

Kinetics of Epichlorohydrin synthesis using Dichloropropanol and Sodium Hydroxide

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Abstract

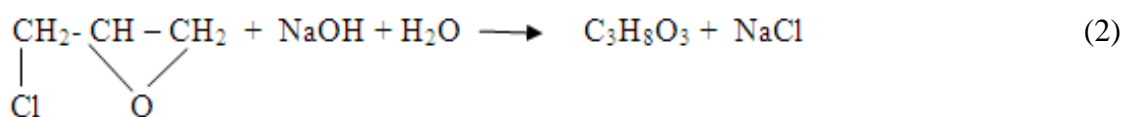
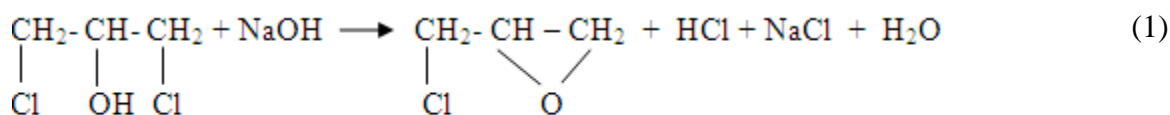
Conventionally epichlorohydrin (EPCH) is made by chlorohydrination of allyl chloride obtained from high-temperature chlorination of propylene. Unfortunately, the method produces a large amount of chlorinated by-products and consumes loads of energy due to high operating temperature. An alternative approach for the production of epichlorohydrin would be to use glycerol from biodiesel production plant. Epichlorohydrin is made by dehydrochlorination of 1,3-dichloropropanol (1,3-DCP) obtained from hydrochlorination of glycerol with aqueous hydrogen chloride. Experimental study on dehydrochlorination reaction was carried out under operating temperatures ranged from 50 to 80°C and reactant molar ratio from 1:1 to 1:12. The optimal reaction conditions were: temperature, 70°C; reactant molar ratio, 1:5 and duration, 10 minutes. Kinetics of dehydrochlorination was then studied in the presence of excess sodium hydroxide solution. The reaction kinetics conformed to pseudo first order with respect to dichloropropanol concentration. The activation energy of the reaction was determined at 38.8 kJ/mol and the pre-exponential factor A was at $1.62 \times 10^7 \text{ sec}^{-1}$. Quantitative analyses of the reaction products were performed using GC-MS.

Keywords: Epichlorohydrin, Dichloropropanol, Dehydrochlorination, Kinetics study, Muriatic acid

1. Introduction

Epichlorohydrin, an organochlorine compound and an epoxide, is commonly used as a raw material in producing several synthetic materials, including epoxy, phenoxy, and polyamide resins, polyether rubber, synthetic glycerin, glycidyl ethers, polythiols, elastomers, surfactants, plasticizers, dyestuffs, pharmaceutical products, oil emulsifiers, lubricants, and adhesives. Other applications of epichlorohydrin are solvent for resins, gums, cellulose, esters, paints, and lacquers. Epichlorohydrin is also widely used as a stabilizer in chlorine-containing substances such as rubber, pesticide formulations, and solvents (Anonymous, 2011). Conventionally (A & Kerkhof, 1994), epichlorohydrin is made by chlorohydrination of allyl chloride, which is obtained by high-temperature chlorination of propylene (Nagato, Mori, Maki, & Ishioka, 1987). 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 (Siano, et al., 2006). Today, the glycerol is in abundance as by-product of biodiesel, thus has provided an opportunity to synthesize epichlorohydrin from glycerol by adding some basic solution. The two-step process, which utilizes glycerol as a feedstock was firstly developed by Solvay's, called Epicerol® technology (Clark & Hartman, 1941), (Plant, 2009), . The first step is the direct hydrochlorination process between glycerol and hydrochloric acid to produce dichloropropanol. The second step is the dehydrochlorination of dichloropropanol obtained from the first step with basic solution, generating the final product, epichlorohydrin (Santacesaria, Tesser, Serio, Casale, & Verde, 2010). Glycerol used in the Solvay process was the byproduct from biodiesel production from rapeseed oil.

Kinetics parameters for the reactions using sodium hydroxide is still lacking but crucial for the design of dehydrochlorination reactor. However, Carra et al. [8] reported the dehydrochlorination kinetics using calcium hydroxide while Ma et al. [9] focused on the kinetics of the side reaction of epichlorohydrin i.e. hydrolysis. In this study, we focus on the second step, the dehydrochlorination reaction between dichloropropanol and sodium hydroxide (Scheme 1) (Ma, Zhu, & Yuan, 2007). Our earlier study on Aspen Plus simulation investigated the effects of process parameters such as temperature and reactant molar ratio on the reaction (Herliati, Yunus, ZZ, & A.S, 2011). The study reported that the second reaction was very fast and could be completed in approximately 4 minutes. The simulation also generated some interesting results for setting the experimental design, pressure, temperature range, molar ratio of reactants, and duration of reaction. The parameters used in simulation can be seen in Table 2.



Scheme 1

2. Materials and methods

2.1 Chemicals

Commercially available sodium hydroxide and 1,3-dichloropropanol were purchased from Merck Chemical Co. While 1,3-dichloropropanol for GC standard calibration was obtained from Sigma Aldrich Co. Singapore.

2.2 Isothermal Experiment

The above-mentioned reactions were carried out in a three-neck flask (500-ml), which was immersed in 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 needed to control the reactor temperature and the mixture inside the reactor was stirred by the magnetic stirred vigorously. The reactor was fed with the base solution, which contains certain amount of sodium hydroxide then the temperature was increased to the desired temperature. When the intended reaction temperature was reached, a known fixed amount of the organic reagent, dichloropropanol, was poured into the reactor-containing base solution. The 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 moles of OH^- during the reaction [14].

The five different reaction temperatures were applied namely 50, 60, 70, and 80°C to investigate the effect of temperature on the reaction rate constants. While 5 different molar ratios 1:1, 1:2, 1:4, 1:6, 1:9 were chosen to investigate the effects of excess NaOH on reaction conversion and yield. The stoichiometric ratio between 1,3 DCP and NaOH is 1:1. 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, in order to stop reaction then the hydrolysis of epichlorohydrin can be prevented. Samples were analyzed for 1,3-dichloropropanol, 1,2-dichloropropanol, and epichlorohydrin by Gas chromatography (GC). Carra et al (Ma, Zhu, & Yuan, 2007) and the earliest study by Zhang et al. (Zhang, Zhang, Lu, Jin, Wang, & Luo, 2012) also used GC method to monitor rate of the reaction. Equations 3 and 4 were used to calculate the conversion of 1,3-DCP and yield of EPCH respectively:

$$\text{Conversion of glycerol (\%)} = \frac{\text{Moles of 1,3-DCP reacted}}{\text{Moles of 1,3-DCP supplied}} \times 100$$

(3)

$$\text{Yield for EPCH (\%)} = \frac{\text{Moles of EPCH produced}}{\text{Moles of 1,3-DCP supplied}} \times 100 \quad (4)$$

2.3 Model development

Kinetics of dehydrochlorination was studied in the presence of sodium hydroxide solution at various temperatures. According to Ma et al. (Ma, Zhu, & Yuan, 2007), and Zhang et al. (Zhang, Zhang, Lu, Jin, Wang, & Luo, 2012) dehydrochlorination of 1,3-DCP in aqueous basic solution is a fast occurring reaction. However, the competing hydrolysis reaction may have taken place, as shown in Equation 2, when the operating temperature reaction was higher than 80°C, presence of excessive base solution and longer reaction time (Ma, Zhu, & Yuan, 2007). The experiments were conducted to determine the kinetics parameters such as reaction rate constants and activation energies for the reactions as shown in Scheme 1. The stoichiometric molar ratio between the dichloropropanol and sodium hydroxide is 1:1. In the analysis of kinetic study, molar ratio of 1:9 was used throughout the experiments. This is to ensure that the rate of reaction was not influenced by the sodium hydroxide concentration (Smith, 1981). The effects of molar ratio dichloropropanol:NaOH on the conversion to epichlorohydrin was conducted at 60°C.

According to Ma et al. (Ma, Zhu, & Yuan, 2007), dehydrochlorination of dichloropropanol with sodium hydroxide is a second order irreversible reaction then the rate equation can be written as follows:

$$-r_{epy} = -\frac{d[DCP]}{dt} = k[DCP]^\alpha [OH^-]^\beta \quad (5)$$

where [1,3-DCP] and [OH⁻] are concentration of 1,3-DCP and OH⁻, respectively.

In this study, we did not consider the formation of 2,3-DCP as an isomer of 1,3-DCP because pure 1,3-DCP (99.9%) was used [17]. Moreover, based on observation studied by Ma et al. [9], 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. Both halogenoalkyls in 1,3-DCP increased the chlorine mobility or the negative charge on the oxygen [18]. Thus, the hydroxyl could attack 1-C and 3-C, but 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 [19]. Furthermore, it is harder for the hydroxyl to attack 2-C in 2,3-DCP due to the space effect [9], which does not even exist in 1,3-DCP. In order to determine the kinetic parameters, the concentration of OH⁻ used was used in large excess, 10 times the initial concentration of 1,3-DCP. Thus, [OH⁻] can be assumed zero order, and the rate law can be described by a pseudo-first-order kinetic model (Smith, 1981), (Laidler, 1987):

$$-r_{epy} = -\frac{d[DCP]}{dt} = k[DCP] \quad (6)$$

3. Results and discussion

3.1 Effect of molar ratio

Following the Le'Chatelier principle, one of the methods to promote a forward reaction as depicted in Equation 1 is by using one of the reactants in excess. Since NaOH is relatively cheaper compared to organic compound dichloropropanol, the reaction was subjected to excess sodium hydroxide. The stoichiometric molar ratio between the dichloropropanol and sodium hydroxide was 1:1.

The effects of molar ratio dichloropropanol:NaOH on the conversion moles of DCP consumed over moles of 1,3-DCP fed to epichlorohydrin was conducted at 60°C and is shown in Fig. 1 and 2. These two figures showed that increasing molar ratio 1,3-DCP:NaOH from stoichiometric to 1:6 can improve the conversion of the reaction. After that there was no benefit of increasing molar ratio where conversion nearly remained constant since the reaction has reached its chemical equilibrium. This result also compared well with the simulation analysis using Aspen Plus as shown in Fig. 2.

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

The effect of molar ratio on yield of epichlorohydrin is shown in Fig. 3 and 4. The results clearly indicate that excessive use of base solution in the dehydrochlorination reaction enhances the hydrolysis of epichlorohydrin, thus lower the yield of epichlorohydrin significantly. The results were also in good agreement with the Aspen Plus simulation results as depicted in Fig. 4.

3.2 Effect of temperature

The effect of temperature on the conversion of 1,3-DCP within the range of 50 – 80°C is shown in Fig. 5. Fig. 6 appraised the effect of temperature on the conversion after 5 minutes of reaction time. Under the operating conditions employed in this study, we can see that the reaction rate was slightly improved as the temperature was increased to 70°C. On the contrary, Ma et al. (Ma, Zhu, & Yuan, 2007) did not find any marked effect of temperature on process performance. Figure 6 also shows that there is no marked improvement on conversion by increasing the temperature above 70°C.

The occurrence of hydrolysis reaction of epichlorohydrin to glycerol may have taken place at temperature above 70°C, thus lowered the yield of epichlorohydrin. The simulation study also confirmed that conducting the reaction above 70°C (343 °K) should be avoided due to the hydrolysis reaction. This finding was in good agreement with the reported data by Ma et al. They concluded that at temperature above 70°C, the hydrolysis reaction may have taken place of which would lower the yield of epichlorohydrin. This study compared well with our earlier simulation study as shown in Fig. 6.

Furthermore, Fig. 7 and 8 illustrated the influence of temperature on the yield of epichlorohydrin at end of reaction. Again, it exhibited similar behavior as the conversion described earlier. These figures showed that the yield of epichlorohydrin was relatively low at 50°C and then increased with temperature up to 70°C. However at temperature above

70°C, the side hydrolysis reaction of epichlorohydrin to glycerol would have been occurred. The insights into the occurrence of this hydrolysis reaction would be further exemplified in the forthcoming kinetics study. However, the peak in the GC chromatogram confirmed the formation of glycerol from the hydrolysis described above as shown in Figure 8.

The results were in good agreement with the Aspen Plus simulation data as can be seen in Fig. 9. Since Ma et al. (Ma, Zhu, & Yuan, 2007) did not study the effect of temperature on product composition, but this study has provided new insights on the effect of temperature on dehydrochlorination of 1,3-DCP to epichlorohydrin.

3.3 Reaction kinetics

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. To analyze the kinetics of dehydrochlorination of 1,3-DCP with sodium hydroxide, two kinetics models including the pseudo-first-order and second-order were used. Linear equations of these models can be seen in Eq. (7) and (8). The parameter, reaction rate constants, in these models (pseudo first and second-order) were estimated from the slope of the linear plot [20].

$$\ln[1,3 - DCP]_o - \ln[1,3 - DCP] = kt \quad (7)$$

$$1/[1,3 - DCP] - 1/[DCP]_o = kt \quad (8)$$

A straight-line plot, as shown in Fig. 10, supports our hypothesis that the dehydrochlorination of 1,3-DCP and sodium hydroxide follows the first order kinetics model with higher value correlation coefficient ($R^2 > 0.99$), compared to the second order model, ($R^2 < 0.90$). The reaction rate constants, k at various temperatures, 50 to 80°C, were obtained from the slopes of these lines and tabulated in Table 1. The indicator which also was used to determine the goodness of fit kinetic models was total sum squared error (SSE) [21]. In this study we found that SSE for the pseudo first order kinetic at 50 – 80°C were 0.00319, 0.00243, 0.00619 and 0.00511 for the total 0.0169 while the SSE for the second order kinetic were 0.1005, 0.0334, 0.401 and 0.249 for the total 0.783. The comparisons of SSE confirm that dehydrochlorination of 1,3-DCP with sodium hydroxide to produce epichlorohydrin fits well with pseudo first order kinetic model.

Table 1 explains the dependence of the rate constant, k , on temperature, T , for the dehydrochlorination of 1,3-DCP. The dependency of rate constant, k , on temperature follows the Arrhenius Equation (Smith, 1981):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

Where A is the frequency factor, E_a is the activation energy for the reaction, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature expressed in K . From the slope of a plot of $\ln(k)$ versus $1/T \times 1000$ we can estimate the activation energy by multiply the negative slope with the universal gas constant. The frequency factor A was determined from the exponential value of y -intercept. Both A and E_a are very useful kinetic parameters to be known because the rate constants can be determined for any temperature once these two parameters are known. The plot of $\ln(k)$ versus $1/T \times 1000$ is shown in Fig. 11.

The activation energy E_a obtained from the plot was 38.8 kJ/moles and the frequency factor A was $1.62 \times 10^7 \text{ sec}^{-1}$. Ma et al. (Ma, Zhu, & Yuan, 2007) reported the activation

energy for the reaction involved in the dehydrochlorination of dichloropropanol with $\text{Ca}(\text{OH})_2$ of which the value of A and E_a are at 10^7 sec^{-1} and 49.18 kJ/mol respectively. 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. The Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$, shows that k value will be higher when the activation energy is lower therefore the rate of reaction proceed faster. In this study, since the activation energy obtained was slightly lower compared to reporting by Ma et al. (Ma, Zhu, & Yuan, 2007) then it may be a reason that time of our reaction to completion the reaction was slightly faster.

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

$$r = 1.62 \times 10^7 e^{-38.8/RT} [\text{DCP}] \quad (10)$$

4. Conclusions

The reaction kinetics of dehydrochlorination of dichloropropanol and sodium hydroxide to epichlorohydrin was investigated. The effect of temperatures (50 to 80°C) on such reaction was observed where the optimum temperature was found to be 70°C. The effect of molar ratio 1,3-DCP:NaOH was also investigated where the best molar ratio in terms of conversion and in terms of yield were found at 1:5 and stoichiometric ratio, respectively. For the kinetic study we used sodium hydroxide in excess 1:10, then reaction rate was found to follow pseudo first order with respect to dichloropropanol concentration. The activation energy of the reaction was also determined at 38.8 kJ/mol and the pre-exponential factor A was at $1.62 \times 10^7 \text{ sec}^{-1}$. The reaction completion was achieved only after 2 minutes of reaction. Under these mild reaction conditions, the occurrence of the competing hydrolysis reaction can be suppressed.

Acknowledgements

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Table 1

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

Temperature (°C)	k (1 st Order) sec ⁻¹	k (2 nd Order) Lmol ⁻¹ sec ⁻¹
50	0.0056	0.026
60	0.008	0.058
70	0.012	0.126
80	0.021	1.243

Table 2: Required Parameters used in the Simulation of dehydrochlorination Reaction [13]

Parameter	Information
Reactor Block	RBatch
Base Method	Wilson
Input Variable	
Temperature (°C)	20 to 60
Pressure (bar)	1.05
Chemical reactions	Scheme 1
Kinetics data	
A, s ⁻¹	10 ⁷
E _a , kJ/mole	49.21
Feed of Reactor	
Reactan mol ratio (1,3-DCP to NaOH))	1:1; 1:1.5; 1:2.3; 1:4; 1: 9

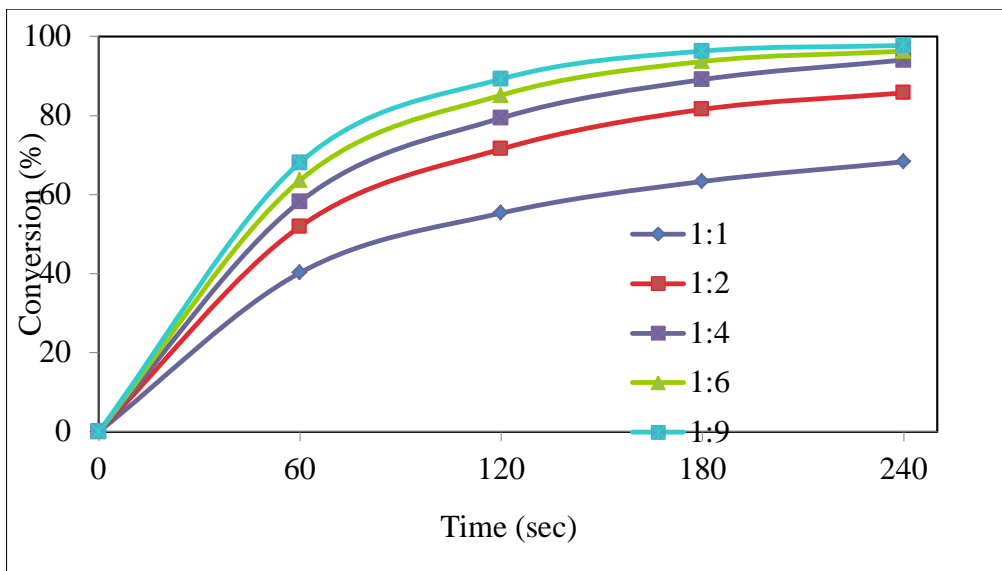


Fig. 1. Trend of conversion vs. time for the dehydrochlorination reaction of 1,3-DCP at different molar ratio

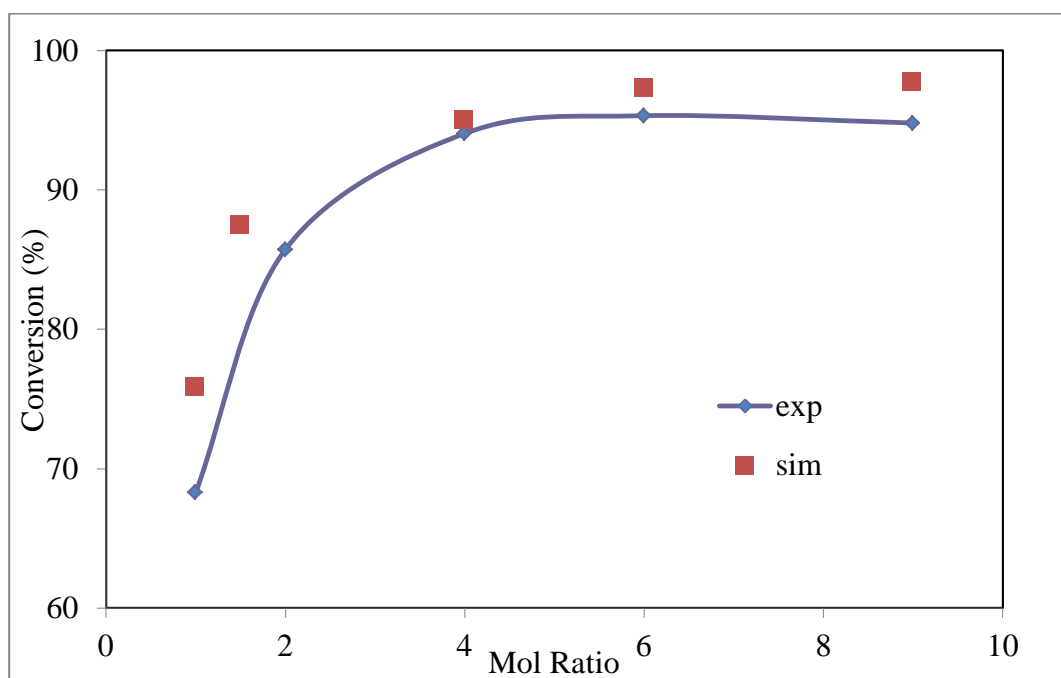


Fig. 2. Effect of mol ratio on conversion of 1,3-DCP: comparison between experimental and simulation

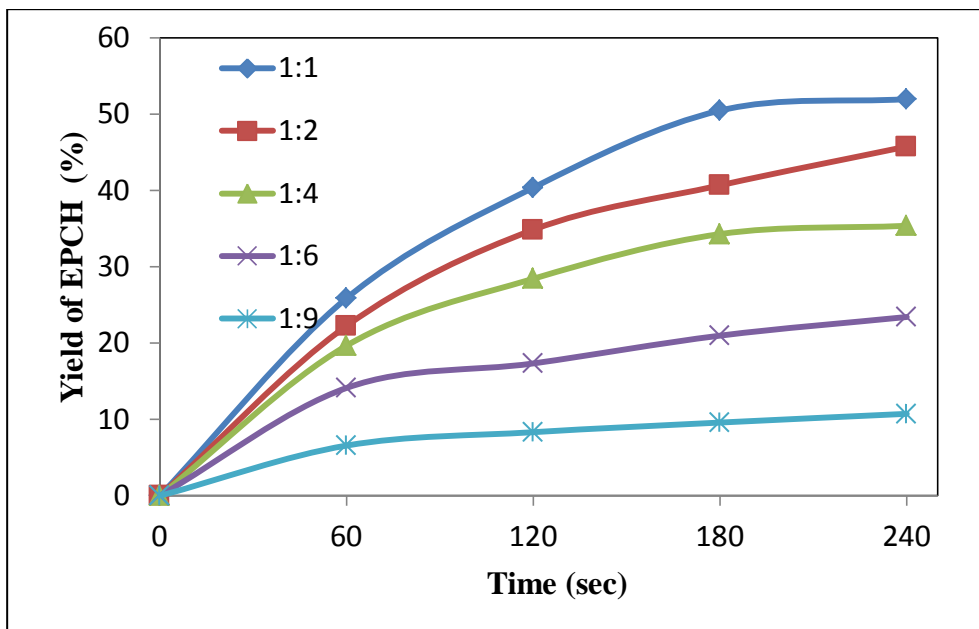


Fig. 3. Trend of yield of EPCH vs. time for the dehydrochlorination reaction of 1,3-DCP at different molar ratio

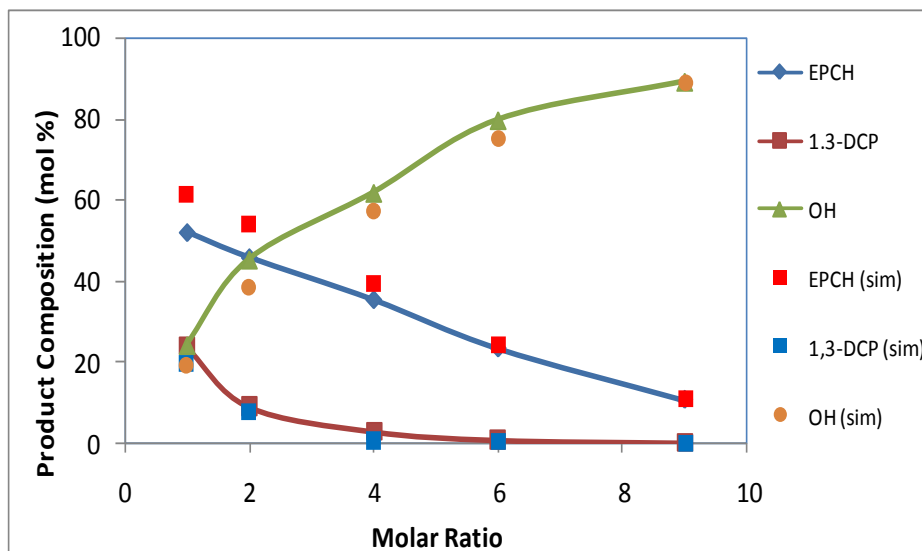


Fig. 4. Effect of mole ratio on product composition: Comparison between experimental data and simulation

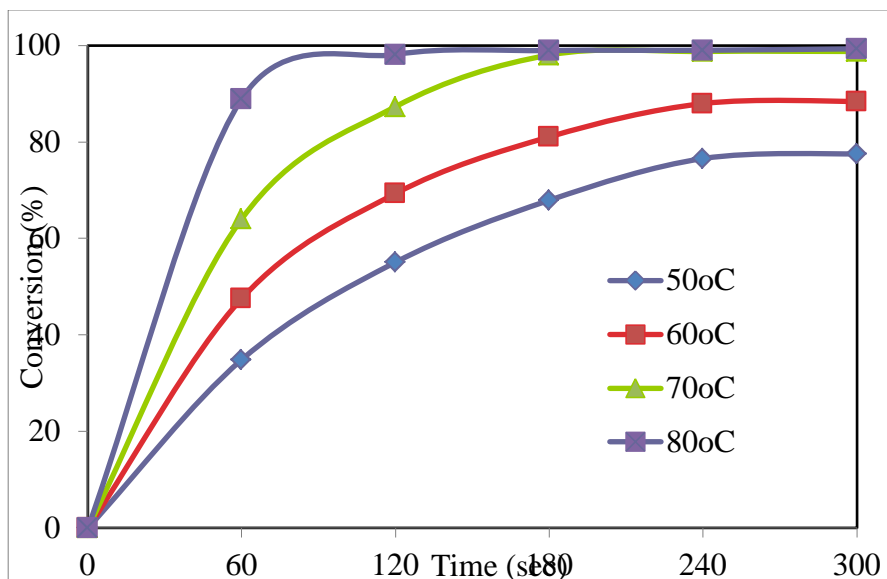


Fig. 5. Trend of conversion vs. time for the dehydrochlorination reaction of 1,3-DCP at different temperature

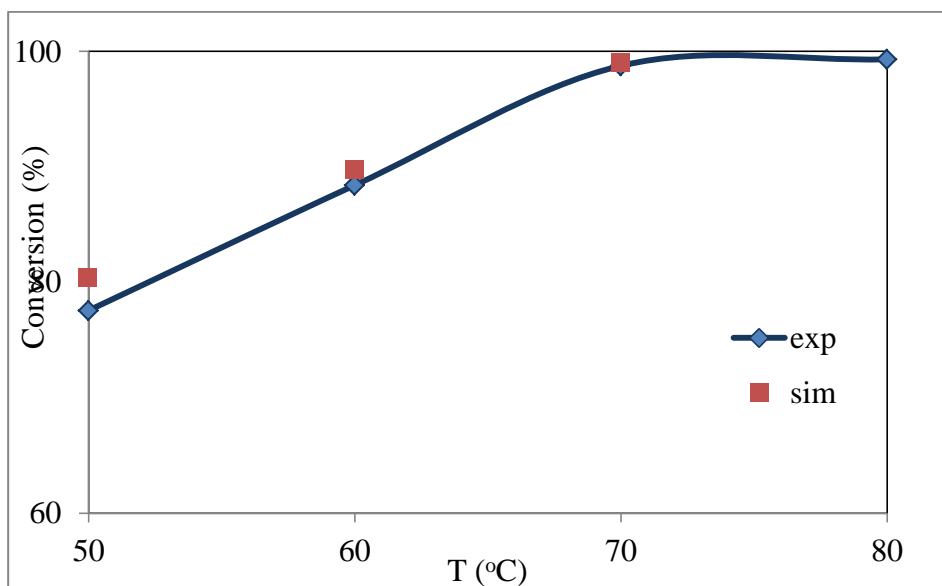


Fig. 6. Effect of temperature on conversion of 1,3-DCP: Comparison between experimental and simulation

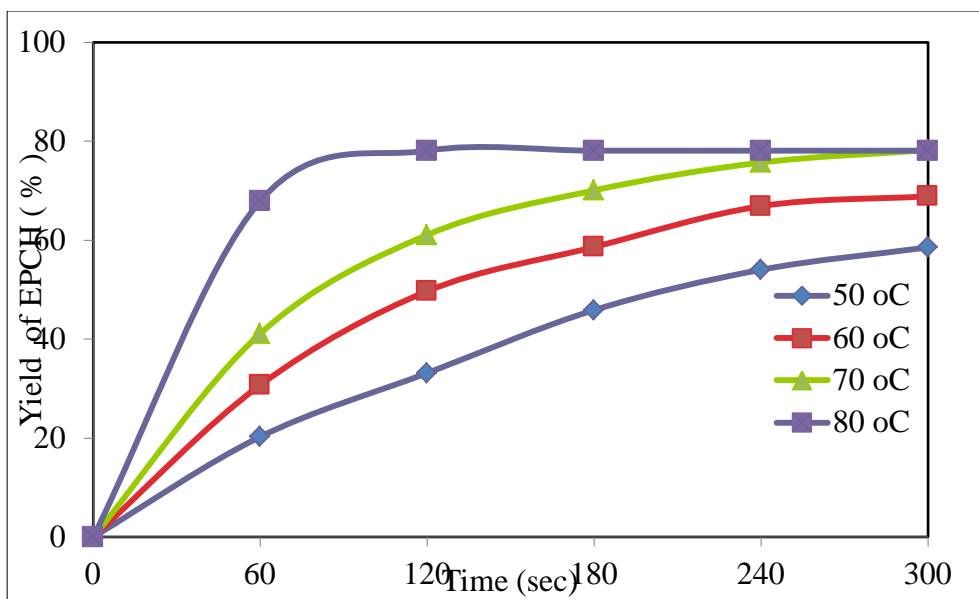


Fig. 7. Effect of temperature and time on yield of epichlorohydrin dehydrochlorination of 1,3-DCP with NaOH, mol ratio 1:10

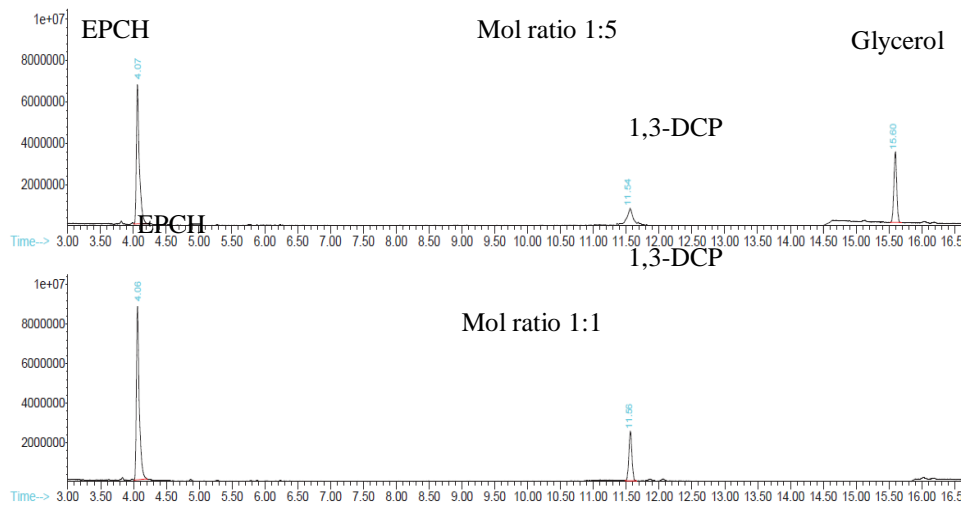


Fig. 8. GC Chromatogram (a) molar ratio 1:1 (b) ratio molar 1:5

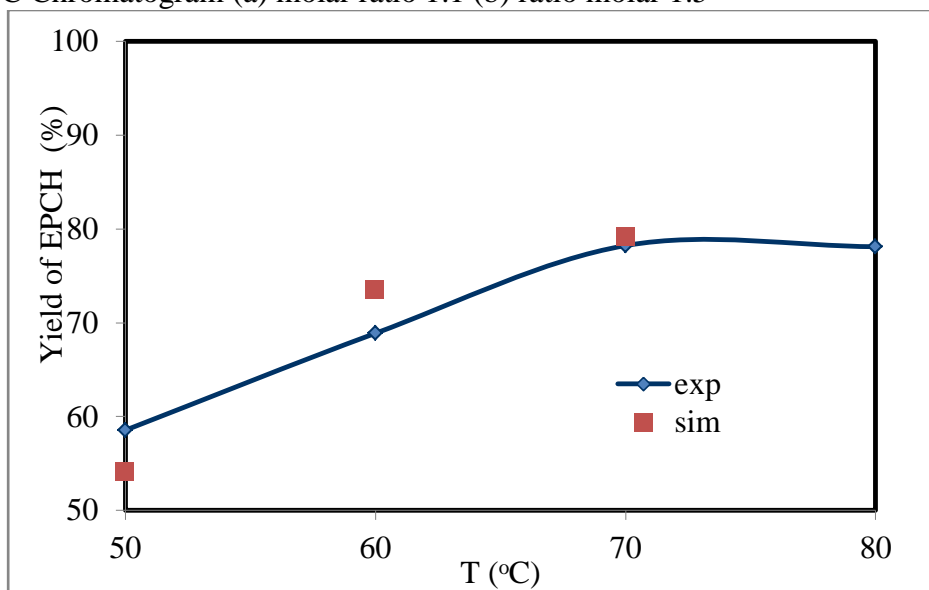


Fig. 9. Effect of temperature on yield of EPCH: Comparison between experimental and simulation using Aspen Plus

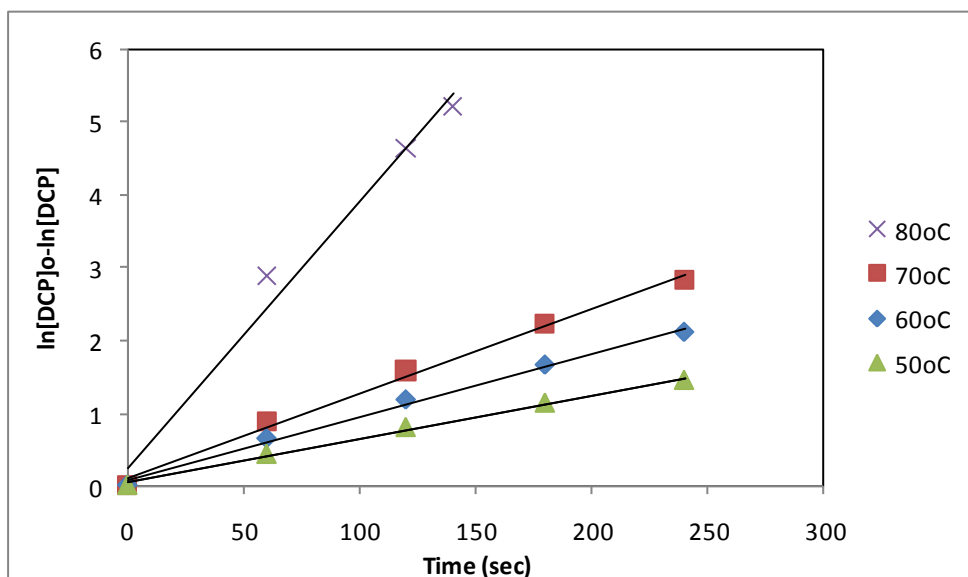


Fig. 10. First-order kinetic model for dehydrochlorination of 1,3-DCP and NaOH

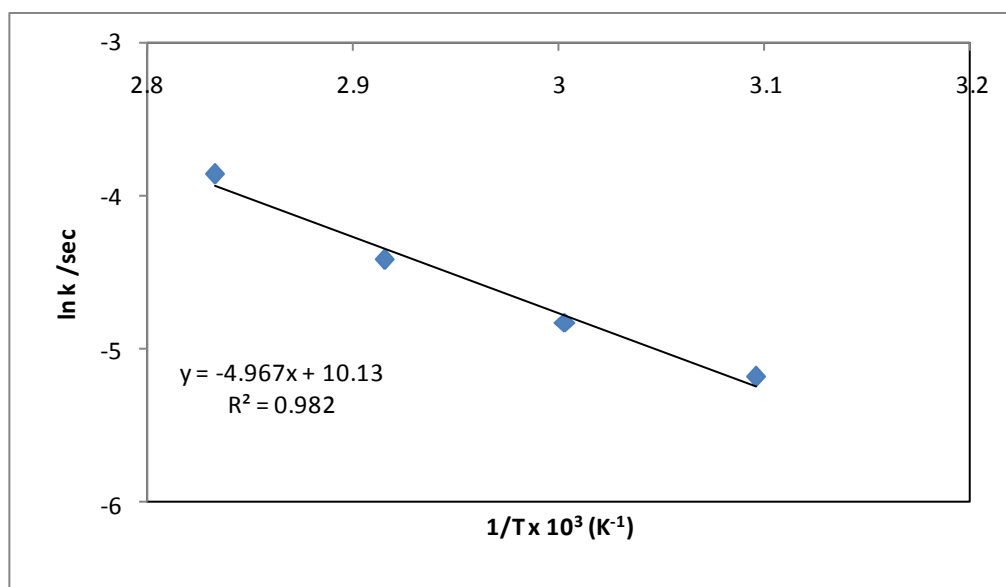


Fig. 11. Plot of $\ln(k)$ versus $1/T$ for the dehydrochlorination reaction

