RECOVERY OF DILUTE ACETIC ACID VIA ESTERIFICATION REACTION CATALYZED BY AMBERLYST 15

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UNIVERSITI MALAYSIA PAHANG

RECOVERY OF DILUTE ACETIC ACID VIA ESTERIFICATION REACTION CATALYZED BY AMBERLYST 15

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Thesis submitted in partial fulfillment of the requirements
for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
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SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I declare that this report is the result of my own research except as cited in the references and summaries which have been duly acknowledge. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

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NOMENCLATURE

AA	acetic acid
C_i	concentration of species I (mol/m^2.s)
Ct	vacant site
E	process efficiency (%)
Ea	activation energy (cal/gmol)
ER	eley-rideal
FID	flame ionization detector
GC	gas chromatograpgy
k	specific reaction rate (constant)
K_C	catalysed reaction rate constant ($m^3/mol^{-1}g_{cat}{}^{-1}s^{-1}$)
Ke	equilibrium constant (dimensionless)
K_i	adsorption equilibrium constant for species *i*
LHHW	langmuir-hinshelwood-hougen-watson
	number of moles of A initially (entering)
PH	pseudo-homogeneous
X	conversion of key constant, A
Θi	ratio of the number of moles of species *i* initially (entering) to the number of moles of A initially (entering)

PENUKARAN ASID ASETIK CAIR MELALUI PROSES PENGEKSTRAKAN DENGAN PEMANGKIN AMBERLYST 15

ABSTRAK

Proses pemulihan asid asetik daripada larutan akueus adalah masalah utama dalam bidang petrokimia dan industri kimia. Proses konvensional pemisahan fizikal seperti penyulingan dan pengekstrakan mengalami beberapa kelemahan. Dalam kerja ini, tindak balas pengesteran asid asetik dengan 2-etil-1-hexanol telah dikaji dalam kehadiran pertukaran ion resin Amberlyst 15. Kesan parameter operasi penting seperti suhu dan kelajuan pergolakan telah diperiksakan. Dalam lingkungan kajian, penukaran maksimum asid asetik mencapai 98.8% pada suhu 100 °C. Untuk kelajuan pergolakan, tiada kesan banyak untuk penukaran asid asetik dari 300rpm untuk 600pm dimana penukaran tertinggi asid asetik adalah 75%. Eksperimen data kinetik tindak balas pengesteran telah dikaitkan dengan pseudo-homogen (PH), Langmuir-Hinserlwood-Hougen-Watson (LHHW) dan Eley-Rideal (ER) model. Model LHHW memberikan keputusan yang terbaik dengan data esperimen. Tenaga pengaktifan bagi tindak balas ini telah ditemui sebanyak 71,08 kJ mol-^{1}.

RECOVERY OF DILUTE ACETIC ACID VIA ESTERIFICATION REACTION CATALYZED BY AMBERLYST 15

ABSTRACT

The recovery of acetic acid from its dilute aqueous solutions is a major problem in both petrochemical and fine chemical industries. The conventional physical separations such as distillation and extraction suffer from several drawbacks. In the present work, the esterification reaction of dilute acetic acid with 2-ethyl-1-hexanol has been studied in the presence of ion-exchange resin Amberlyst 15. The effect of important operating parameters such as speed of agitation and reaction temperature has been examined. Within the range of study, the maximum conversion of acetic acid reached 98.8% at temperature of 100 ℃. For speed of agitation, there is no much effect to the conversion of acetic acid ranging from 300rpm to 600pm where the highest conversion of acetic acid was 75%. Experimental kinetic data of the esterification reaction were correlated with the pseudo-homogeneous (PH), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) models. The LHHW model gave the best agreement with the data. The activation energy for the reaction was found to be 71.08 $kJmol^{-1}$.

CHAPTER 1

INTRODUCTION

1.1 Background of the Proposed Study

Aqueous solutions of acetic acid are produced as by-products or waste streams of many important chemical processes. A large amount of acetic acid containing waste is produced if the reaction is involving with acetic anhydride as well as in the production of cellulose esters, terephthalic acid and dimethyl terephthalate (Bianchi et al., 2002). The waste containing acetic acid is a major issue for those petrochemical and fine chemical industries in term of disposal. From the past, the waste containing acetic acid was sent to incinerator which is commonly practiced by industries. Nevertheless, it is not environmental friendly. Carbon dioxide and other hazardous compounds are released from incineration process and cause the pollution issues.

Several methods or patents have been proposed and published by researchers to recover the acetic acid. The methods include extraction, distillation, pervaporation, ion exchange, membrane separation and so forth. These methods are not promising due to some drawbacks in issue of economic (Ragaini et al., 2005). Apart from that, further treatments and some technical limits are the factors for the conventional methods which are being rejected. In view of these constraints, it is necessary the researchers to explore more alternative methods to replace the current methods in the recovery of acetic acid from waste stream.

In the present work, dilute acetic acid (20% w/w) was recovered using esterification method. The dilute acetic acid was reacted with 2-ethyl-1-hexanol to produce 2-ethyl-1-hexyl acetate as main product.

1.2 Research Objectives

The research objectives of the research study are:

i) The effect of important parameters such as temperature and speed of agitation were examined.

ii) The kinetic model was developed based on the data obtained from experiment.

1.3 Scope of Proposed Study

The scope of the present study focused on the conversion of acetic acid in a wastewater to a more valuable ester product via esterification process. Effect of the important of operating parameters on the process was studied. The range of operating parameters for temperature and speed of agitation were varied from 70 ℃ to 100 ℃ and 300rpm to 600rpm respectively. In kinetic model part, the experimental data was fitted with the suitable kinetic model such as Pseudo-homogeneous model (PH), Langmuir-Hinshelwood-Watson model (LHHW) and Eley-Rideal model (ER).

1.4 Significance of Proposed Study

In esterification reaction, carboxylic acid reacts with alcohol to produce ester and water. In the present work, 2-ethyl-1-hexyl acetate is produced via this reaction. 2-ethyl-1-hexyl acetate has a good market value as raw materials for the sunscreen cream and anti-aging cream (Ragaini et al., 2005).

Incineration has been widely applied by the industries for the past since it was a cheap, easy operation, and a common method to remove the acetic acid from waste stream. By adopting this method, large amount of carbon dioxide gaseous will be produced from the incineration of hydrocarbon compounds to the atmosphere. Thus, the issue of air pollution is concerned. The method of recovery of acetic acid via esterification reaction is more environmental friendly and worth to be explored.

CHAPTER 2

LITERATURE REVIEW

This review of literature is about the recovery methodologies of the acetic acid from wastewater, reactant used, type of catalyst, and kinetic models for esterification of wastewater containing acetic acid with alcohol.

2.1 Recovery Methodology

Extraction, distillation, pervaporation, esterification, membrane separation and reactive distillation are the example methods proposed to recover the acetic acid from waste stream. In fact of conventional physical separation methods, extraction and distillation show several drawbacks.

An application of reactive extraction has been applied to recover the acetic acid from aqueous pyrolysis oil. Rasrendra et al., (2011) shows that 84% of acetic acid recovery was achieved at equilibrium condition (room temperature) by selecting proper amine and diluents combination. Apart from that, more than 80% of acetic acid is recovered in term of efficiency with less energy requirement has been proven by Katikaneni & Cheryan, (2002) and Mahfud et al., (2008). Although this method has high recovery efficiency rate, but further treatment is required. Some significant efforts have been contributed for looking other suitable alternatives to recover acetic acid.

Bipolar membrane electrolysis is one of the methods that less researchers would like to adopt to recovery the acetic acid from dilute wastewater. Yu et al., (2000) claimed that 0.2% (wt%) of acetic acid was recovered quite successfully with up to 70% of conversion. Unfortunately, recovery of acetic acid by using membrane is always a costly technology to the industry. Azeotropic distillation is a quite interesting method to be adopted to recovery the acetic acid from waste stream, but it generates the environmental issues (Gualy et al., 1996).

Esterification is one of the popular methods that often practiced by researches to recovery the acetic acid from wastewater. Jermy & Randurangan., (2005) had carried out esterification reaction by recovering the acetic acid using n-butyl alcohol. The experiment was studied over various type of protonated AL-MCM-41 with different Si/Al ratio. Furthermore, several kinetic studies had been done by recovering the acetic acid through esterification reaction. Robert et al., (1997) and Blagov et al., (2005) both had developed their kinetic model by fitting the experimental data via esterification. The reaction was carried out by using methanol in the presence of hydrogen iodide. In the present work, the esterification reaction was carried out to recover the acetic acid by reacting with 2-ethyl-1-hexanol over the Amberlyst 15 (dry).

2.2 Catalyst

In esterification reaction, catalyst is usually used in the process. There are three common types of catalyst used in the reaction. They are homogeneous catalyst, heterogeneous catalyst and enzyme. The function of the catalyst is providing alternative path by lowering the activation energy required for the reaction. In industry, the mineral liquid acids are widely applied in the past for esterification such as sulphuric acid and *p*-toluenesuphonic. By using these homogeneous catalysts, the catalytic activity and yield of the acetic acid are high (Peters et al., 2005). However, these acid catalysts are found to be toxic, corrosive, and the catalysts cannot be easily separated from the product mixture (Teo & Saha, 2004; Akbay et al, 2011; Lilja et al., 2002). Furthermore, Shaojun & Brent., (2010) claimed that the neutralization and separation step are required to neutralise and remove the homogenous catalyst from the product mixture.

Due to the several disadvantages of homogeneous catalysts, the ion-exchange resin is become an attractive alternative catalyst. The ion-exchange resin may be Amberlyst 15, Dowex 50W, Smopex 101, Nb_2O_5, Sulphated ZrO_2, and so forth. The ion-exchange resins are not corrosive, has long activity life and easily to be separated from the product mixture (Altiokka & Citak., 2002; Toor et al., 2011). Some researchers have compared the process efficiency (*E* %) among the homogeneous catalyst and heterogeneous catalyst. Bianchi et al., (2002) has done the process efficiency (*E* %) comparison between homogeneous and heterogeneous catalysts for the esterification of acetic acid and 2-ethyl-1-hexanol. Their research findings are shown in Table 2.1.

Table 2.1 Process Efficiency Comparison between Homogeneous and Heterogeneous Catalysts

Catalyst used	E %
H_2SO_4	69.2
Nafion NR 50	45.6
Amberlist 15	44.7
Amberlist 200	43.6
Amberlist IR 120	42.6
SO_4 – Zirconia	31.9

From the Table 2.1, sulphuric acid gives the highest percentage of process efficiency. Unfortunately, sulphuric acid is not easily to be removed from the product mixture as stated above. Another paper has examined a comparison of commercial solid acid catalysts for esterification (Peters et al., 2005) and their findings are shown in Table 2.2.

Table 2.2 The Activity of the Different Heterogeneous Catalyst Used in the Esterification Reaction

The K_C value shown by using different heterogeneous catalyst in the esterification reaction between acetic acid and butanol at 75 ℃.		
Catalyst	Amount (g)	K_C (m^3 mol^{-1} g_{cat}^{-1} s^{-1})
Amberlyst 15	1.90	1.6 x 10^{-8}
Smopex-101	1.85	2.4 x 10^{-8}
H-USY-20	2.88	9.8 x 10^{-10}
H-ZSM-5-12.5	2.82	5.9 x 10^{-11}
H-BETA-12.5	2.81	7.7 x 10^{-10}
H-MOR-45	2.79	1.0 x 10^{-10}
ZrO2	5.00	8.8 x 10^{-9}
Nb_2O_5	5.07	9.8 x 10^{-11}

From the Table 2.2 Smopex-101 and Amberlyst 15 both gives the first and second highest number of Kc among the zeolites and ion-exchange resins. The amount Smopex-101 and Amberlyst 15 used in gram is only 1.85 and 1.90 respectively.

In the present work, Amberlyst 15 is chosen as heterogeneous catalyst for the esterification reaction of dilute acetic acid with 2-ethyl-1-hexanol. Saha & Sharma. (1995), Teser et al. (2009) and Peter et al. (2005) have provided the physical properties of Amberlyst 15. The physical properties include shape, size, porosity, temperature, acidity and so forth which are shown in Table 2.3.

Table 2.3 The Properties of Amberlyst 15

Physical Properties	Amberlyst 15
Shape	Bead
Size (mm; min 90%)	0.5
Internal Surface Area (m^2 / g)	55.0
Acidity (mequiv. / g)	4.7
Cross Link Density (% DVB)	20-25
Porosity (vol %)	36
Functional Group	Sulphonics
Matrix	Macroreticular copolymer styrene-DVB
Temperature Stability (K)	293

2.3 Reactants used

In the esterification reaction, carboxylic acid is reacted with alcohol to produce ester and water. Most of the published papers covered the esterification of the concentrated acetic acid. Only few of the papers have discussed about dilute acetic acid.

In the chemical process, there are some dilute acetic acid are produce as a by-product. 35% (w/w) aqueous solution of acetic acid was produce from the manufacture of cellulose acetate from acetylation of cellulose. Furthermore, the dilute acetic acid (5-20% w/w) has also being produced from the process of synthesis of glyoxal acetaldehyde and nitric acid (Teo & Saha., 2004). Therefore, an esterification reaction between acetic acid and *n*-butanol / *iso*-amyl alcohol was investigated in a reactive distillation column by using microporous ion-exchange resin, Indion 130. The reactions were found to be equilibrium limited (Saha et al., 2000). Esterification of acetic acid with various alcohols such as *n*-butyl alcohol, isobutyl alcohol and tertiary butyl alcohol has been studied in the presence of Mesoporous Al-MCM-41 molecular sieves as heterogeneous catalyst. From the observation, the *n*-butyl alcohol conversion was found to be higher than isobutyl alcohol and tertiary butyl alcohol (Jermy & Pandurangan., 2005).

Kirumakki et al., (2005) have reported that the degree of liquid phase esterification on the type of alcohols and the acidity of the zeolites. This research has been done on the liquid phase esterification of *n*-propyl, *n*-butyl, *iso*-propyl and *iso*-butyl alcohols on acetic acid over the various zeolite types of Hβ, HY and HZSM5. In the present work, 2-ethyl-1hexanol will be served as one of the reactants to be reacting with acetic acid. There are not many researchers study the esterification reaction using 2-ethyl-1-hexanol. Ragaini et al., (2005) claimed that the reaction took place in the organic phase and the conversion of acetic acid reached 70%. Besides, kinetic model was performed. The result brought to the hypothesis that the diffusion of the reagents and products in and out the catalyst pores is not a rate-determining step. Table 2.4 shows the several reactants that have been used to produce different acetate ester.

Table 2.4 The Summary of Common Alcohol Reactants Used for Esterification reaction

References	Reactant used
Bianchi et al., (2003)	*n*-butanol, 2-ethyl-1-hexanol
Dash & Parida., (2006)	*n*-butanol
Jazi (2010)	Benzyl Alcohol
Hasanoglu et al., (2009)	Ethanol
Kirumakki et al., (2005)	*n*-propyl, *n*-butyl, *iso*-propyl, *iso*-butyl

2.4 Kinetics Model

In Gangadwala et al., (2003) research, the esterification reaction was conducted in the presence of the ion-exchange resin Amberlyst 15. This heterogeneous kinetics model including Pseudo-Homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) were applied to correlate kinetics data available for different operating parameters. For the ER model, the esterification reaction was assumed that the adsorbed butanol and acetic acid species on the catalyst surface are taken places. But for LHHW model, all of the components were assumed in their adsorbed phases. Teo & Saha., (2004) stated that, the model with the least sum of squares and random residuals would be the most suitable from the statistical standpoint. The researchers claimed that the LHHW model is applicable when the rate determining step is the surface reaction between adsorbed molecules. For ER model, it is applicable if the rate limiting step is surface reaction where it takes place between one adsorbed species and one non-adsorbed reactant from the bulk liquid phase.

In the published papers, the most common models that have been developed by researchers are Pseudo-Homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW). This kind of kinetics model is only applied to heterogeneous reaction. Gangadwala et al., (2003) stated that the LHHW models explain the data successfully over a wide range of catalyst loading and temperature for esterification reaction under the reaction between acetic acid and n-butanol. Apart from that, ER and LHHW model yielded a better result under the reaction between acetic acid and methanol catalyzed by amberlyst 36 among IQH, the NIQH, the ER, and the LHHW models (Tsai et al., 2011). Altiokka & Citak (2002) stated that ER model is suitable the reaction has been found to occur between an adsorbed alcohol molecule and a molecule of acid in the bulk phase under the reaction between acetic acid and isobutanol catalyzed by strong acidic ion-exchange acid.

Based on the review, LHHW model is prefer compare to the other two models. In most of the papers, LHHW model gives the best representation of kinetic behavior for all practical purposes under a given condition and explain the data successfully over a wide range of temperature for esterification reaction.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Research Design

This study focuses on the conversion of dilute acetic acid via esterification process. In a batch reactor by varying the temperature and speed of the concentration of the samples was analyzed by gas chromatography using flame ionization detector. The details procedure for the execution is shown in the subsequent section.

3.2 Chemicals and Materials Preparation

3.2.1 Acetic acid

Acetic acid (20% w/w) with 99.7% purity was prepared for the esterification reaction which was reacting with 2-ethyl-1-hexanol. The total volume of acetic acid which was prepared is 60ml for each run of reaction.

3.2.2 2-ethyl-1-hexanol

The 2-ethyl-1-hexanol with its purity 99.0% was used to react with acetic acid (20% w/w). As much as 240ml of 2-ethyl-1-hexanol was prepared for each run of esterification reaction.

3.2.3 Amberlyst 15

Amberlsyt 15 was used in the esterification reaction to provide the alternative path by lowering the activation energy. The Amberlyst 15 was washed with ethanol. Then, it was placed in a ventilated oven with 100 ℃ for at least 24 hours for drying process.

3.2.4 Stock Solution for Calibration Curve

Stock solution was prepared for calibration curve of acetic acid. There were five solutions with different concentration were prepared where the information is shown in Table 4.1. The solutions then were diluted with hexane where the hexane was served as solvent. After that, the solutions were filtered and injected into 2ml vial for gas chromatography analysis.

3.2.5 Sample preparation for GC-FID

The samples from esterification reaction were kept in a freezer once they were withdrawn from the batch reactor. Then, 0.5ml of sample was diluted into 0.5ml of hexane. Next, a mixed solution was filtered and injected into 2ml vial for gas chromatography analysis.

3.3 Equipment and Apparatus Used

In this section, the equipment and the apparatus that was used for esterification reaction and gas chromatography analysis will be discussed here.

3.3.1 Esterification Reaction

Table 3.1 presents the equipment and apparatus that were used for esterification reaction. Besides, the functions for major equipment are listed as below.

Table 3.1 Equipment or the Apparatus Used for the Esterification Reaction Study and Its Function

Equipments/Apparatus	Function
3-necked flask (500ml)	To store the reactants and act as batch reactor
Mechanical Stirrer	To stir the reactants with desired agitation speed
Thermometer	To measure temperature
Condenser	To condense the vaporized vapours
Heating Mantle	To supply heat to the esterification reaction

3.3.2 Gas Chromatography

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analysing compounds that can be vaporized without decomposition. In the current work, the GC-FID is used to analyse the concentration of acetic acid appear in the sample of esterification reaction. Table 3.2 shows the operating parameter of GC analysis column for acetic acid.

Table 3.2 The operating parameters for GC column

Column	BD-200, 125-2032 30 m x 0.53 mm, 1.00 µm
Carrier	Helium at 34.5 cm/sec Measured at 35°C
Oven	35°C for 5 min, 30 - 200°C at 10 °/ min
Injection	Split, 230°C Split ratio 1:10
Detector	FID, 250°C

3.4 Experimental Procedure for Esterification Reaction Study

Figure 3.1 presents the equipment and apparatus set-up for esterification reaction. There are few major types of equipment that will be used in the reaction.

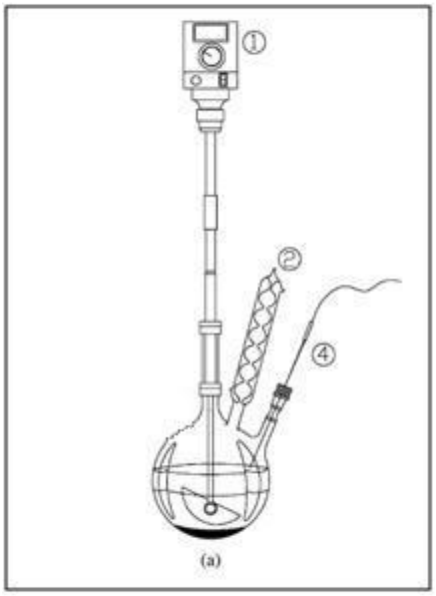


Figure 3.1 Experimental Set-up for the Reaction Study

The esterification reaction experimental set up was located to the tapped water source. A 500ml of 3-necked round flask was placed into the heating mantle. The water flow direction of the condenser was from bottom up to upper part once the water tap is opened. 240ml of 2-ethyl-1-hexanol with 3g of Amberlyst 15 was poured into the 3-necked round flask and heat is started to be supplied to the batch reactor. At the same time, 60ml of acetic acid is heated in a beaker. Once both reactants have achieved 60 ℃, the acetic acid is poured into the 3-necked round flask. Time is started to run. 1ml of sample is taken out by micro pipette every 10 minutes for the first hour time. The sample has to be cooled down as soon as possible in order to stop the reaction. Next, the samples will be taken every 30 minutes for the next two hours time. Then, the samples will be taken again every one hour for the next eight hours time. When all the samples are taken, then the esterification reaction can be fully stopped. There are two important parameters for the present esterification reaction. Table 3.3 presents the range of parameter studied for reaction temperature and speed of agitation. Fomr Table 3.3, the temperature for esterification reaction will be started with 60 up to 100℃. Besides, the speed of agitation will be studied with 300rpm to 600rpm.

Table 3.3 The range of parameters studied

Parameter	Range of study
Temperature (℃)	60, 70, 80, 90, 100
Speed of agitation (rpm)	300, 400, 500, 600

3.5 Kinetics Model Development

In the presence work, the proposed reaction scheme based on LHHW model is shown in Eq. 3.1, 3.2, 3.3, 3.4 and 3.5.:

Adsorption: $$A + S \xrightarrow{k_A} A.S \qquad (3.1)$$

$$B + S \xrightarrow{k_B} B.S \qquad (3.2)$$

Surface reaction: $$A.S + B.S \xrightarrow{k_S} C.S + D.S \quad \text{(Dual Site)} \qquad (3.3)$$

Desorption: $$C.S \xrightarrow{k_C} C + S \qquad (3.4)$$

$$D.S \xrightarrow{K_D} D + S \qquad (3.5)$$

S represents a vacant active catalyst site;

Where A: Acetic acid; B: 2-ethyl-1-hexanol; C: 2-ethyl-hexyl acetate; D: water

If the rate limiting step is surface reaction between adsorbed molecules, then the rate expression for LHHW model is

$$-r_s = \frac{k_A {C_t}^2 K_A K_B \left(C_A C_B - \frac{K_c K_B}{K_A K_B K_S} C_C C_D\right)}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2}$$

$$= \frac{k \left(C_A C_B - \frac{C_C C_D}{K_e}\right)}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \qquad (3.5)$$

For the proposed reaction scheme based on ER model is shown in Eq.3.6, 3.7 and 3.8. :

Adsorption: $B + S \xrightarrow{k_A} A.S$ (3.6)

Surface reaction: $B.S + A \xrightarrow{K_S} C.S + D$ (3.7)

Desorption: $C.S \xrightarrow{K_D} C + S$ (3.8)

S represents a vacant active catalyst site;

Where A: Acetic acid; B: 2-ethyl-1-hexanol; C: 2-ethyl-hexyl acetate; D: water

If the rate limiting step is surface reaction where it takes place between one adsorbed species and one non-adsorbed reactant from the bulk liquid phase, the rate expression for ER model is

$$-r_s = \frac{k_s C_t K_A \left(C_A C_B - \frac{K_C C_C C_D}{K_S K_A}\right)}{1 + K_A C_A + K_C C_C}$$

$$= \frac{k\ (C_A C_B - \frac{C_C C_D}{ke})}{1 + K_A C_A + K_C C_C} \tag{3.9}$$

For proposed reaction scheme based on PH model is shown in Eq. 3.10:

$$-r_s = k\ (C_A C_B - \frac{C_C C_D}{K_{eq}}) \tag{3.10}$$

The model is applicable if all the components are not adsorbed molecules.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sample Analysis using Gas Chromatography

4.1.1 Calibration Curve

A calibration curve is a common method for determining the concentration of an unknown sample by achieving accurate quantitative measurement. The calibration curve is usually calibrated using standard samples of known composition. In the present work, a calibration curve where the area versus concentration of acetic acid is plotted. The initial concentration of acetic acid is 3.493mol/dm^3 or 209580ppm. The conversion of acetic acid in the reaction of esterification is predicted between the ranges from 0.5 to 1.0. Table 4.1 shows the corresponding area to the acetic acid concentration while Figure 4.1 represents the data graphically.

From Figure 4.1, a calibration curve of acetic acid is plotted with 0.9627 of R-squared value where the line intercepts zero. By using the equation Y=0.2989X, the concentration samples of acetic acid from the reaction of esterification are determined.

Table 4.1 The Area and Concentration Values of AA for Calibration Curve

Concentration (ppm)	Area (pA*s)
31025	1.15E+04
46875	1.46E+04
62500	1.82E+04
78125	1.98E+04
93750	2.71E+04
109375	3.46E+04
125000	3.81E+04

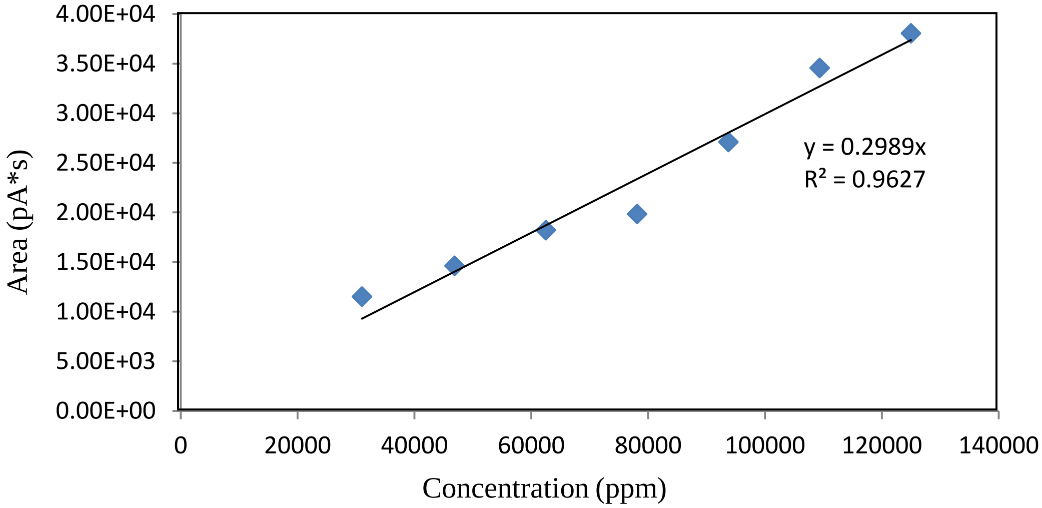


Figure 4.1 Calibration Curve of Acetic Acid

4.1.2 Sample Analysis

Gas chromatography with FID is used to identify the compound of acetic acid in a sample. The concentration of acetic acid sample can be calculated once the area of acetic acid sample is obtained and with the help of calibration curve. Besides, the identities of solvent (Hexane), 2-ethyl-1-hexanol and 2-ethyl-1-hexyl acetate are identified too.

Figure 4.2 shows chromatogram obtained from the analysis of GC-FID for the sample of 80 ℃ and 500rpm at 40th min. Based on the retention time shown, few main compounds are identified and grouped according to the chromatography and spectroscopy catalogue 2012 (Refer to appendixes A1) provided by Agilent Technologies (Agilent 2012) in Table 4.2 as below.

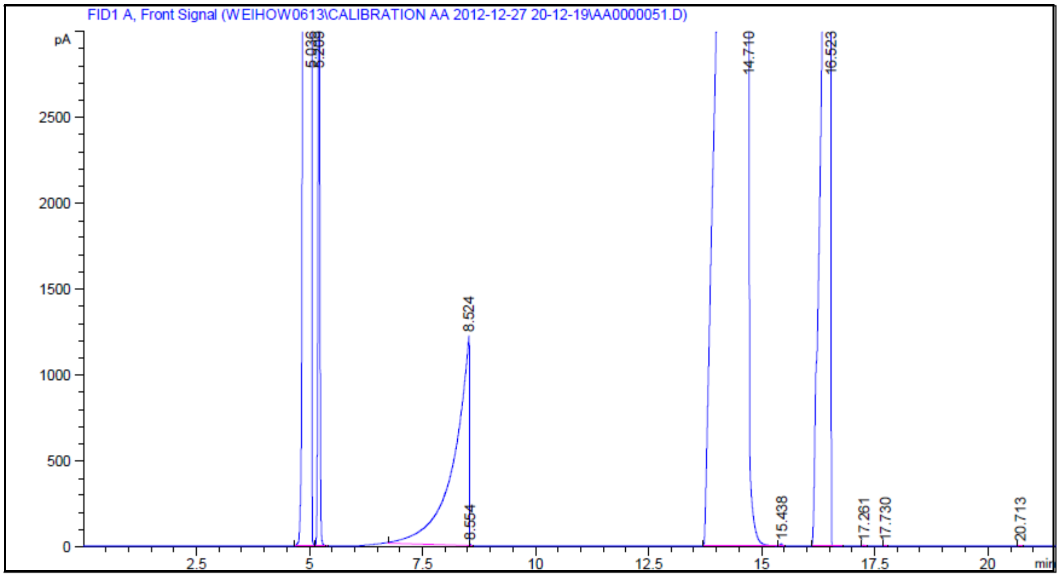


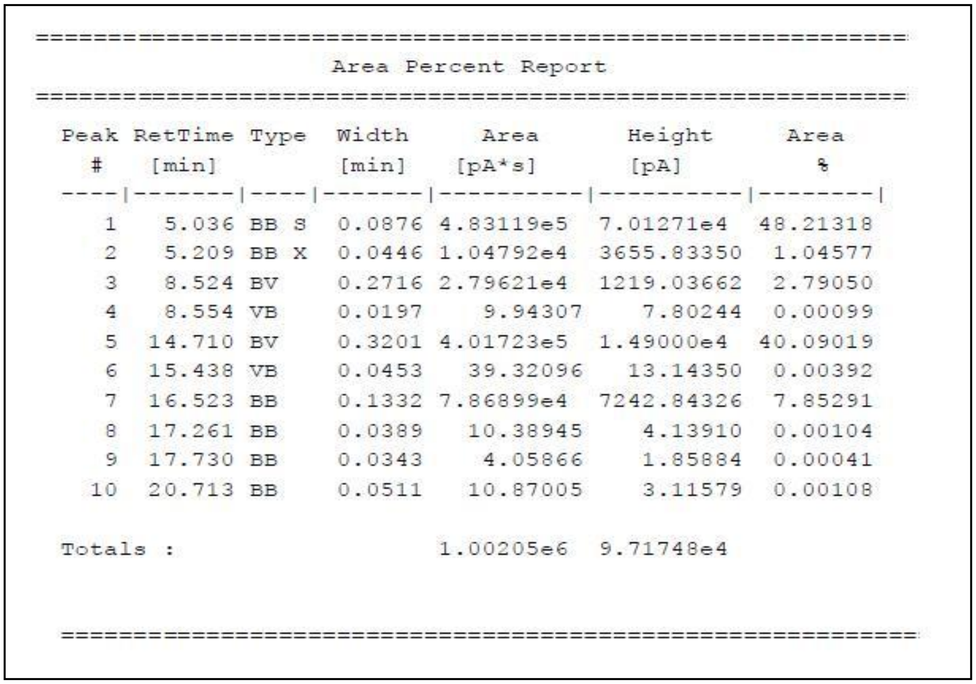
Figure 4.2 The Peaks Shown for the Sample of 80 ℃, 500rpm At 40 min by GC-FID

Table 4.2 The Groups and Compound Identities That Appeared In Sample

Ranges of Retention Time	Group of Compound	Compound Identity
5.0 – 5.9	Hydrocarbon	Hexane, C_6H_{14}
7.0 – 8.9	Carboxylic Acid	Acetic Acid, CH_3COOH
14.0 – 15.9	Alcohol	2-ethyl-1-hexanol, $C_8H_{18}O$
16.0 – 16.9	Ester	2-ethyl-1-hexyl Acetate, $C_{10}H_{20}O_2$

From Figure 4.3, the peak of acetic acid is chosen based on the area between the range of 7.0 and 8.9 in carboxylic acid group. In this group, there are two peaks shown which are 8.524 and 8.554 respectively in term of retention time. The peak with both the highest value of height and area is the real peak of acetic acid.

By using the equation of Y=0.2989X, the concentration of the acetic acid from the sample can be calculated once the area of acetic acid is figured out from the area percent report.



```
============================================================
                     Area Percent Report
============================================================

  Peak RetTime Type  Width     Area      Height     Area
    #   [min]        [min]   [pA*s]      [pA]        %
  ----|-------|----|-------|----------|----------|--------|
     1    5.036 BB S  0.0876 4.83119e5  7.01271e4  48.21318
     2    5.209 BB X  0.0446 1.04792e4  3655.83350  1.04577
     3    8.524 BV    0.2716 2.79621e4  1219.03662  2.79050
     4    8.554 VB    0.0197    9.94307    7.80244  0.00099
     5   14.710 BV    0.3201 4.01723e5  1.49000e4  40.09019
     6   15.438 VB    0.0453   39.32096   13.14350  0.00392
     7   16.523 BB    0.1332 7.86899e4  7242.84326  7.85291
     8   17.261 BB    0.0389   10.38945    4.13910  0.00104
     9   17.730 BB    0.0343    4.05866    1.85884  0.00041
    10   20.713 BB    0.0511   10.87005    3.11579  0.00108

  Totals :                   1.00205e6  9.71748e4


  ============================================================
```

Figure 4.3 The Area Percent Report from GC-FID Analysis

4.2 Studies on the Effect of Esterification Reaction Parameters

The esterification of acetic acid with 2-ethyl-1-hexanol is an electrophilic substitution. Since the reaction is slow and reversible, the effects of parameters such as temperature and speed agitation were studied. This reaction was carried out in the presence of dry Amberlyst. A series of comparison for the both parameters will be discussed in the subsequent section.

4.2.1 Effect of Speed Agitation

The effect of the speed agitation is studied over a wide range of 300 to 600 rpm for esterification reaction was shown in Figure 4.4. Gangadwala et al., (2003) stated that speed of agitation in a reaction is related to mass-transfer resistances. In the present work, it is clear that the external mass transfer resistance is smaller at both 400 and 600 rpm if compared to the speed agitation of 300 and 500 rpm. From the figure, the trends of 300 and 500 rpm are almost identical as well as for the other two speed agitation of 400 rpm and 600 rpm. Based on the observation, all of the rest parameters should be performed at the speed of agitation with 600 rpm which provides the highest conversion of acetic acid and eliminates the external mass transfer resistance.

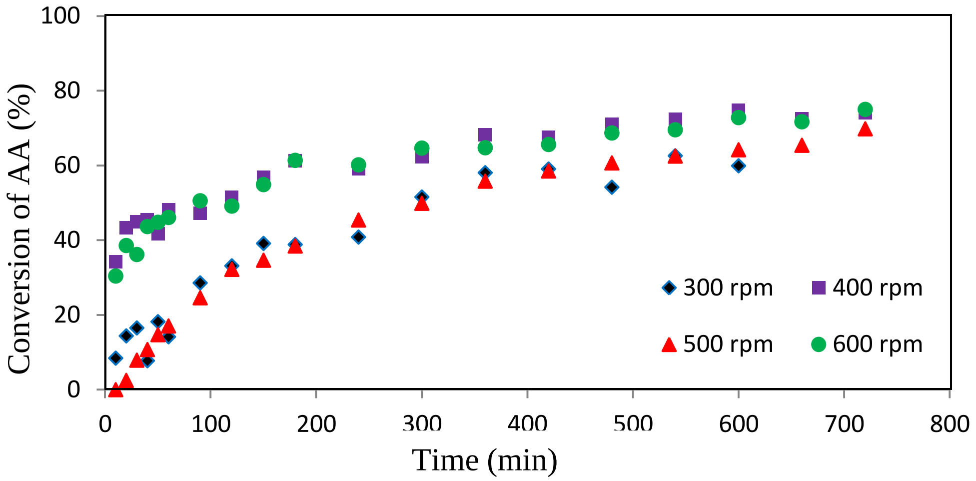


Figure 4.4 Effect of the Speed of Agitation (rpm) on the Conversion of AA (Temperature = 80 ℃, Catalyst Loading = 3g)

Table 4.3 Conversion of AA with Different Speed of Agitation at 80 ℃

Speed of Agitation (rpm)	Conversion of Acetic Acid (%)
300	59.90
400	74.08
500	69.80
600	74.99

Table 4.3 shows the conversion of acetic acid with various speed of agitation in a esterification reaction. From the table, the speed of agitation with 600 rpm gives the highest conversion of acetic acid compare to others. The conversion of 500rpm reaction was lower than the conversion of 400rpm reaction. The reaction rate for 400rpm is higher than the reaction rate of 400rpm from initial to the time of 400 minutes. At 400 min onward, the reaction rate was slow down especially for the reaction of 400rpm. If the reaction for 400rpm and 500rpm are continued to be carried, the conversion of both reaction are close to each other in prediction.

A comparison of speed of agitation has been made with Ragaini et al., (2005). The reaction runs with 60rpm, 100rpm and 200rpm were performed. The result showed that that best speed is 100rpm with the high concentration of ester. He claimed that a very high stirring speed could produce bubbles and may hinder the reagent diffusion inside the catalyst. On the other hand, Gangadwala et al., (2003) has different view about the effect of speed of agitation. He concluded that 1300rpm is the best speed for his reaction between acetic acid and n-butanol over Amberlyst 15. The influence of an external mass transfer did not bring any effect to the reaction once the speed of agitation is above 1000rpm.

4.2.2 Effect of Reaction Temperature

The effect of various temperatures on the rate of reaction were studied by conducting from 70 to 100 ℃ at a given alcohol to acetic acid ratio of 4:1, agitation speed of 500rpm for 12 hours over Amberlyst 15 (dry). The acetic acid conversion obtained at different reaction temperature and the conversion profiles for different temperature are shown as in Table 4.4 and Figure 4.5 respectively.

Table 4.4 Conversion of AA with Different Reaction Temperatures

Temperature (℃)	Conversion of Acetic Acid (%)
70	56.85
80	69.80
90	79.05
100	98.86

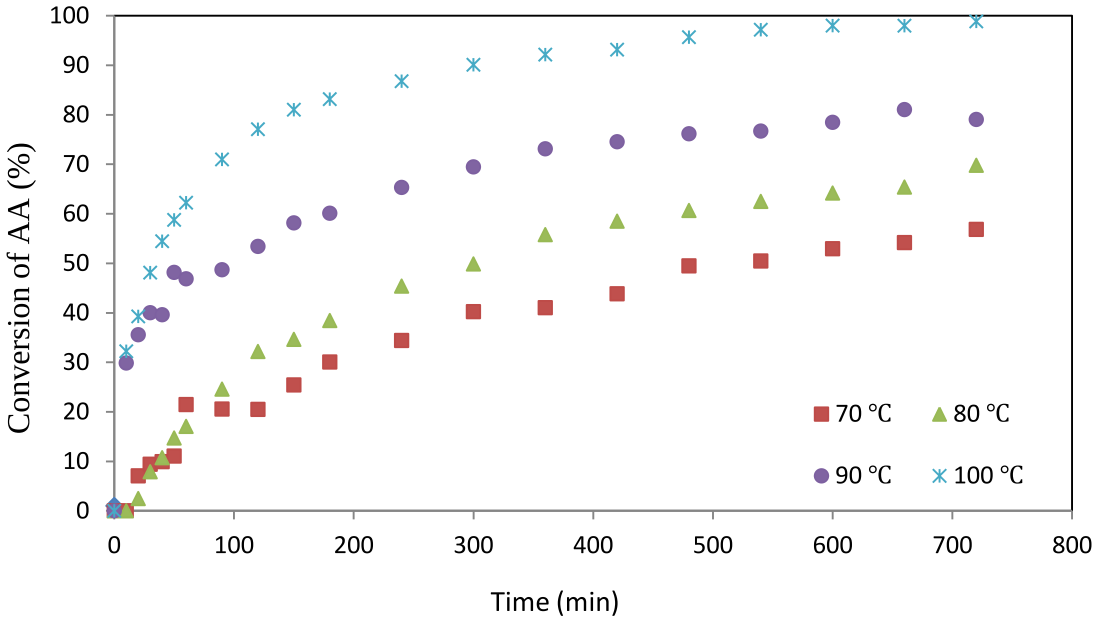


Figure 4.5 Conversion Profile of AA for Different Temperature (Catalyst Loading = 3.0g; stirrer speed = 500rpm, Alcohol to AA ration=4:1)

Table 4.4 presents the change of acetic acid conversion at different reaction temperature. The conversion of acetic acid is increasing from 56.9% to 98.86% as the temperature is increased from 70 to 100 ℃. It shows that the higher temperature yields the greater conversion of acetic acid at a fixed condition. The frequency of the collision is increased when the temperature is increased. Once the molecules have enough energy, the molecules are able to break the bond and from all new bonds with right orientation collision. Thus, more collisions may happen by rising the temperature can lead the increasing of rate of reaction.

Figure 4.5 shows the effect of temperature on the conversion of acetic acid where each reaction temperature is compared along the reaction time. The lines of acetic acid conversion from 70 to 100 ℃ are considered stable without any fluctuation except the line for 60°C. From the overall observation, the rates of reaction for all the temperatures are high from the beginning with time equal to zero to the time of 200 minutes. The rates of reactions start to slow gradually from the time of 200 minutes to 720 minutes. From the other way of observation, the highest rate of reaction is the reaction with 100 ℃, then following by 90 ℃, 80 ℃ and 70 ℃ respectively.

From the paper of Kirbaslar et al., (2000), the effect of temperature on the conversion of acetic acid was studied. The conversion of acetic acid was increasing as the temperature was increased. The reaction was done by reacting the acetic acid with ethanol over Amberlyst 15. Besides, Teo & Saha, (2004) concluded that the higher temperature yields the greater conversion of acetic acid at fixed contact time. Increasing the temperature is apparently favorable for the acceleration of the forward reaction. In conclusion, the trend of the effect of the temperature to the conversion of acetic acid is same with the statement in other papers which is higher temperature yields the greater conversion of acetic acid.

4.3 Kinetics Model

Pseudo-Homogeneous (PH), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (RE) are the three general kinetic models for esterification reaction that can be expressed in the absence of any intraparticle different fusional limitation. These models can be assumed as heterogeneous kinetic models since the catalyst used in the reaction is ion-exchange resins (Amberlyst 15). The models were applied to correlate the kinetic data available for different temperatures ranging from 70 to 100 ℃ of acetic acid to 2-ethyl-1-hexanol.

4.3.1 Langmuir-Hinshelwood-Hougen-Watson (LHHW)

Langmuir-Hinshelwood-Hougen-Watson (LHHW) is derived from the ideas proposed by Hinshelwood based on Langmuir's principles for adsorption (Hougen & Watson., 1943). This approach in determining catalytic and heterogeneous mechanism is usually termed as *Langmuir-Hinshelwood approach*.

In LWWH model, all of the components involved in the reaction are assumed in their adsorbed phases. So, it is only applicable whenever the rate limiting step is surface reaction between the adsorbed molecules. The rate of reaction for this model is expressed as:

$$-r_s = \frac{dC_A}{dt} = \frac{k\ (C_A C_B - \frac{C_C C_D}{k_e})}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \qquad (4.1)$$

where K_A, K_B, K_C and K_D are the adsorption equilibrium constants for acetic acid, 2-ethyl-1-hexanol, 2-ethyl-1-hexyl acetate and waster respectively. A total number of four adsorption equilibrium constants and the values of k, ke, and Ct will be determined based on the experimental data using Polymath Fogler 6.10 for simulation.

4.3.1.1 LHHW Model Fitting using POLYMATH

With the aid of POLYMATH software, the adsorption equilibrium constants, unknown constants and graphs can be determined and plot according to the experimental data. Before the model is generated, the concentration for all the reactants and product are calculated based on the equations as shown in Eq. 4.1 to Eq. 4.5.:

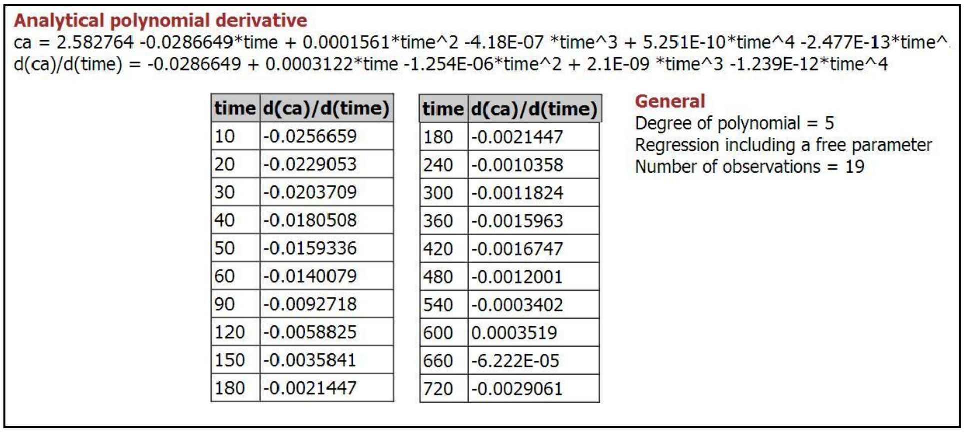
$$C_A = C_{AO}(1-X) \tag{4.2}$$

$$C_B = C_{BO}(\Theta_B-X) \tag{4.3}$$

$$C_C = C_{AO}(\Theta_C+X) \tag{4.4}$$

$$C_D = C_{AO}(\Theta_D+X) \tag{4.5}$$

Besides, the change of the concentration of acetic acid over the time is calculated based on the five degree of analytical polynomial derivative. An example of esterification reaction will be taken for the development of LWWH model with the reaction condition: 100℃, 500rpm with 3g of catalyst loading. Figure 4.6 shows the data of the change of the concentration of acetic acid over the time. The derivative data is also obtained.



Analytical polynomial derivative

```
ca = 2.582764 -0.0286649*time + 0.0001561*time^2 -4.18E-07 *time^3 + 5.251E-10*time^4 -2.477E-13*time^
d(ca)/d(time) = -0.0286649 + 0.0003122*time -1.254E-06*time^2 + 2.1E-09 *time^3 -1.239E-12*time^4
```

time	d(ca)/d(time)
10	-0.0256659
20	-0.0229053
30	-0.0203709
40	-0.0180508
50	-0.0159336
60	-0.0140079
90	-0.0092718
120	-0.0058825
150	-0.0035841
180	-0.0021447

time	d(ca)/d(time)
180	-0.0021447
240	-0.0010358
300	-0.0011824
360	-0.0015963
420	-0.0016747
480	-0.0012001
540	-0.0003402
600	0.0003519
660	-6.222E-05
720	-0.0029061

General

Degree of polynomial = 5
Regression including a free parameter
Number of observations = 19

Figure 4.6 The Data of dCa/dt Over the Time under the Five Degree of Analytical Polynomial Derivative (Reaction condition: 100 ℃, 500 rpm with 3g catalyst)

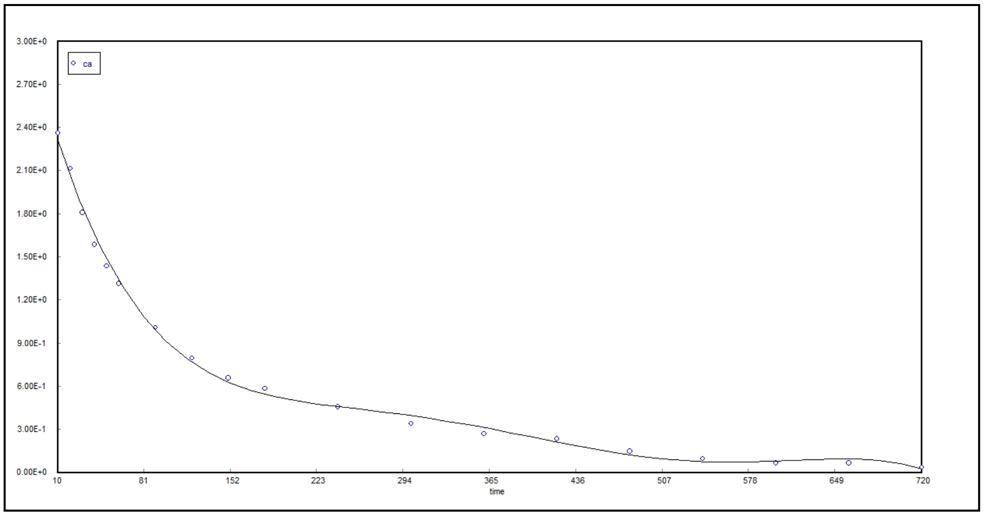


Figure 4.7 Polynomial Regression Graph for Predicted and Experimental Data

Table 4.5 The Statistics Values Shown for Analytical Polynomial Derivative

R^2	0.9973834
R^2adj	0.996377
Rmsd	0.0085583
Variance	0.0020339

Figure 4.7 presents the polynomial regression graph for predicted and experimental data. From the graph, the dot stands for the experimental concentration of acetic acid over the time whereas the line is the predicted concentration of acetic acid by polymath. The closer the dot to the line, the better the experimental data obtained. Based the statistics on Table 4.5, the accuracy (R^2) of the experimental data to the predicted data is as high as 0.9973834.

Then, LWWH model is inserted into polymath where the data obtained from experimental work are fitted with it. The model is belonging to non-linear model and the model variables are fitted with initial guess. Table 4.6 shows the valuables values for LWWH model under nonlinear regression.

Table 4.6 The variables values for LWWH model under nonlinear regression

Variable	Initial guess	Value	95% confidence
k	1	10.19338	0.0019218
ke	1	101.9987	1.936002
Ka	1	7.961235	0.0021111
Kb	1	7.988544	0.0021111
Kc	1	3.452258	0.0021903
Kd	1	3.350794	0.0021903

From the observation throughout Table 4.6, all the absorption equilibrium constants and values of k and ke are determined with 95% confidence and initial guess = 1. All the values obtained for all variables must be bigger than the values shown in the column of 95% confidence. If it does not, then the initial guess has to be adjusted to get a better result.

Table 4.7 The Statistics Values Shown of Nonlinear Regression for LHHW Model

R^2	0.9823054
R^2adj	0.9754998
Rmsd	0.0002606
Variance	1.886E-06

Table 4.7 presents a statistics values of nonlinear regression for LHHW model. The value of R^2 is 0.982305. R^2 is stand for how precision the data being fitted into a LWWH model. The higher the value of R^2, the more precise the data fitted into the LWWH model.

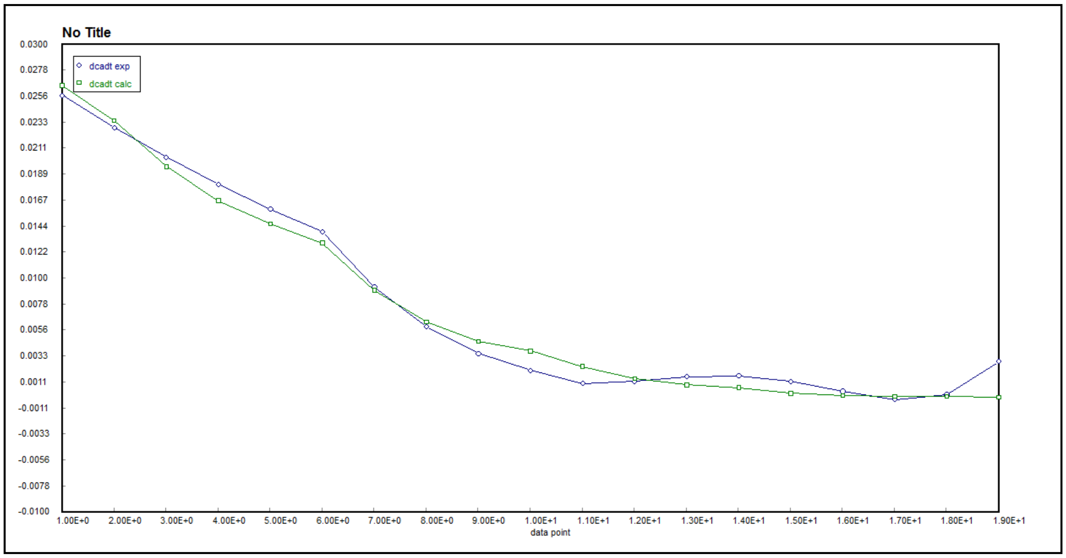


Figure 4.8 The dCa/dt for Both Experimental and Predicted Lines for LHHW Model

Figure 4.8 is the graph for dCa/dt for both experimental and predicted data for LHHW model by polymath. The blue line represents the experimental data whereas the green line represents the predicted data by polymath itself. Based from the observation, the blue line is very close to the green line over the time. The precisions of R^2 shown in Table 4.7 is correct and being supported by this graph.

Table 4.8 presents the data information of k values and the R^2 value for the model of LHHW for the temperature from 70 to 100 ℃. The values of k are increased as the temperature of reaction is increased. For R^2, the value should be as high as possible. For equilibrium constant, ke, the values should be decreasing as the temperature increases. The ke in Table 4.8 does not show the trend that the ke values are decreased as the temperature is increased. The last two values for temperature 90 and 100 are 102.0000 and 101.9987 respectively. If the both values are smaller than previous value, then this esterification reaction can be claimed as endothermic reaction.

Table 4.8 The k, ke and R^2 Values for different temperatures under LHHW Model

Temperature	k	ke	R^2
70	0.6771332	101.9993	0.9322739
80	0.7684141	101.9963	0.9666379
90	1.6999260	102.0000	0.9421096
100	10.1933800	101.9987	0.9823054

4.3.2 Eley-Rideal (ER)

Eley-Rideal (ER) is a mechanism that proposed by D. D. Eley and E. K. Rideal in the year of 1938. The reaction only takes place between adsorbed molecules of alcohol and the molecules of acid in the bulk solution which is based on the mechanism. Korumakki et al., (2005) claimed that the saturation of the catalyst surface with alcohol is the reason blocking the acid adsorption. By using this statement, the adsorbed molecules will be alcohol.

The rate of reaction for ER model is expressed as Eq. 4.6.:

$$-r_s = \frac{dC_A}{dt} = \frac{k\ (C_A C_B - \frac{C_C C_D}{ke})}{1 + K_A C_A + K_C C_C} \qquad \text{Eq. (4.6)}$$

A number of adsorption equilibrium constants and the unknown constants will be determined based on the experimental data using Polymath Fogler 6.10 for simulation.

4.3.2.1 ER Model fitting using POLYMATH

The values of absorption equilibrium constants and graphs will be determined and tabulated by using Polymath Folger 6.1. The rate of reaction for ER model will be inserted into the programme. The procedures for the generation of ER model are exactly the same with the procedures shown in 4.4.1.1 Polymath Simulation for LHHW Model.

Based on the observation from Table 4.9, the k values are increasing as the temperature is increased from 70 to 100 ℃. The kinetic energy posses by the molecules were enough for them to take place to have chemical reaction. The higher the temperature for the reaction, the faster the molecules possesses sufficient kinetic energy to take place. By sufficient kinetic energy, the equilibrium is shift right hand side easily to form products. For ke, the results obtained are not favorable. The ke values should be decreasing but it does not as the temperature is increased. Besides, the R^2 values from 70 to 100 ℃ are not consistent. The R^2 should be as close as possible to 1. This might due to the errors made during the reaction time when the experimental samples were collected.

Table 4.9 The k, ke and R^2 Values for different temperatures under ER Model

Temperature	k	Ke	R^2
70	0.0185838	1.01E4	0.9318441
80	0.2813998	5.386366	0.7896166
90	0.7548546	7.967297	0.8331095
100	1.3661310	101.999100	0.9582823

4.3.3 Pseudo Homogeneous (PH)

Pseudo Homogeneous model is the reaction that the adsorption of the reactants onto the catalyst surface is assumed to be negligible. The rate of reaction for PH is expressed as Eq. 4.7.:

$$-r_A = k\ (C_A C_B - \frac{C_C C_D}{k_e}) \qquad (4.7)$$

The k and ke values will be determined based on the experimental data using Polymath Fogler 6.10 for simulation.

Table 4.10 The k, ke and R^2 Values for Different Temperatures under PH Model

Temperature	k	ke	R^2
70	0.000798	2.360591	0.8684412
80	0.001192	12.803280	0.9540991
90	0.001964	28.799920	0.9745121
100	0.005461	101.998800	0.8920435

4.3.3.1 PH Model fitting using POLYMATH

The k and ke values are determined by Polymath Folger 6.1 by inserting the rate of reaction PH model into the programme. The procedures for the generation of PH model are exactly the same with the procedures shown in 4.4.1.1 Polymath Simulation for LHHW Model.

Table 4.10 shows the k, ke and R^2 values for different temperatures under PH Model. Based from the observation, the k value is increasing gradually as the reaction temperature is increasing every 10 ℃. For ke value, the trend of these values is out from the expectation. The values of ke suppose should be decreasing as the reaction temperature increases. Besides, this PH model shows that it is an exothermic reaction but not an endothermic reaction. Besides, the R^2 values for temperature for both 70°C and 100 ℃ are not favorable since they both are not close enough to 1.

4.3.4 Comparison between LWWH, ER and PH Model

From Table 4.8, Table 4.9 and Table 4.10, most of the regression lines fitted the data well where the R^2 is close to 1. Unfortunately, there are many exceptional cases. However, one among the three models has to be chosen to be the best model which fits the data well. Table 4.11 presents the comparison of R^2 between LHHW, ER and PH model.

From Table 4.11 presents the values of R^2 based on the models and the reaction temperatures respectively. For ER model, there performance of R^2 is not nice where there is a negative value of R^2 appeared for temperature 70 ℃. So, ER model is not suitable to be the best kinetic model to fit the data. For both LHHW and PH model, the values of R^2 for LHHW model are closer to 1 if compare to the values of R^2 for PH model. In this kinetic model comparison, it is clear that LHHW model is the best model to be fitted with the data available from experimental work.

The reaction was happened between all adsorbed molecules. The molecules of acetic acid and 2-ethyl-1-hexanol were adsorbed to the catalyst surface. In the catalyst, the reaction was taken place to produce 2-ethyl-1-hexyl acetate and water. After the reaction, the both products were desorbed from the catalyst. The mechanism explained the reaction where the LHHW model was fitted.

Table 4.11 Comparison of R^2 between LHHW, ER and PH model

		R^2	
Temperature	**LHHW**	**ER**	**PH**
70	0.9322739	0.9318441	0.868441
80	0.9666379	0.789617	0.954099
90	0.9421096	0.83311	0.974512
100	0.9823054	0.958282	0.892044

4.4 LHHW Model Mechanism

The mechanism of the esterification reaction for the present work was described according to the LHHW model. The 2-ethyl-1-hexanol molecule first is adsorbed on the active site on the internal surface of Amberlyst 15 while the acetic acid molecule is also adsorbed on the catalyst site and forms oxonium ion intermediate, which is attacked from the back by the 2-ethyl-1-hexanol adsorbed from the catalyst site. 2-ethyl-1-hexyl acetate (ester) and water are formed in adsorbed state. Then, all the adsorbed molecules are desorbed and give rise to a vacant catalyst site in the reaction. Therefore, the surface reaction is the rate limiting step.

4.5 Activation Energy

Activation energy is the least amount of energy that needs to overcome in order for a chemical reaction to take place. This energy is introduced in 1889 by the Swedish scientist Svante Arrhenius. From the Arrhenius equation, the activation energy can be expressed as Eq. (4.8):

$$k = Ae^{-Ea/RT} \qquad (4.8)$$

where A = frequency factor for the reaction

R = universal gas constant, 8.314 J/mol.K or 1.987 cal/mol.K

T = temperature (K)

K= reaction rate coefficient

Based on the Table 4.8 for LHHW model, a calculation is shown on Table 4.12 and the graph of ln k versus 1/T is plotted in Figure 4.9. Activation energy of LHHW model can be calculated based from the Figure 4.9.

Table 4.12 The Values of ln k and 1/T for LHHW Model

k (min)	T (K)	ln k	1/T	$1/T*10^5$
0.6771332	343	-0.3898873	0.0029155	291.55
0.7684141	353	-0.2634265	0.0028329	289.29
1.699926	363	0.53058472	0.0027548	275.48
10.19338	373	2.32173849	0.0026810	268.10

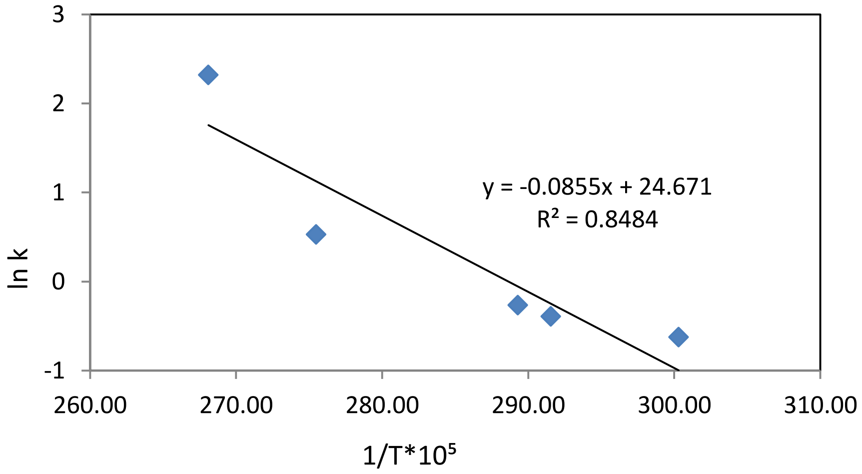


Figure 4.9 The Graph of ln k versus 1/T for Activation Energy Calculation

From Figure 4.9, the slope is equal to –E/R where the slope can be obtained from the equation of Y=-0.0855X + 24.671.

Slope = -0.0855*1E5 = -Ea/R

Ea = 8550 K (8.314 J/mol.K)

= 71.08 kJ/mol (16.99 kcal/mol)

ln A = 24.671, therefore A = 5.1817×10^{10} min^{-1}

A comparison of activation energy was compared between other findings and the present activation energy. Table 4.13 shows the activation energy for the esterification reaction using different alcohols and catalysts.

Table 4.13 The Activation Energy for the Esterification Reaction using Different Alcohols and Catalysts

Researcher	Alcohol	Catalyst	Activation energy
Liu et al (2006)	Methanol	H_2SO_4	52.7 kJ/mol
Gogoi & Dutta (2009)	Isoamyl alcohol	CT-175	47.0 kJ/mol
Tarihi (2011)	Ethyl alcohol	Lewatit	84.9 kJ/mol
Toor et al (2011)	Iso-butanol	Amberlyst 15	23.3 kJ/mol

From the Table 4.13, the activation energy is shown based on the types of alcohol and catalyst used in the esterification reaction. The range of activation energy for the esterification reaction is normally fall between 20 kJ/mol and 80 kJ/mol. In order to ensure that present activation energy is rational, a comparison for activation energy is made with other findings.

4.6 Adsorption Equilibrium Constant

There are four adsorption equilibrium constants in the LWWH model. They are K_A, K_B, K_C and K_D where A, B, C and D are acetic acid, 2-ethyl-1-hexanol, 2-ethyl-1-hexyl acetate and water respectively. The values of adsorption equilibrium constants are presented in Table 4.14 ranging from 70°C to 100°C. The values were predicted using POLYMATH. The KA and KB values were found to increase from 3.61 to 7.96 and 7.98 respectively. The increase in both KA and KB values with temperature indicates a higher heat of adsorption with increasing temperature. It is clear that the adsorption of Langmuir model is endothermic process (He et al., 2010).

Table 4.14 Adsorption Equilibrium Constants for LHHW Model

Temp	K_A	K_B	K_C	K_D
70	3.61	3.61	7.48	7.48
80	3.34	3.35	4.68	4.76
90	4.81	4.81	5.42	7.47
100	7.96	7.98	3.45	3.35

4.7 Heat of Adsorption for Equilibrium Constant

Graphs of ln K*i* vs 1/T were plotted for each adsorption equilibrium constants which are shown in Appendix C. The heat of adsorption can be calculated from the plotted graph. The slope of each graph is equal to $-\Delta H_{ad}/R$ for each adsorption equilibrium constants. Table 4.14 presents the heat of adsorption for each adsorption equilibrium constants.

Table 4.15 The Heat of Adsorption for Each Adsorption Equilibrium Constants on LHHW Model

Adsorption Equilibrium Constant	Slope*1E5	Heat of adsorption, ΔH_{ad}
K_A	-0.0333	27.69kJ/mol
K_B	-0.0333	27.69kJ/mol
K_C	0.0213	-17.7kJ/mol
K_D	0.0175	-14.55kJ/mol

CHAPTER 5

CONCLUSION AND RECOMMENTATION

5.1 Conclusion

The kinetic behaviour has been studied for the esterification reaction of diluted acetic acid with 2-ethyl-1-hexanol over Amberlyst 15 at temperature from 70 to 100 ℃ and speed of agitation from 300rpm to 600rpm. The highest conversion reached 98.86% when the reaction was carried out at the temperature of 100 ℃ with 500rpm over 3g of catalyst. The conversion of acetic acid was found to increase gradually with an increase in temperature. On the other side, there is no much different in term of conversion for the effect of speed of agitation ranging from 300rpm to 600rpm. The highest conversion for agitation speed was 74.9% with 600rpm. The mass transfer resistance for both 300rpm and 500rpm were high compare to the reaction for 400rpm and 600rpm. PH, LWWH and ER models were applied to correlate with the experimental data. LHHW model gave the best representation of the kinetic behavior for all practical purposes on the reaction kinetics studied under the given condition.

5.2 Recommendation

Apart from the effect of reaction temperature and the speed of agitation, there are many others important parameters that can be studied for esterification reaction. They are catalyst loading, molar ratio, reaction time and particle size of catalyst. Besides, the reaction time for reaction should be longer until equilibrium is achieved. Then, the equilibrium data can be obtained.

On top of that, other alcohol compounds that being used to react with acetic acid should be explored. The complex alcohols such as 2-methyl-pentanol and benzyl alcohol can be studied. Amberlite 200, MCM-141-41 and other ion-exchange resins can be used in the further study for comparison purposes.

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APPENDIX A

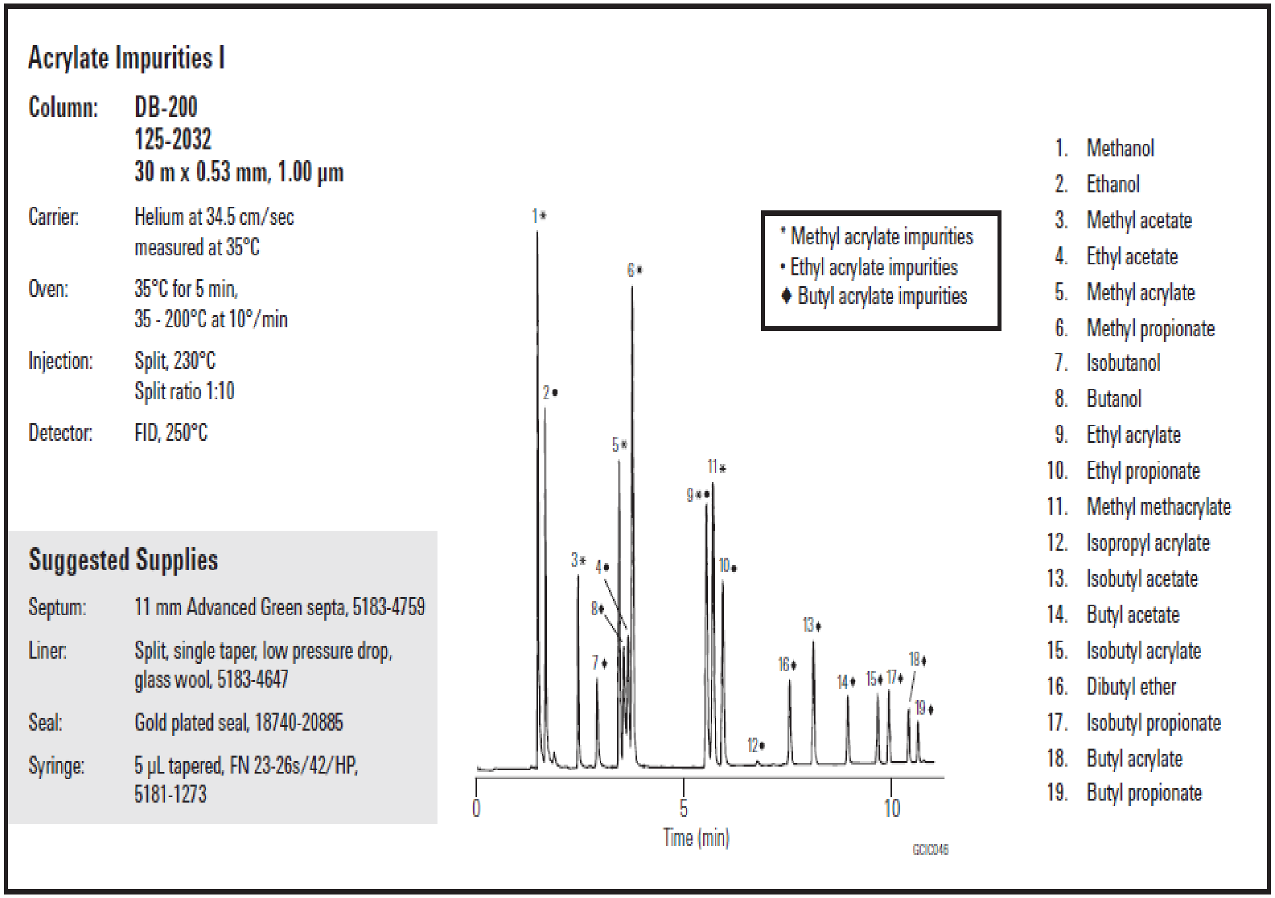
Table A.1 The concentration (ppm) for each sample at various temperature with 500rpm and 3g catalyst.

Samples No	Reaction Temperature			
	70 ℃	80 ℃	90 ℃	100 ℃
1	209547.67	224708.60	147013.72	142034.79
2	194776.85	204390.77	135029.11	127279.36
3	189860.82	193049.85	125708.93	108757.44
4	188766.81	187100.03	126563.40	95460.02
5	186400.80	178754.10	108637.00	86423.55
6	164598.19	173842.09	111360.32	79149.55
7	166491.13	158057.54	107518.90	60825.65
8	166639.68	142133.82	97643.36	48040.25
9	156287.72	136998.33	87687.52	39784.05
10	146582.80	129024.42	83605.22	35305.55
11	137467.38	114452.33	72676.48	27709.85
12	125268.65	105078.62	63987.05	20760.19
13	123586.48	92667.11	56334.28	16457.98
14	117708.93	86961.53	53343.19	14360.56
15	105889.60	82434.93	49960.64	9075.87
16	103820.01	78602.88	48823.15	5930.72
17	98626.30	75058.55	45121.47	4182.86
18	96032.79	72533.29	39721.99	4218.42
19	90441.62	63302.02	43905.15	2399.23

Table A.2 The concentration (ppm) for each sample at various speed of agitation with 80 ℃ and 3g catalyst.

Samples No	Speed of Agitation			
	300rpm	400rpm	500rpm	600rpm
1	191909.00	137854.13	224708.60	145870.86
2	179429.24	118760.12	204390.77	128752.09
3	174970.89	115458.68	193049.85	133781.20
4	193340.92	114434.26	187100.03	118127.80
5	171462.03	122075.61	178754.10	115734.36
6	179933.76	108651.72	173842.09	113031.78
7	149731.01	110683.17	158057.54	103663.43
8	140157.91	101795.25	142133.82	106639.01
9	127595.85	90597.52	136998.33	94592.84
10	128209.43	81090.67	129024.42	81011.04
11	124012.04	85838.74	114452.33	83506.86
12	101546.34	78844.43	105078.62	74139.18
13	87917.70	66760.35	92667.11	73928.40
14	85841.42	67939.78	86961.53	72104.38
15	96062.23	60637.72	82434.93	65648.04
16	78437.60	58051.55	78602.88	63862.54
17	84050.18	53029.12	75058.55	57024.60
18	76498.01	57761.04	72533.29	59355.43
19	75109.23	54315.68	63302.02	52423.78

APPENDIX B



Acrylate Impurities I

Column:	**DB-200** **125-2032** **30 m x 0.53 mm, 1.00 µm**
Carrier:	Helium at 34.5 cm/sec measured at 35°C
Oven:	35°C for 5 min, 35 - 200°C at 10°/min
Injection:	Split, 230°C Split ratio 1:10
Detector:	FID, 250°C

Suggested Supplies

Septum:	11 mm Advanced Green septa, 5183-4759
Liner:	Split, single taper, low pressure drop, glass wool, 5183-4647
Seal:	Gold plated seal, 18740-20885
Syringe:	5 µL tapered, FN 23-26s/42/HP, 5181-1273

* Methyl acrylate impurities
• Ethyl acrylate impurities
♦ Butyl acrylate impurities

1. Methanol
2. Ethanol
3. Methyl acetate
4. Ethyl acetate
5. Methyl acrylate
6. Methyl propionate
7. Isobutanol
8. Butanol
9. Ethyl acrylate
10. Ethyl propionate
11. Methyl methacrylate
12. Isopropyl acrylate
13. Isobutyl acetate
14. Butyl acetate
15. Isobutyl acrylate
16. Dibutyl ether
17. Isobutyl propionate
18. Butyl acrylate
19. Butyl propionate

Figure B.1 The characteristics of column for gas chromatography

APPENDIX C

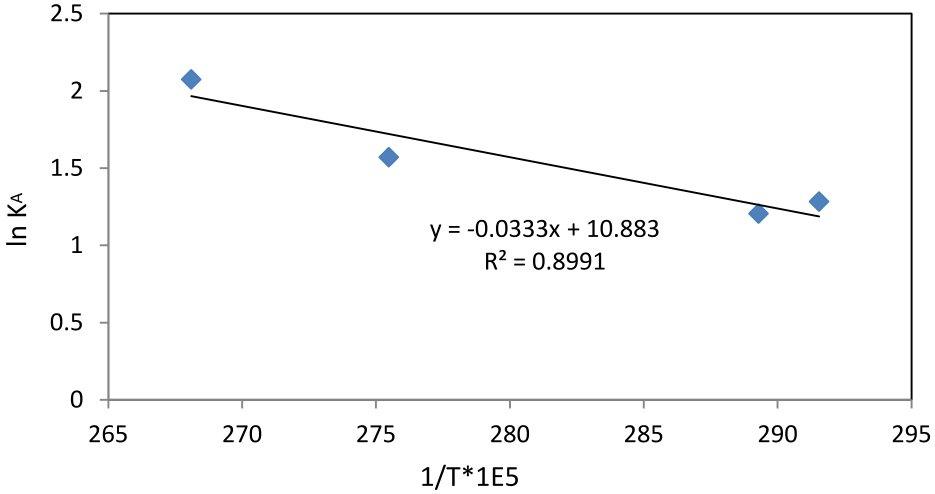


Figure C.1 Graph of ln K_A vs 1/T

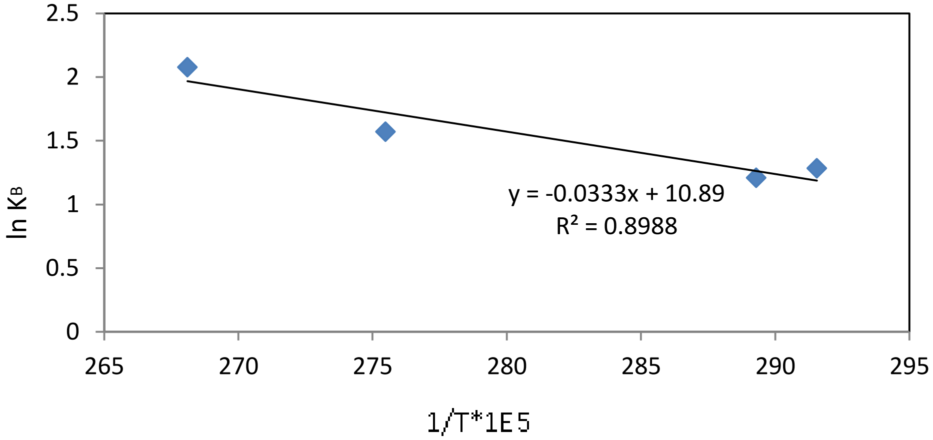


Figure C.2 Graph of ln K_B vs 1/T

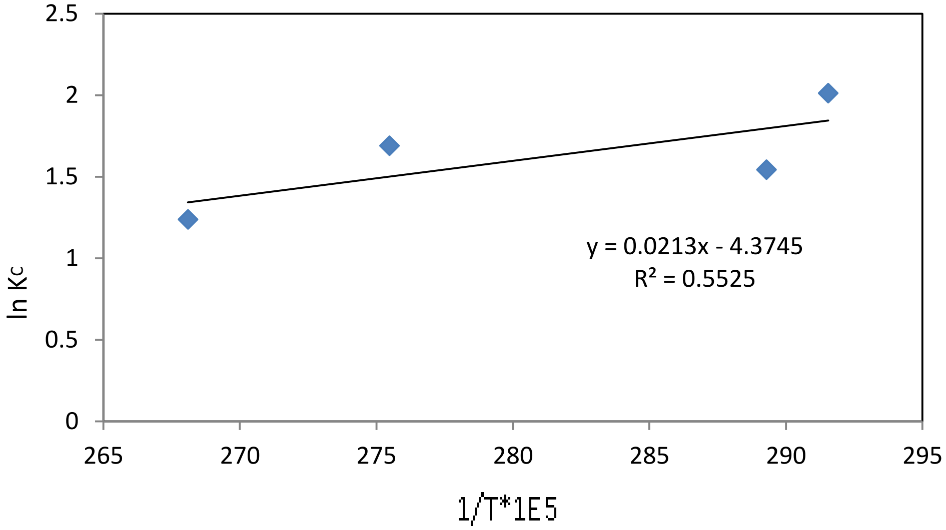


Figure C.3 Graph of ln K_C vs 1/T

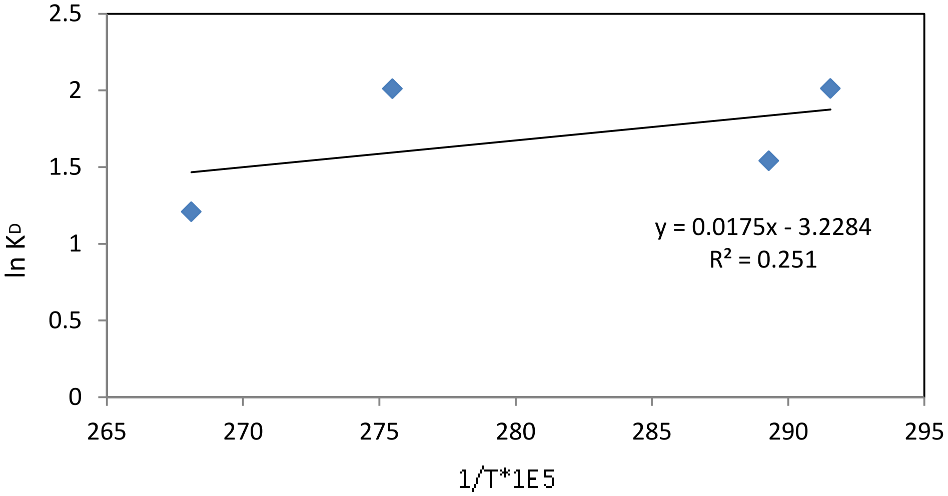


Figure C.4 Graph of ln K_D vs 1/T