.009568
260	0.003691	0.001918	0.00355	0.009849
280	0.003341	0.001967	0.003504	0.0101
300	0.003028	0.00201	0.003462	0.010325
320	0.002748	0.002049	0.003425	0.010526
340	0.002497	0.002085	0.003392	0.010706
360	0.00227	0.002116	0.003362	0.010869
380	0.002066	0.002145	0.003335	0.011015
400	0.001882	0.00217	0.003311	0.011147
420	0.001716	0.002194	0.003289	0.011267
440	0.001565	0.002215	0.003269	0.011375
460	0.001428	0.002234	0.003251	0.011473
480	0.001304	0.002251	0.003235	0.011562
500	0.001191	0.002267	0.00322	0.011643
520	0.001088	0.002281	0.003206	0.011716
540	0.000995	0.002294	0.003194	0.011783
560	0.00091	0.002306	0.003183	0.011844
580	0.000832	0.002317	0.003173	0.0119
600	0.000762	0.002327	0.003163	0.011951
620	0.000697	0.002336	0.003155	0.011997
640	0.000638	0.002344	0.003147	0.012039
660	0.000584	0.002352	0.00314	0.012078
680	0.000535	0.002359	0.003134	0.012113
700	0.00049	0.002365	0.003128	0.012146
720	0.000449	0.002371	0.003122	0.012175
740	0.000412	0.002376	0.003117	0.012202
760	0.000377	0.002381	0.003113	0.012227
780	0.000346	0.002385	0.003109	0.012249
800	0.000317	0.002389	0.003105	0.01227
820	0.000291	0.002393	0.003101	0.012289
840	0.000266	0.002396	0.003098	0.012306

860	0.000244	0.002399	0.003095	0.012322
880	0.000224	0.002402	0.003093	0.012337
900	0.000205	0.002405	0.00309	0.01235
920	0.000188	0.002407	0.003088	0.012362

304 K

Time sec	1,3-DCP Time kg	WATER kg	OH- kg	EPCH kg
0	0.133669		0.312026	0
20	0.105795		0.284141	0.02788
40	0.085487		0.263824	0.048194
60	0.070116		0.248446	0.063568
80	0.058166		0.236492	0.07552
100	0.048683		0.227005	0.085005
120	0.041036		0.219354	0.092654
140	0.034787		0.213103	0.098904
160	0.029628		0.207941	0.104065
180	0.025331		0.203642	0.108363
200	0.021726		0.200036	0.111968
220	0.018684		0.196993	0.115011
240	0.016105		0.194412	0.117591
260	0.013908		0.192214	0.119789
280	0.01203		0.190336	0.121666
300	0.010421		0.188726	0.123276
320	0.009038		0.187342	0.124659
340	0.007847		0.186151	0.12585
360	0.006819		0.185123	0.126879
380	0.005931		0.184234	0.127767
400	0.005161		0.183464	0.128537
420	0.004495		0.182797	0.129204
440	0.003916		0.182218	0.129783
460	0.003413		0.181715	0.130286
480	0.002976		0.181278	0.130723
500	0.002595		0.180897	0.131104
520	0.002264		0.180566	0.131435
540	0.001976		0.180277	0.131723
560	0.001725		0.180026	0.131974
580	0.001505		0.179806	0.132194
597.419	0.001338		0.179639	0.132362

314 K

Time sec	1,3-DCP Time kg	WATER kg	OH- kg	EPCH kg
0	0.131941		0.307991	0
20	0.095561		0.271596	0.036388
40	0.07173		0.247755	0.060224
60	0.055129		0.231147	0.076829
80	0.043089		0.219102	0.088872
100	0.034095		0.210104	0.097868
120	0.027227		0.203233	0.104737
140	0.021896		0.197901	0.110069
160	0.017707		0.193709	0.114259
180	0.014382		0.190384	0.117585
200	0.011723		0.187723	0.120245
220	0.009583		0.185582	0.122386
240	0.007851		0.183849	0.124118
260	0.006444		0.182442	0.125525
280	0.005296		0.181294	0.126673
300	0.004358		0.180355	0.127612
320	0.003589		0.179585	0.128381
340	0.002958		0.178954	0.129012
360	0.00244		0.178435	0.12953
380	0.002013		0.178009	0.129957
400	0.001662		0.177658	0.130308
420	0.001372		0.177368	0.130598
424.044	0.00132		0.177316	0.13065

322 K

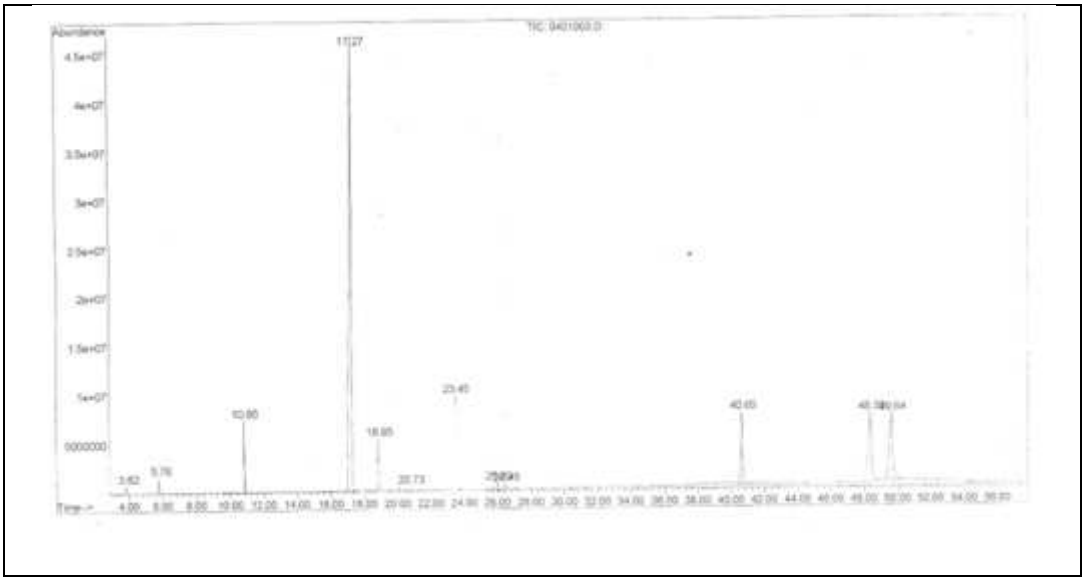
Time sec	1,3-DCP Time kg	WATER kg	OH- kg	EPCH kg
0	0.130598		0.304857	0
20	0.055104		0.229331	0.075511
40	0.027306		0.201522	0.103315
60	0.014456		0.188666	0.116168
80	0.007905		0.182112	0.122721
100	0.004396		0.178602	0.126231
120	0.002465		0.176671	0.128162
140	0.001389		0.175594	0.129238
142.1414	0.001307		0.175511	0.12932

332 K

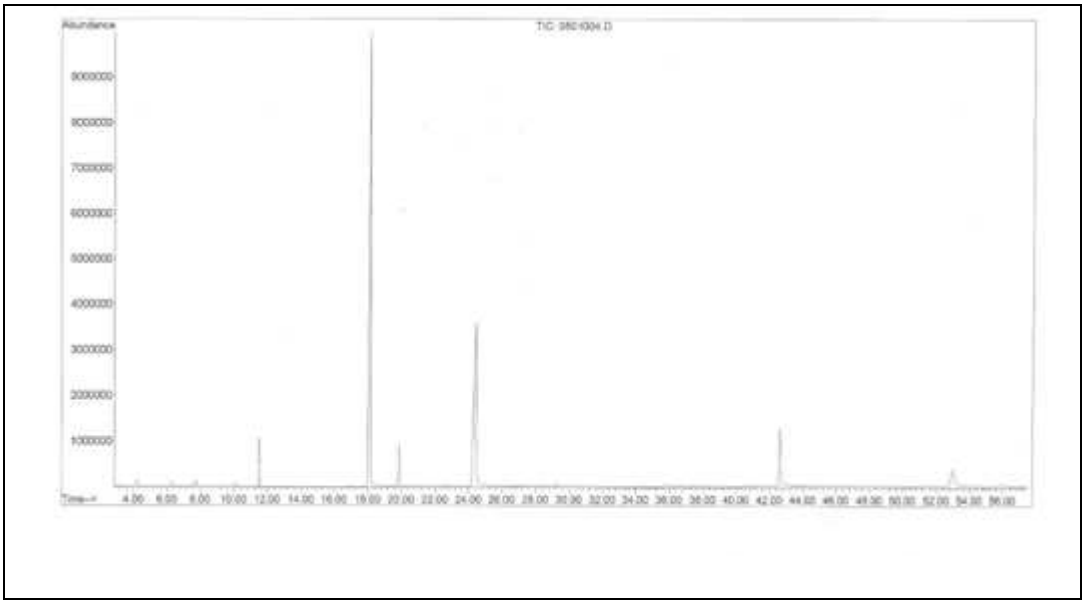
Time sec	1,3-DCP Time	WATER	OH-	EPCH
	kg	kg	kg	kg
0	0.128761		0.300568	0
20	0.020928		0.192689	0.107857
40	0.004857		0.176612	0.123931
60	0.001294		0.173047	0.127496

Appendix C

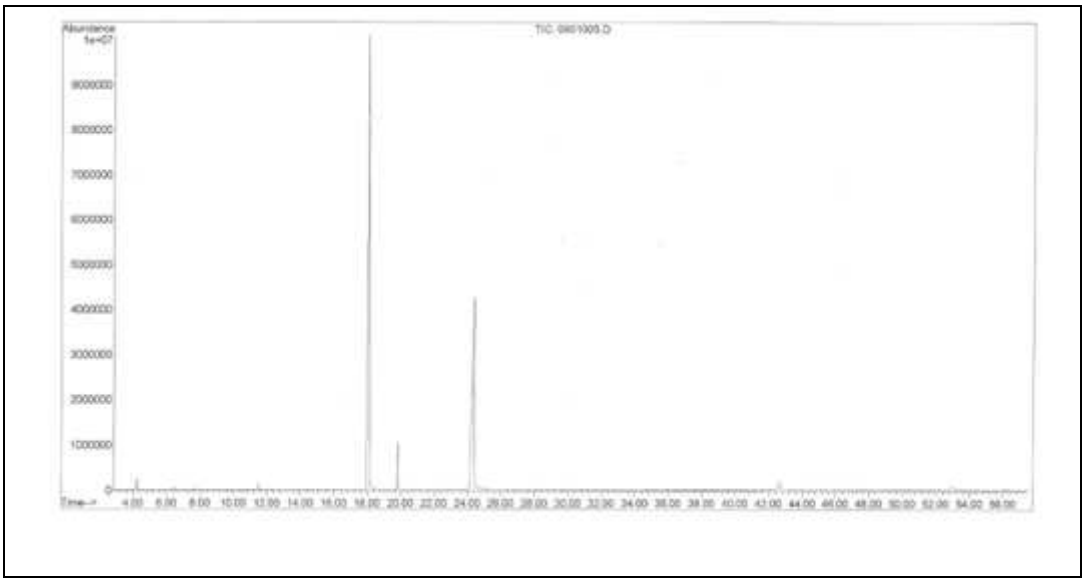
Gas Analysis



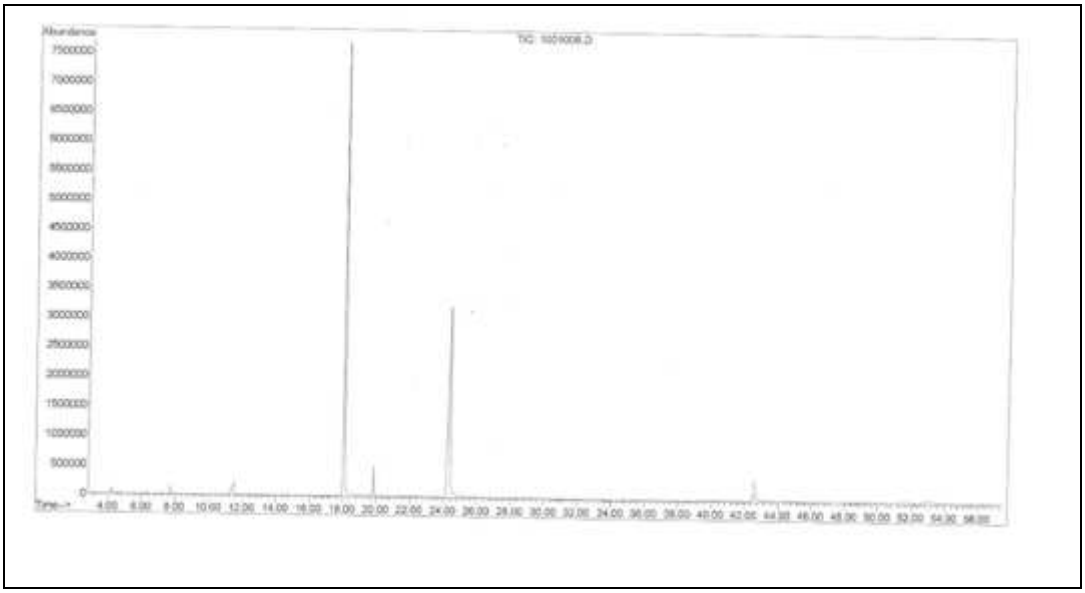
T = 70°C



T =80°C



T = 90^{o}C



T = 100^{o}C

Lab doping Library Search Report

Data Path : C:\msdchem\1\DATA\110812-a\
Data File : 02.D
Acq On : 12 Aug 2011 15:42
Operator : rgt
Sample : 70 oC
ALS Vial : 1 Sample Multiplier: 1

Search Libraries: C:\Database\W8NO8.L Minimum Quality: 100

Unknown Spectrum: Apex
Integration Events: ChemStation Integrator – events.e

Pk#	RT	Area %	Library/ID	Ref#	CAS#	Qual
1	11.460	1.67	C:\Database\W8NO8.L			
			1,2-propanediol, 3-chloro- $$.alpha,-monochlorohydrin $$ Glycerin epichlorohydrin	131536	000096-23-1	83
			1,2-Propanediol, 3-chloro-$$ .alpha. –Chlorohydrin $$ Glycerin .alpha.-monochlorohydrin $$Glycerin epichlorohydrin	131539	000096-23-1	83
			1,2-PROPANEDIOL, 3-CHLORO-$$ 3-CHLOROPROPANE-1,2-DIOL $$ (+-)-2,3-DIHYDROXYCHLOROPROPANE $$.ALPHA,-CHLOROHYDRIN	131545	000096-23-1	83
2	18.014	92.45	C:\Database\W8NO8.L			
			2-Propanol, 1.3-dichloro- $$ .alpha.-Dichlorohydrin $$ .alpha., .gamma. – Dichlorohydrin $$ S-Dichloroisopropyl alcohol	43247	000096-24-2	90
			2-Propanol, 1,3-dichloro- $$ .alpha. Dichlorohydrin $$ .alpha., gamma. –Dichlorohydrin $$ S-Dichloroisopropyl alcoholl	43245	000096-24-2	90
			2-PROPANOL, 1,3-DICHLORO- $$ 1,3-DICHLOROPROPAN-2-OL $$ .ALPHA., GAMMA. –DICHLOROHYDRIN $$ .ALPHA. -DICHLOROHYDRIN	43248	000096-24-2	90
3	19.761	5.88	C:\Database\W8NO8.L			
			1-CHLOROETHENE $$ ETHENE, CHLORO- $$ CHLOROETHENE $$ CHLOROETHYLEN	87150	000075-01-4	83
			Ethene, chloro- $$ Ethylene, chloro- $$ Chloroethene $$ Chloroethylene	87141	000075-01-4	83
			1-Propanol, 2,3-dichloro- $$ .alpha., ,beta.-Dichlorohydrin $$ .beta. –Dichlorohydrin $$ Glycerol .alpha.,.beta. -dichlorohydrin	87204	000616-23-9	83

PRDIADHA.M Tue Aug 16 09:19:43 2011

Lab doping Library Search Report

Data Path : C:\msdchem\1\DATA\110812-a\
Data File : 03.D
Acq On : 12 Aug 2011 16:43
Operator : rgt
Sample : 80°C
ALS Vial : 2 Sample Multiplier: 1

Search Libraries: C:\Database\W8NO8.L Minimum Quality: 100

Unknown Spectrum: Apex
Integration Events: ChemStation Integrator – events.e

Pk#	RT	Area %	Library/ID	Ref#	CAS#	Qual
1	4.060	89.58	C:\Database\W8NO8.L			
			epichlorohydrin Glycerin epichlorohydrin	131539	000096-23-1	83
			1,2-Propanediol, 3-chloro-$$ .alpha. –Chlorohydrin $$ Glycerin .alpha.-monochlorohydrin $$Glycerin epichlorohydrin	131536	000096-23-1	83
			1,2-PROPANEDIOL, 3-CHLORO-$$ 3-CHLOROPROPANE-1,2-DIOL $$ (+-)-2,3-DIHYDROXYCHLOROPROPANE $$.ALPHA,-CHLOROHYDRIN	131545	000096-23-1	83
2	18.076	89.55	C:\Database\W8NO8.L			
			2-Propanol, 1.3-dichloro- $$ .alpha.-Dichlorohydrin $$ .alpha., .gamma. –Dichlorohydrin $$ S-Dichloroisopropyl alcohol	43247	000096-24-2	78
			2-Propanol, 1,3-dichloro- $$ .alpha. Dichlorohydrin $$ .alpha., gamma. –Dichlorohydrin $$ S-Dichloroisopropyl alcoholl	19383	000096-24-1	78
			2-PROPANOL, 1,3-DICHLORO- $$ 1,3-DICHLOROPROPAN-2-OL $$ .ALPHA., GAMMA. –DICHLOROHYDRIN $$ .ALPHA. -DICHLOROHYDRIN	43245	000096-24-2	78
3	19.761	6.88	C:\Database\W8NO8.L			
			1-CHLOROETHENE $$ ETHENE, CHLORO- $$ CHLOROETHENE $$ CHLOROETHYLEN	87208	000616-23-9	83
			Ethene, chloro- $$ Ethylene, chloro- $$ Chloroethene $$ Chloroethylene	87204	000616-23-9	83
			1-Propanol, 2,3-dichloro- $$ .alpha., ,beta.-Dichlorohydrin $$ .beta. –Dichlorohydrin $$ Glycerol .alpha.,.beta. -dichlorohydrin	87150	000075-01-4	83

PRDIADHA.M Tue Aug 16 09:20:01 2011

Lab doping Library Search Report

Data Path : C:\msdchem\1\DATA\110812-a\
Data File : 04.D
Acq On : 12 Aug 2011 17:45
Operator : rgt
Sample : 90 oC
ALS Vial : 3 Sample Multiplier: 1

Search Libraries: C:\Database\W8NO8.L Minimum Quality: 100

Unknown Spectrum: Apex
Integration Events: ChemStation Integrator – events.e

Pk#	RT	Area %	Library/ID	Ref#	CAS#	Qual
1	4.200	1.39	C:\Database\W8NO8.L			
			2-Propanone, 1-hydroxy- $$ Acetol $$ CH3C (O)CH2OH $$ Hydroxyacetone	18195	000116-09-9	59
			1-HYDROXYACETONE $$ 2-PROPANONE, 1-HYDROXY- $$ 1-HYDROXY-2-PROPANONE $$ 2-KETOPRYL ALCOHOL	18216	000116-09-6	59
			2-Propanone, 1-hydroxy- $$ Acetol $$ CH3C(O) CH2OH $$ Hydroxtacetone	18188	000116-09-6	45
2	18.076	89.55	C:\Database\W8NO8.L			
			2-Propanol, 1.3-dichloro- $$ .alpha.-Dichlorohydrin $$ .alpha., .gamma. – Dichlorohydrin $$ S-Dichloroisopropyl alcohol	43248	000096-24-2	90
			2-Propanol, 1,3-dichloro- $$ .alpha. Dichlorohydrin $$ .alpha., gamma. –Dichlorohydrin $$ S-Dichloroisopropyl alcoholl	43245	000096-24-2	90
			2-PROPANOL, 1,3-DICHLORO- $$ 1,3-DICHLOROPROPAN-2-OL $$ .ALPHA., GAMMA. –DICHLOROHYDRIN $$ .ALPHA. -DICHLOROHYDRIN	43247	000096-24-2	90
3	19.761	6.88	C:\Database\W8NO8.L			
			1-CHLOROETHENE $$ ETHENE, CHLORO- $$ CHLOROETHENE $$ CHLOROETHYLEN	87150	000075-01-4	83
			Ethene, chloro- $$ Ethylene, chloro- $$ Chloroethene $$ Chloroethylene	87180	000497-04-1	83
			1-Propanol, 2,3-dichloro- $$ .alpha., ,beta.-Dichlorohydrin $$ .beta. –Dichlorohydrin $$ Glycerol .alpha.,.beta. -dichlorohydrin	552	000075-01-4	83

PRDIADHA.M Tue Aug 16 09:20:19 2011

Lab doping Library Search Report

Data Path : C:\msdchem\1\DATA\110812-a\
Data File : 05.D
Acq On : 12 Aug 2011 18:46
Operator : rgt
Sample : 100 oC
ALS Vial : 4 Sample Multiplier: 1

Search Libraries: C:\Database\W8NO8.L Minimum Quality: 100

Unknown Spectrum: Apex
Integration Events: ChemStation Integrator – events.e

Pk#	RT	Area %	Library/ID	Ref#	CAS#	Qual
1	4.200	1.68	C:\Database\W8NO8.L			
			2-Propanone, 1-hydroxy- $$ Acetol $$ CH3C (O)CH2OH $$ Hydroxyacetone	18216	000116-09-6	59
			1-HYDROXYACETONE $$ 2-PROPANONE, 1-HYDROXY- $$ 1-HYDROXY-2-PROPANONE $$ 2-KETOPRYL ALCOHOL	18195	000116-09-6	59
			2-Propanone, 1-hydroxy- $$ Acetol $$ CH3C(O) CH2OH $$ Hydroxtacetone	18188	000116-09-6	45
2	18.052	89.92	C:\Database\W8NO8.L			
			2-Propanol, 1.3-dichloro- $$ .alpha.-Dichlorohydrin $$ .alpha., .gamma. – Dichlorohydrin $$ S-Dichloroisopropyl alcohol	43249	000096-24-2	83
			2-Propanol, 1,3-dichloro- $$ .alpha. Dichlorohydrin $$ .alpha., gamma. –Dichlorohydrin $$ S-Dichloroisopropyl alcoholl	43246	000096-24-2	78
			2-PROPANOL, 1,3-DICHLORO- $$ 1,3-DICHLOROPROPAN-2-OL $$ .ALPHA., GAMMA. –DICHLOROHYDRIN $$ .ALPHA. -DICHLOROHYDRIN	43246	000096-24-2	78
3	19.761	8.40	C:\Database\W8NO8.L			
			1-CHLOROETHENE $$ ETHENE, CHLORO- $$ CHLOROETHENE $$ CHLOROETHYLEN	87180	000497-04-1	83
			Ethene, chloro- $$ Ethylene, chloro- $$ Chloroethene $$ Chloroethylene	87150	000075-01-4	83
			1-Propanol, 2,3-dichloro- $$ .alpha., ,beta.-Dichlorohydrin $$ .beta. –Dichlorohydrin $$ Glycerol .alpha.,.beta. - dichlorohydrin	87141	000075-01-4	83

PRDIADHA.M Tue Aug 16 09:20:40 2011

BIODATA OF STUDENT

Herliati was born on 14th September 1969 in Palembang, Indonesia. She received her first degree in Bachelor of Chemical Engineering from Department of Chemical Engineering, Faculty of Technology, Universitas Sriwijaya (UNSRI) in year 1993. She then continued her study for Master of Chemical Engineering at Department of Chemical Engineering, Faculty of Technology, Universitas Indonesia (UI) and graduated in 2003. Following the author's graduation, she enrolled as a full time candidate for Doctor of Philosophy in the same field as previous of Chemical Engineering, at the department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia (UPM) in December 2006. She is as a senior lecturer at Universitas Jayabaya Jakarta since 1994.

LIST OF PUBLICATIONS

The articles that were published and submitted by the author during her PhD study are as follows:

Journal Publication

1. Robiah Yunus, **Herliati**, A.S. Intan & Z.Z.Abidin, Dzulkefly Kuang. Preliminary Design of Semi-Batch Reactor for Synthesis 1,3-Dichloro-2-Propanol Using Aspen Plus, *International Journal of Chemistry* 3 (1): 196-201, 2011

Proceeding Publications

1. **Herliati**, Robiah Yunus, A.S. Intan, Z.Z.Abidin, Dzulkefly Kuang. Preliminary design Of Semi-Batch Reactor For 1,3-Dichloro-2-propanol Production from Natural Glycerol. *Symposium of Malaysian Chemical engineers (SOMChe) in conjunction with Regional Symposium on Chemical Engineering* (*RSCE),* 689-698, 2008.

2. **Herliati**, Robiah Yunus, A.S. Intan, Z.Z.Abidin, Dzulkefly Kuang. Simulation of Epichlorohydrin Synthesis from Dichloropropanols in Reactive Distillation Column Using Aspen Plus. *International Conference on Quality in Research (QIR) in conjunction with ICSERA*, 39-42, 2011

3. **Herliati**, Robiah Yunus, Dzulkefly Kuang, Lubena. Direct Preparation of Dichloropropanol from Glycerol Biodiesel Based Using HCl 37%: a Preliminary Study. *International Seminar on Energy Science and Technology*, 295-301, 2011