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RESEARCH REPORT UMP GRANT

Laporan Prestasi Skim Geran UMP

Progress	
Final	/

√ *Please tick*

A

GRANT RDU NO : RDU 140313

RESEARCH TITLE : Kinetics and Mass Transfer of Esterification of Diluted Acrylic Acid with 2-Ethyl Hexanol in a Tubular Packed Bed Reactor

PROGRESS PERIOD : 01/04/2014 - 31/03/2016

PROJECT LEADER : Chin Sim Yee

PROJECT MEMBERS :

1. **Hayder A. Abdul Bari**
2. **Cheng Chin Kui**
3.
4.
5.

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE				
Project progress according to milestones achieved up to this period	**0 - 25%**	**26 - 50%**	**51 - 75%**	**76 - 100%**
Percentage (please state %)				100

RESEARCH OUTPUT		
	ISI	**SCOPUS**
Number of articles/ manuscripts/ books *(Please attach the First Page of Publication)*	1. One in KCEJ (Attachment 1) 2. 3. 4. 5.	1. 2. 3. 4. 5.
	International	**National**
Conference Proceeding *(Please attach the First Page of Publication)*	1. One in SOMChE Proceeding (Attachment 2) 2. 3. 4. 5.	1. 2. 3. 4. 5.
Intellectual Property *(Please specify)*	None	

HUMAN CAPITAL DEVELOPMENT

Human Capital	Number				Others (please specify)
	On-going		Graduated		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
PhD Student	1				
Master Student					
Undergraduate Student	1				
Total	2				

Name of Student:	Mohd Amirul Asyraf B. Ahmad
ID Matric No:	PKC15006
Faculty:	FKKSA
Thesis title:	Kinetic and Simulation Studies of the Estefication of Waste Water Containing Acrylic Acid with 2-Ethyl Hexanol
Graduation Year:	2018
Name of Student:	Heamamalini A/P Parathethasan
ID Matric No:	KA13038
Faculty:	FKKSA
Thesis title:	Esterification of Acrylic Acid and 2-Ethyl Hexanol in Tubular Reactor for the Synthesis of 2-Ethyl Hexyl Acrylate
Graduation Year:	2017
** *enter for more space*	

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *(Peruntukan diluluskan)* : **RM 37,800.00**
Amount Spent *(Jumlah Perbelanjaan)* : **RM 24,054.86**

Balance *(Baki)* : **RM 13,745.14**
Percentage of Amount Spent *(Peratusan Belanja)* : 64 %

ASSET

D

Bil	Peralatan *(Equipment)*	Model	No Daftar Aset *(Asset Tagging No)*	Amount (RM)	Lokasi *(Location)*
1	Thermal oil pump		FTA1000-PB104(R)-1602-0001-00004	2,200.00	Unit Operation Lab
2	Peristaltic pump for transfering raw material		FTA1000-PB104(R)-1602-0001-00001	400.00	Unit Operation Lab
3	Peristaltic pump for transfering raw material		FTA1000-PB104(R)-1602-0001-00002	400.00	Unit Operation Lab
4	Furnace		FTA1000-PB104(R)-1602-0001-00007	900.00	Unit Operation Lab

PRODUCT DESCRIPTION FOR UMP R&D DIRECTORY (SHORT & BRIEF) *Only for Final Report*

E 2-ethylhexyl acrylate (2EHA) was produced through the esterification of pure and diluted acrylic acid with 2-ethyl hexanol in a tubular packed bed reactor.

PRODUCT PICTURE FOR UMP R&D DIRECTORY *Only for Final Report*

F The tubular packed bed reactor setup as shown in Figure 1 and Photo 1, comprises a reactant tank which is made of stainless steel. The reactant tank was connected to a heat exchanger, a coil immersed in oil bath for heating up the inlet stream of the reactor (feed solution) to desired temperature. A peristaltic pump was used to pump the reactants to the reactor system.

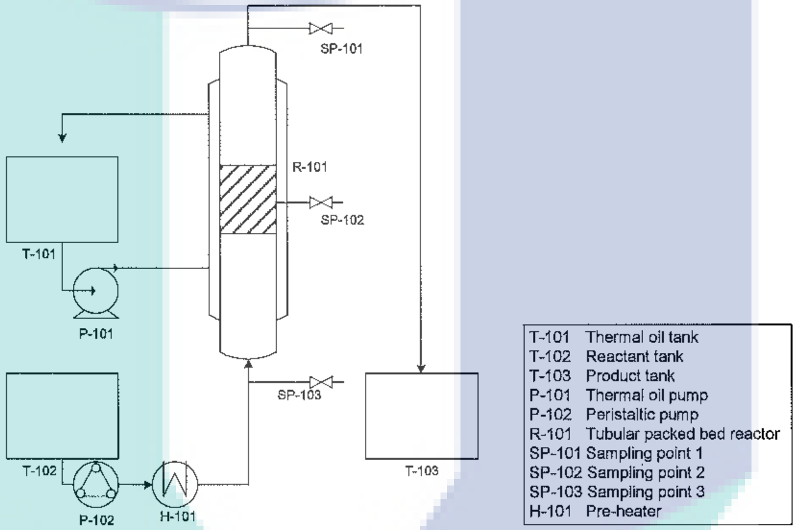

Figure 1. Schematic diagram of the tubular packed bed reactor.

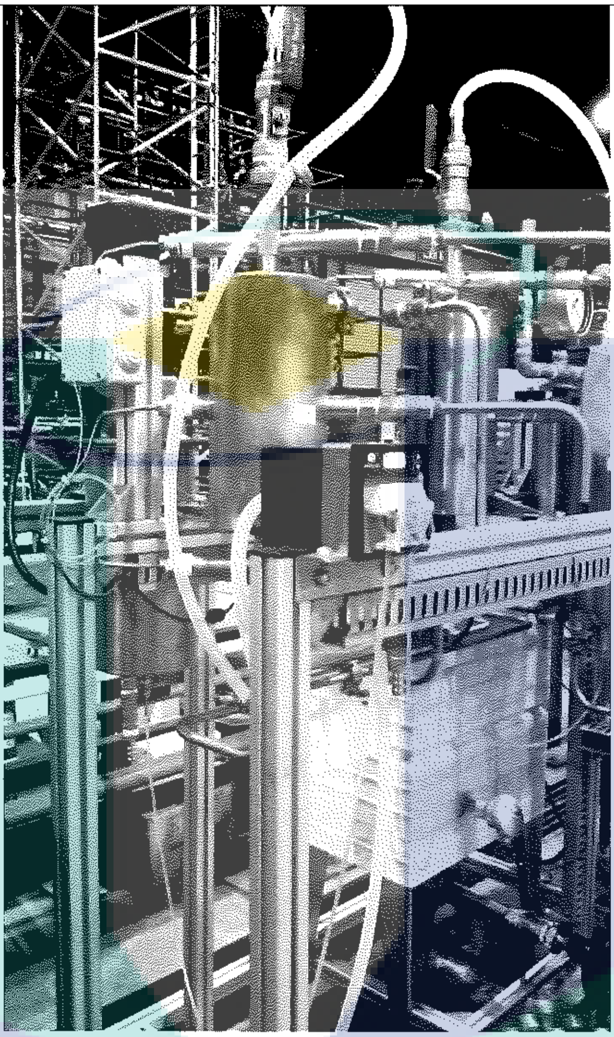

Photo 1. Photo of the tubular packed bed reactor.

SUMMARY OF RESEARCH FINDINGS *(Ringkasan Penemuan Projek Penyelidikan)*

G	The global demand of 2-ethylhexyl acrylate (2EHA) market has witnessed a significant growth in the past few years and this growth is anticipated to increase in the coming years. 2EHA is one of the basic organic building blocks that mainly used in the production of coatings, adhesives, super-absorbents, thickeners and plastic additives. As the demand increases, the productions of 2EHA need to be innovated so that it can be produced in a cheaper price. The use of homogeneous catalyst in the commercial process shows that these catalysts are hard to separate from the reaction medium, hence unable the reuse of the catalysts and complicate the separation process. It also promotes side reaction which resulting in expensive downstream processes. The employment of heterogeneously catalysed process in a tubular reactor is anticipated to a cheaper process since it can enable the reuse of catalyst, minimise the hazardous waste generation due to the homogeneous catalyst, and eliminate the occurrence of side reaction and hence increasing the yield of desired product. In the present study, the best catalyst was identified and the residence time distribution of the tubular packed bed reactor was examined prior the study on the effect of important operating parameters on the esterification of Acrylic Acid (AA) with 2-Ethyl Hexanol (2EH) for the production of 2EHA in a tubular packed bed reactor. The reaction kinetics were also evaluated. Employing the best catalyst, DIAION PK-208 in a tubular packed bed reactor for the esterification of AA and 2EH, the highest yield and conversion, 3.29% and 44.3 % respectively were obtained at the reaction temperature of 95°C, initial feed molar ratio of AA:2EH of 1:3 and catalyst loading of 5 g. The discrepancy of the yield and conversion was ascribing to the AA adsorbed on the resin. The tubular packed bed reactor was non-ideal in mixing. The kinetic studies show that the Eley-Rideal (ER) was the best kinetic model to correlate the rate of consumption AA and production of 2EHA. As a continuaty of this work, a grant under TORAY Science Foundation Malaysia was approved for my PhD student to cover a wider scope of this research (approval letter as in Attachment 3).

PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

H	-

IR. DR. CHIN SIM YEE
Assoc. Professor
Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang
Lebuhraya Tun Razak, 26300 Gambang, Pahang

Date : 17/11/17
Tarikh

Project Leader's Signature:
Tandatangan Ketua Projek

COMMENTS, IF ANY/ ENDORSEMENT BY FACULTY
(Komen, sekiranya ada/ Pengesahan oleh Fakulti

Recommend / Not Recommend / KIV / Need Ammendment

....

....

....

Name:
Nama:

Signature:
Tandatangan:

Date:
Tarikh:

**** Dean/TDR**

COMMENTS, IF ANY/ ENDORSEMENT BY RMC PNI *(Komen, sekiranya ada/ Pengesahan oleh RMC PNI*	
I	**Recommend / Not Recommend / KIV / Need Ammendment** …………………………………………………………………………………………… …………………………………………………………………………………………… …………………………………………………………………………………………… **Name:** **Signature:** *Nama:* *Tandatangan:* **Date:** *Tarikh:*

Attachment 1

Korean Journal of Chemical Engineering

KINETIC STUDIES OF THE ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL CATALYSED BY DIAION RESINS

--Manuscript Draft--

Manuscript Number:	KJCE-D-17-00034
Full Title:	KINETIC STUDIES OF THE ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL CATALYSED BY DIAION RESINS
Article Type:	Original Article
Corresponding Author:	Sim Yee Chin Universiti Malaysia Pahang Faculty of Chemical and Natural Resources Engineering MALAYSIA
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Funding Information:

Funder	Recipient
Universiti Malaysia Pahang (short-term grant scheme (RDU130313))	Dr. Sim Yee Chin
Universiti Malaysia Pahang (Postgraduate Graduate Research Scheme (GRS150397))	Mr Mohd Amirul Asyraf Ahmad
Malaysia Toray Science Foundation	Mr Mohd Amirul Asyraf Ahmad
Mitsubishi Chemical Holding Group	Not applicable

Abstract:

Homogenous acid catalysts are often used in the industries producing acrylate esters. In addition to their toxicity and corrosiveness, they are hard to remove from the reaction medium. The heterogeneously catalysed esterification that uses the poly(styrene-divinylbenzene) sulfonated resin as catalyst can overcome the drawbacks of homogeneous catalysts. In the present work, activity and kinetic studies of the esterification of acrylic acid (AA) and 2-ethylhexanol (2EH) catalysed by DIAION acidic ion exchange resins were carried out in a batch system. DIAION resins PK208 out-performed the other resins due to its low percentage of crosslinkage that enhancing the accessibility of the reactant and its comparative ion exchange capacity. It was used subsequently in the kinetic studies. It shows the highest yield of 41% was obtained at the temperature of 388K, initial reactant molar ratio of AA to 2EH of 1:3 and catalyst loading of 10 wt% after 4 hour reaction. The kinetic studies adopting PK208 as catalyst show that the Eley-Rideal (ER) was the best kinetic model to correlate the rate of consumption and production of AA and 2-ethylhexyl acrylate respectively. The increase of the equilibrium constant with temperature indicated that the esterification of AA with 2EH an endothermic reaction.

Suggested Reviewers:

Emine Sert, PhD
Ege Universitesi
emine.buyuran@ege.edu.tr
Expertise in this field

Basu Saha, PhD

KINETIC STUDIES OF THE ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL CATALYSED BY DIAION RESINS

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ABSTRACT

Homogenous acid catalysts are often used in the industries producing acrylate esters. In addition to their toxicity and corrosiveness, they are hard to remove from the reaction medium. The heterogeneously catalysed esterification that uses the poly(styrene-divinylbenzene) sulfonated resin as catalyst can overcome the drawbacks of homogeneous catalysts. In the present work, activity and kinetic studies of the esterification of acrylic acid (AA) and 2-ethylhexanol (2EH) catalysed by DIAION acidic ion exchange resins were carried out in a batch system. DIAION resins PK208 out-performed the other resins due to its low percentage of crosslinkage that enhancing the accessibility of the reactant and its comparative ion exchange capacity. It was used subsequently in the kinetic studies. It shows the highest yield of 41% was obtained at the temperature of 388K, initial reactant molar ratio of AA to 2EH of 1:3 and catalyst loading of 10 wt% after 4 hour reaction. The kinetic studies adopting PK208 as catalyst show that the Eley-Rideal (ER) was the best kinetic model to correlate the rate of consumption and production of AA and 2-ethylhexyl acrylate

Attachment 2

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2016

29th SYMPOSIUM OF MALAYSIAN CHEMICAL ENGINEERS 2016

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and 0.0024, respectively. The wide peak and small value of n (lower than 2) suggests the continuation of the hydrate formation in the bulk of liquid with the dendritic shape of the crystals. It also indicates that the secondary growth step of slow crystallization process which may be due to thickening the crystal edges or crystal completeness forming a plate-like crystal. Moreover, the relatively low values of n also indicates heterogeneous nucleation is taking place in the systems during hydrate formation. In addition, the half time of the crystallization process, $t_{1/2}$, is calculated by using Avrami parameters. The calculated $t_{1/2}$ for the two samples are in agreement with their experimental values. The analysis also indicates that 97% of the crystallization rate of methane hydrate is governed by the enclathration reaction.

Keywords: hydrate; Avrami model; isothermal kinetic; induction time

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Screening of Catalyst and Important Variable for The Esterification of Acrylic Acid with 2 Ethylhexanol

[Paper ID: RE-08]

Mohd Amirul Asyraf Bin Ahmad[1], Chin Sim Yee[1,2*]

[1]Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia
[2]Center of Excellence for Advanced Research in Fluid Flow, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia
*Corresponding author: chin@ump.edu.my

Abstract: The global demand of 2-ethylhexyl acrylate (2EHA) market has witnessed a significant growth in the past few years and this growth is anticipated to increase in the coming years. 2EHA is one of the basic organic building blocks that mainly used in the production of coatings, adhesives, superabsorbents, thickeners and plastic additives. Homogenous acid-catalysed esterification of acrylic acid (AA) with 2-ethylhexanol (2EH) is commonly used for the production of 2EHA. The homogeneous catalysts such as sulfuric and para-toluene sulfonic acid have resulted the costly and complicated downstream process that generates acidic, corrosive and non-environmental friendly waste. Therefore, it is importance to develop a cheaper process that employing heterogeneous catalysts and alternative raw material from wastewater containing acrylic acid. In this research, the study for the esterification of AA with 2EH catalysed by ion-exchange resin was conducted. The best sulfonic acid functional cation-exchange resin among SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160 was screened. PK208 outperformed the other resins and it was used subsequently in the parametric studies. The effect of important parameters (initial concentration of acrylic acid (AA), temperature, molar ratio of reactant (AA and 2EH), catalyst loading, and polymerisation inhibitor loading) was studied using 2 factorial design to determine the significant parameters to the esterification. It was found that the initial concentration of AA and temperature were most significantly affecting the esterification of AA with 2EH.

Keywords: Acrylic Acid, 2-ethylhexyl acrylate, 2 ethylhexanol, Esterification, Resin

RDU 140313

KINETICS AND MASS TRANSFER OF ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL IN A TUBULAR PACKED BED REACTOR

CHIN SIM YEE
HAYDER A. ABDUL BARI
CHENG CHIN KUI

RESEARCH VOT NO.: RDU140313

Fakulti Kejuruteraan Kimia dan Sumber Asli
Universiti Malaysia Pahang

2017

ACKNOWLEDGEMENT

We would like to thank Universiti Malaysia Pahang, for the Short-Term Grant Scheme (RDU130313) and the Postgraduate Graduate Research Scheme (GRS150397) to support this research work. Gratitude is given especially to Mitsubishi Chemical Holding Group for sponsoring the resin catalysts.

KINETICS AND MASS TRANSFER OF ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL IN A TUBULAR PACKED BED REACTOR

(Keywords: Kinetic, esterification, acrylic acid, packed bed reactor, 2-ethyl hexyl acrylate)

The global demand of 2-ethylhexyl acrylate (2EHA) market has witnessed a significant growth in the past few years and this growth is anticipated to increase in the coming years. 2EHA is one of the basic organic building blocks that mainly used in the production of coatings, adhesives, super-absorbents, thickeners and plastic additives. As the demand increases, the productions of 2EHA need to be innovated so that it can be produced in a cheaper price. The use of homogeneous catalyst in the commercial process shows that these catalysts are hard to separate from the reaction medium, hence unable the reuse of the catalysts and complicate the separation process. It also promotes side reaction which resulting in expensive downstream processes. The employment of heterogeneously catalysed process in a tubular reactor is anticipated to a cheaper process since it can enable the reuse of catalyst, minimise the hazardous waste generation due to the homogeneous catalyst, and eliminate the occurrence of side reaction and hence increasing the yield of desired product. In the present study, the best catalyst was identified and the residence time distribution of the tubular packed bed reactor was examined prior the study on the effect of important operating parameters on the esterification of Acrylic Acid (AA) with 2-Ethyl Hexanol (2EH) for the production of 2EHA in a tubular packed bed reactor. The reaction kinetics were also evaluated. Employing the best catalyst, DIAION PK-208 in a tubular packed bed reactor for the esterification of AA and 2EH, the highest yield and conversion, 3.29% and 44.3 % respectively were obtained at the reaction temperature of 95℃, initial feed molar ratio of AA:2EH of 1:3 and catalyst loading of 5 g. The discrepancy of the yield and conversion was ascribing to the AA adsorbed on the resin. The tubular packed bed reactor was non-ideal in mixing. The kinetic studies show that the Eley-Rideal (ER) was the best kinetic model to correlate the rate of consumption AA and production of 2EHA. The data obtained can be used as a baseline information to develop a bigger scale of packed bed reactor for the production of 2EHA.

KINETIK DAN PEMINDAHAN JISIM UNTUK PENGESTERAN ASID AKRILIK DENGAN ETIL HEXANOL DALAM REAKTOR TIUB LAPISAN TERPADAT

(Keywords: Kinetik, pengesteran, asid akrilik, reaktor tiub lapisan terpadat, 2-etil hexil akrilat)

Permintaan pasaran dunia terhadap ester akrilik menunjukkan peningkatan yang ketara pada kebelakangan ini dan dijangkakan akan terus meningkat pada masa akan datang. Ester akrilik merupakan unit asas bahan dalam kebanyakan penghasilan bahan penyalut, gentian, penyerap berkuasa tinggi, bahan penebal, dan bahan tambahan dalam penghasilan plastic. Seiring dengan peningkatan permintaan, pengeluaran ester akrilik perlu lebih inovatif supaya ia boleh dihasilkan dengan harga yang lebih murah. Penggunaan pemangkin homogen dalam proses komersial menunjukkan bahawa pemangkin ini sukar untuk dipisahkan dari medium tindak balas, menyebabkan ia tidak dapat digunakan semula selain juga merumitkan proses pemisahan bahan. Ia juga menggalakkan tindak balas sampingan yang mengakibatkan kos pemisahan lebih tinggi. Penggunaan pemangkin heterogen dalam proses reaktor tiub lapisan terpadat dijangka dapat merendahkan kos kerana ia membenarkan penggunaan semula pemangkin, mengurangkan penghasilan sisa berbahaya disebabkan pemangkin homogen, seterusnya mengelakkan berlakunya tindak balas sampingan hatta meningkatkan hasil produk yang diingini. Dalam kajian ini, kesan parameter operasi yang penting untuk proses pengesteran asid akrilik (AA) dengan 2-Ethyl Hexanol (2EH) untuk menghasilkan 2-ethyl hexyl akrilat dalam reaktor tiub telah dilaksanakan. Kinetik tindak balas juga turut dinilai. Dengan menggunakan pemangkin yang terbaik, DIAION PK-208 di dalam reactor tiub lapisan terpadat untuk proses esterifikasi antara AA dan 2EH, hasil dan tukaran terbaik ialah 3.29% dan 44.3% masing-masing yang didapati pada suhu reaksi 95 ℃, nisbah molar AA:2EH ialah 1:3, dan berat pemangkin 5g. Perbezaan hasil dan tukaran menunjukkan wujudnya penyerapan AA pada resin pemangkin. Reaktor tiub lapisan terpadat menunjukkan pencampuran yang tidak ideal. Kajian kinetik menunjukkan model Eley-Rideal (ER) merupakan model kinetic yang terbaik untuk mengkorelasikan hubungan kadar penggunaan AA dan penghasilan 2EHA..

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

2EH	2 ethyl hexanol
2EHA	2 ethyl hexyl acrylate
AA	Acrylic acid
GC	Gas chromatography
FID	Flame ionization detector
PH	Pseudo-homogeneous
ER	Eley Rideal
LHHW	Langmuir Hinshelwood Hougen Watson

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

2-ethylhexyl acrylate (2EHA) is a clear , volatile liquid that slightly soluble in water but fully soluble in alcohol, ethers and most organic solvent (Komoń *et al.*, 2013). It has very good film formation property for which it is used in paints, adhesives, and coating applications (Haloi & Singha, 2011). In 2013, the acrylic esters had a total demand of 3,055KT globally. The Asia-Pacific region is that the largest market of acrylic esters products, accounting or more than 40% of the total world demand. The conventional production process for 2-ethylhexyl acrylate is catalytic dehydration of 2-ethyl hexanol and acrylic acid in a continuous process.

1.2 Motivation

2EHA was produced through the esterification of acrylic acid (AA) with 2EH in the presence of catalyst. The function of catalyst in the esterification process is to accelerate the chemical reaction by lowering the activation energy required for the reaction. In previous studies, homogeneous chemical catalysts, biocatalyst and enzymatic catalyst have been used in esterification reaction of AA.

Homogeneous catalysts are preferred in the conventional esterification reaction due to its higher catalytic activity. Homogeneous catalyst is used in the conventional method to accelerate the esterification reaction which takes days to achieve equilibrium (Ahmad, Kamaruzzaman, & Chin, 2014). Typical catalysts include sulfonic acid type catalysts such as benzene sulfonic acid, methane sulfonic acid, p-toluene sulfonic acid, or sulfuric acid, and phosphoric acid or phosphonic acid catalysts have been used for industrial esterification reaction. This reaction claimed to have several drawback such as corrosion problem, difficult to be separated from the reaction mixture, time consuming and necessity to be neutralized after reaction (Ahmad *et al.*, 2014; Akbay & Altiokka, 2011; Lilja *et al.*, 2002; Liu, Lotero, & Goodwin, 2006) . A cheaper process is required to benefit the society as the demand of 2EHA is increasing.

1.3 Problem Statement

In previous studies, the esterification of AA with alcohol has been carried out using homogeneous catalyst such as sulfuric acid, hydrofluoric acid and para-toluenusulfuric acid (Altiokka & Ödeş, 2009). Homogeneous catalysts are preferred in the conventional esterification reaction due to its higher catalytic activity and cheaper price. However this method have several drawbacks such as difficult to separate from reaction medium and has corrosion problem (Akbay & Altiokka, 2011). Moreover, homogeneous catalyst can’t be reused and the use of strong acid in homogeneous system give negative effect towards the reaction since it can cause corrosion, pollution of environment and catalyst recovery problem. To overcome this, heterogeneous catalyst is recommended as the substitute to these homogeneous catalysts because it is insoluble, good in selectivity and inexpensive because it can be reused.

As for heterogeneous catalyst, the catalyst is usually in solid form and the reaction can take place either in liquid or gasses phase (Farnetti, Monte, & Kašpar, 1999). Heterogeneous catalyst are insoluble, have good selectivity and specificity, can easily recovered and have good thermal stability (Farnetti *et al.*, 1999). One of the important characteristics of the heterogeneous catalysts is water resistance since the by-product during the esterification of AA with alcohol is water. A few of heterogeneous catalysts have been found to be water resisted which including organic functional polymers , zeolites, salts of heteropolyacids, some of the sulfated oxides , and other solid oxides (Izumi, 1997; Okuhara *et al.*, 1998). Some of it such as salts of heteropolyacids were not used in the commercial process due to the leaching problems (Komon *et al.*, 2013).

Ion exchange resins (IER) have attracted considerable attention in the researches about the esterification of organic acid with alcohol. Amberlyst, Dowex, Nafion, and Purolite are among the commonly used IER catalysts in the esterification of organic acid with alcohol. Altiokka and Odes (2009), Essayem *et al.* (2007), Okuhara *et al.* (1998) and (Sert *et al.*, 2013) employed several type of heterogeneous catalysts in the esterification of AA with propylene glycol, butane and butanol respectively. They found that IER type of catalyst outperformed the other type of catalyst for the esterification reaction. The esterification of acrylic acid with n-butanol with different type of heterogeneous catalyst such as Amberlyst-15, Amberlyst-131 and Dowex 50Wx-400 was studied.

The research on heterogeneously catalysed 2EHA synthesis is still rare. Komon *et al.* (2013) performed the best catalyst screening among the Amberlyst group (Amberlyst 39, Amberlyst 46, Amberlyst 70, and Amberlyst 13) before carrying out the kinetics study of the esterification of AA with 2EHA catalysed by Amberlyst 70. Meanwhile, Chin *et al.* (2015) has done the kinetic and one factorial at time (OFAT) parametric study for the identical reaction catalysed by Amberlyst 15. In previous study, esterification of AA with 2EH was studied using batch reactor. In the case of mass production in the commercial process, a continuous reactor such as tubular reactor should be used.

To date, the study on the esterification of acrylic acid with 2-ethyl hexanol in tubular reactor with DIAION PK-208 (heterogeneous catalyst) as catalyst has not been reported in the literature. This reaction would contribute to the development of a feasible 2EHA production with cheaper price.

1.4 Objectives

In the present work, esterification of acrylic acid (AA) and 2-ethyl hexanol (2EH) catalysed by DIAION PK-208 in a tubular packed bed reactor was studied with the objectives of:

(a) To investigate the effect of reaction temperature, reactants feed molar ratio, reactor aspect ratio L/D and polymerisation inhibitor on the system performance.

(b) To study the reaction kinetics of the heterogeneously catalysed esterification of AA with 2EH.

1.5 Scopes of Study

The scopes of study for the present work included the residence time distribution analysis to examine the quality of mixing of the tubular packed bed reactor before it was used to investigate the effect of important operating parameters on the AA conversion and 2EHA yield. These parameters were reactant initial molar ratio of AA to 2EH (1:1, 1:3, and 1:5), temperature (75°C to 95°C) and catalyst loading (5 to 15g). Furthermore, the reaction kinetics were evaluated by fitting kinetic data to the Pseudo-Homogeneous model, Eley-Rideal model and Langmuir Hinshelwood Hougen Watson model.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter review on the type of catalysts used for the esterification reaction, particularly on AA esterification. There are also reviews on the operating conditions of the esterification of AA with different alcohol.

2.2 Esterification of Acrylic Acid

To the best of our knowledge, only the esterification of the concentrated acrylic acid was reported in the open literature research. Work on esterification reaction of waste water containing acrylic acid has not been studied so far.

Catalyst is used in the esterification process to enhance or accelerate chemical reaction process by lower the activation energy required for reaction. Catalysts can be divided into 3 types, that is homogenous catalysts, commonly use is acidic compound such as sulphuric acids (H_2SO_4), sodium hydroxide (NaOH) and hydrochloric acids (HCl) (Malshe and Chandalia, 1977; Chubarov *et al.*, 1984), heterogeneous catalyst such as solid acid catalysts sulfated zirconia (ZS), zeolites, alumina and commercialized ion exchange resins such as Amberlyst, Nafion and Dowex family (Chen *et al.*, 1999) and also biocatalyst, mostly consist of enzyme group such as lipase (Tsukamoto and Franco, 2004).

Acrylic esters such as methyl acrylate, ethyl acrylate, and butyl acrylate are generally manufactured by esterifying acrylic acid with the corresponding alcohol. Previously, homogenous acid catalysts are often use in industrial processes for this purpose. For example, sulphuric acid, hydrofluoric acid, para-toluenesulfonic acid (Olah, 1973; Jaques and Leisten, 1964; Khurana *et al.*,1990) and heteropolyacid (Kozhevnikov, 1987; Schwegler *et al.*, 1991; Paumard, 1990) However, these acid catalysts are found to be toxic and corrosive and, in addition, are hard to remove from the reaction medium. So, the challenge was to replace them by solid catalysts such as zeolites, alumina or resins, which are easier to separate from the products and also less toxic.

Farnetti *et al.*, (1999) have stated the advantages and disadvantages of homogeneous and heterogeneous catalyst. Homogeneous catalyst seem to be quite expensive and difficult to be recover from the process beside have poor thermal stability which limit the optimum condition for the reaction even though have excellent conversion and selectivity. Heterogeneous catalyst claimed to be more relevant and appropriate as it is easy and cheap for recovery purpose, good in thermal stability, beside have good conversion and selectivity. Kiss (2011) stated that biocatalyst/enzymatic catalyst consumed low energy which contribute to low operating cost. However, because the poor thermal stability (about 50-55 ℃) the process need longer reaction time to be completed (Demirbas, 2008; Feofilova *et al.*, 2005; Gerpen, 2005).

A few researchers have studied the esterification of acrylic acid with several alcohols such as methanol, 1-butanol, using cation-exchange resins as catalysts (Darge and Thyrion, 1993; Chen *et al.*, 1999; Zaleskova *et al.*, 1983; Iizuka *et al.*, 1986).

Esterification reaction between acrylic acid and 2-ethylhexanol was investigated in an isothermal semi-batch reactor by using sulfuric acid as a homogeneous catalyst. The reaction kinetics was found to be second order (Fomin *et al.*, 1991). Esterification of acrylic acid with 1-butanol has been studied in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, solid oxides and organic resins as heterogeneous catalysts. In this solid–liquid reaction system it was found that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ exhibited the highest catalytic activity, in the unit of catalyst weight, among the solid oxide catalysts, while the activity $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was less than those of organic resins such as Nafion and Amberlyst-15 (Chen *et al.*, 1999).

Kuusk and Faingol’d (1974) have reported that esters can be prepared by the reaction of acrylic acid with an excess of cyclohexene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 2-octene at 333-383 K using 95% H_2SO_4 as catalyst. lnoe and Iwasaki (1994) have claimed that cyclohexyl acrylate can be prepared with good yield in a short time by reacting acrylic acid with cyclohexene in the presence of heteropolyacids containing MO oxides and W oxides as main components (Inoe and Iwasaki, 1994).

In view of the industrial importance of these esterification reactions, it was thought desirable to conduct a systematic investigation to optimise the reaction conditions with emphasis on the selectivity towards the desired product. The suitability of commercially available solid acid catalysts such as macroporoussulphonic acid resin (Indion 130 and Amberlyst 15), gelular or microreticularcation-exchange resin (Amberlite IR 120) and acid-treated montmorillonite clay (Engelhard F 24) was assessed. Chen *et al.* (1999) has reported the preliminary studies on the efficiency of different catalyst on the reaction of acrylic acid. Chen *et al.* (1999) stated that, organic acid is more preferable compared with solid oxides as the conversion is much more higher and the Amberlyst 15 shown the second highest conversion after Nafion-H

In another study it has been reported that heteropoly acids (heterogeneous catalyst), such as phosphorous tungstic acid, show higher activities than the conventional acids in the esterification of methacrylic acid with tripropylene glycol (Shanmugam *et al.*, 2004). The role of Mn and Fe as promoters of sulfated zirconia has been studied in the reaction of acrylic acid esterification by 1-butene to sec-butyl acrylate at 343 K. It was reported that Mn and Fe did not improve the catalytic activity and selectivity to sec-butyl acrylate compared with Amberlite resins or sulfuric acid but they strongly resist deactivation (Essayem *et al.*, 2007).

Amberlyst-15 and Amberlyst-36 and cesium salt of phosphorous tungstic acid were used as the heterogeneous catalysts for the esterification of acrylic acid with propylene glycol. The best catalyst among them was to be determined in point of activity and selectivity towards hydroxypropyl acrylate. Thereafter, the kinetic study of esterification was to be studied at the present of the selected catalysts among the catalysts tested.

Although the catalytic activities of the various types of catalysts were compared with each other, kinetic information has not been given in these studies (Saha and Streat,1999; Malshe and Chandalia, 1977; Chubarov *et al.*, 1984; Fomin *et al.*, 1991; Dupant *et al.*, 1995; Chen *et al.*, 1999; Shanmugam *et al.*, 2004). Tables 2.1 and 2.2 show literatures of the range of the parameter that contribute toward effectiveness of acrylic acid esterification reaction and esterification with other carboxylic acid compound.

Table 2.1 : Review on the operating condition of acrylic acid esterification (acrylic acid esterification).

References	Reaction time (h)	Temperature (K)	Molar Ratio (Acid to alcohol)	Catalyst loading	Remarks
Altiokka & Odes (2009)	8.33	333-358	1:1-4:1 1:1-1:3	3.11-8.46 wt%	Propylene glycol Amberlyst-15
Nowak (1999)	4	353-403	1:2-1:10	0.1-1.0 % wt	2-ethyl hexanol Sulphuric acid
Nowak (1999)	5	333-403	1:2-1:10	0.1-1.5 % wt	n-butanol Sulphuric acid
Chen *et al.* (1999)	5	N/A	N/A	0-2 g	1-butanol Various catalyst (Amberlyst, Nafion, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$)
Ahmad *et al.* (2014) ; Chin *et al.* (2015)	N/A	338-388	1:3	10wt%	2-ethyl hexanol Amberlyst-15
Akbay & Altiokka (2011)	N/A	323-393	1:10	0.26 mol H^+/L	n-amyl alcohol
Komoń *et al.* (2013)	N/A	353-393	1:1	1-10wt%	2-ethylhexan-1-ol
Constantino *et al.* (2015)	N/A	323 and 363K	3:1	N/A	N-butanol
Sert *et al.* (2013)	N/A	338-358	1:1,1:2, and 1:3	10,15 and 20 g/L	N-butanol

Table 2.2: Review on the operating condition of various carboxylic acid esterification in concentrated solution.

References	Reaction time (h)	Temperature (K)	Molar Ratio (Acid to alcohol)	Catalyst loading	Remarks
Garcia *et al.* (2000)	2	343-353	10:1-1:10	3-7%	Cethyl alcohol Immobilized lipase
Teo&Saha (2004)	4-6	333-358	1:2-1:10	2.5-10% w/w	Isomyl alcohol Purolite CT-175
Akbay&Altiokka (2011)	8	333-358	N/A	0.12-0.65 mol H^+/L	N-amyl alcohol Amberlyst-36
Izci&Bodur (2007)	12	318-348	N/A	0.5-1.5 g	Isobutanol Dowex 50 Wx2 Amberlite IR-120

2.3 Catalyst for the Esterification

Catalyst is used in the esterification process to enhance or accelerate chemical reaction process by lower the activation energy required for reaction. Catalysts can be divided into 3 types; there are homogenous catalysts (Sert *el al.*, 2013; Malshe and Chandalia, 1977; Chubarov *et al.*, 1984), heterogeneous catalyst (Chen *et al.*, 1999), and biocatalyst (Tsukamoto and Franco, 2004).

2.3.1 Homogeneous Catalyst

Carboxylic esters such as methyl carboxylate, ethyl carboxylate, and butyl carboxylate are generally manufactured by esterifying the corresponding carboxylic acid with the corresponding alcohol. Homogenous acid catalysts are often used in these processes. It can be classified into Brønsted acid catalysts and Lewis acid catalysts.

Homogeneous catalysts for the esterification of other carboxylic acids

Simple Brønsted acid catalysts are the most frequently used catalyst especially when the esterification is generally slower due to more sterically hindered alcohol or acid, as in the case of long-chain fatty alcohols, or of the tertiary acid abietic acid. These catalysts include sulphuric acid, hydrochloric acid, hydrofluoric acid, dissolved arylsulfonic acids, para-toluenesulfonic acid, heteropolyacid, polyphosphoric acid and the mixtures of these catalysts (Khurana *et al.*,1990; Schwegler *et al.*, 1991; Paumard, 1990).

Sulfonic acid detergent such as dodecylbenzenesulfonic acid (DBSA) was used to catalyse the esterification of lauric acid with 3-phenyl-1-propanol. The equilibrium conversion of 84% was reached within 2 h using 10 mol% of DBSA at 40 ℃. Tensioactive and acid properties of this catalyst can be combined. This detergent formed micelles in the aqueous solution, and the interior of these micelles was sufficiently apolar to drive the reaction of two hydrophobic reactants to the right (Manabe *et al.*, 2002).

Several groups of Lewis acids, containing titanium, tin, hafnium or zirconium were applied with clear advantages over protonic acids. Titanium compounds include $TiCl_4$, $TiCl_2(ClO_4)_2$ and $TiCl(OTf)_3$, titanium alkoxides, and even peroxy titanium complexes have acceptable activity, but their selectivity for the esterification of primary versus secondary alcohols is poor, since they also have pronounced transesterification activity (Thil *et al.*, 2002). In the group of tin catalysts, Me_2SnCl_2, Ph_2SnCl_2, n-BuSnO, and especially 1,3disubstituted tetraorganodistannoxanes have received attention (Otera *et al.*, 1991).

Distannoxanes were applied as catalysts in the esterification, albeit at high tin concentration at 80 ℃. The reactions were susceptible to steric bulk, especially for the acid. Since the distannoxane core was surrounded by hydrophobic groups, water can hardly access the active sites, and this seems to impede the reverse hydrolytic reaction. Consequently, reactions can be driven almost to completion with just heating, without specific water removal (Otera *et al.*, 1991).

High ester yields have also been obtained with hafnium (IV) chloride tetrahydrofuran complex ($HfCl_4.2THF$), zirconium(IV) chloride tetrahydrofuran complex ($ZrCl_4.2THF$), cyclopentadienyl hafnium (IV) dichloride (Cp_2HfCl_2) and with the alkoxides of zirconium and hafnium (Ishihara *et al.*, 2002). Particularly, $HfCl_4.2THF$ was effective for the alcohol : acid mixtures (molar ratio 1:1) at concentrations between 0.2 and 1 mol%. These compounds were rather moisture stable. Strong preference for esterification of primary versus secondary or aromatic alcohols was observed. Secondary alcohols like menthol, or aromatic acids like benzoic acid were converted for over 95%. It was assumed that hafnium or zirconium carboxylates are the actual active catalysts.

Similar with the tris(methoxyphenyl)bismuthanes (Ogawa *et al.*, 1994), high concentrations of hydrated NiCl can be used to obtain moderate ester yields (Ram and Charles, 1997). Cerium (IV) triflate ($Ce(OTf)_4$) has been used for menthol esterification, with retention of the configuration at the secondary alcohol group (Iranpoor and Shekarriz, 1999).

Homogeneous catalysts for the esterification of AA

Saha and Sharma (1996) reported that the acrylate esters could be produced through the reaction of acrylic acid with an excess of cyclohexene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 2-octene at 333-383 K using 95% H_2SO_4 as catalyst. H_2SO_4 was employed as a catalyst by Fomin *et al.* (1991) and Sert *et al.* (2013) for the esterification of acrylic acid and 2-ethylhexanol and hexanol respectively in the isothermal semi-batch reactor. Reaction conversion of more than 95% was observed. H_2SO_4 with different concentrations was also adopted as the catalyst for the esterification of acrylic acid with n-octanol and 2-ethyl hexanol (Nowak, 1999) in an isothermal semibatch reactor. Hydroquinone (0.2 wt%) was used as an effective polymerization inhibitor. The initial molar ratios of acrylic acid : n-octanol (or 2-ethyl hexanol) 1:2 – 1:10 were used while the temperatures were varied between 333-403 K. A 95% conversion was obtained at the temperature of 403 K, initial molar ratio of acid: alcohol of 1:5 of and 0.1%wt catalyst

Saha and Sharma (1996) stated in their paper that cyclohexyl acrylate could be prepared with good yield in a short time by reacting acrylic acid with cyclohexene in the presence of heteropoly acids supported on molybdenum oxides and tungsten oxides with conversion of 95% with 99% selectivity.

Even though homogeneous has shown the higher activity in the esterification reaction, it is found to be toxic and corrosive and hence increasing the maintenance cost. In addition, homogeneous catalyst was also difficult to be recovered from the process (Farnetti *et al.*, 1999; Essayem *et al*, 2007). Heterogeneous acidic catalyst such as zeolite, alumina or resin could be the alternative to substitute the homogenous catalysts in order to overcome the drawbacks of homogeneous catalyst (Chen *et al.*, 1999; Saha and Sharma, 1996; Komon *et al.*, 2013).

2.3.2 Heterogeneous Catalyst

The use of heterogeneous catalyst could promote the advantages of reducing equipment corrosion and ease of product separation. The most attractive part is most of this solid catalyst are more facile regeneration of used catalyst (Essayem *et al*, 2007).

Heterogeneous catalysts for the esterification of other carboxylic acid

The suitability of commercially available solid acid catalysts such as macroporous sulphonic acid resin (Indion 130 and Amberlyst 15), gelular or microreticular cation-exchange resin (Amberlite IR 120) and acid-treated montmorillonite clay (Engelhard F 24) was commonly studied (Yadav and Rahuman 2003; Gangadwala *et al.*, 2003; Osorio-Viana *et al.*, 2013; Merchant *et al.*, 2013; Saha and Streat, 1999).

Pappu *et al.* (2013) has studied the esterification of butyric acid with various types of alcohol with different length of carbon chain (methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, 3-butanol, iso-butanol and 2-ethylhexanol). The reactions were catalysed by the commercial ion exchange resin catalysts (Amberlyst 15, Amberlyst 36, Amberlyst BD 20, and Amberlyst 70). It was found that the rate of reaction decreased with the increase of the length of alcohol carbon chain. Amberlyst 70 showed the best performance for the reaction of butyric acid with 2-ethylhexanol attributing to the higher activity per active site (H^+) and higher thermal stability. Teo and Saha (2004), Izci & Bodur (2007) and Akbay and Altiokka (2011) have studied the esterification of acetic acid with isoamyl alcohol, isobutanol and n-amyl alcohol catalysed by ion exchange resin. Amberlyst 70 has given the maximum conversion in the range of 85 – 93% within 5 hours. The operating condition for the heterogeneously catalysed esterification reaction of carboxylic acid other than AA is included in Table 2.3.

Table 2.3: The heterogeneously catalysed esterification of carboxylic acids other than AA.

Catalyst loading	Molar Ratio (Acid to alcohol)	Temperature (K)	Reaction time (h)	References	Remarks
0.01-0.04 g/cm^3	1:12-1:100	373-393	5	Gangadwala *et al.* (2003)	Reactant: Phthalic anhydride and methanol Catalyst: Amberlyst 36
0.008-0.05 g/cm^3	1:12-1:100	373-393	5	Yadav and Rahuman (2003)	Reactant: Anthranilic acid and methanol Catalyst: Amberlyst 36
20-60 g/L	3:1-1:3	322–362	8	Osorio-Viana *et al.* (2013)	Reactant: Acetic acid with isoamyl alcohol Catalyst: Amberlite IR 120
5% w/w	3:1-1:3	298-328	5	Merchant *et al.* (2013)	Reactant: acetic, propanoic and pentanoic acids and ethanol Catalyst: Amberlite IR 120
5-10% w/w	1:2-1:4	393-433	5	Saha and Streat (1999)	Reactant: cyclohexyl acrylate n-butanol Catalyst: Engelhard F-24
2.5-10% w/w	1:2-1:10	333-358	4-6	Teo & Saha (2004)	Reactant : Acetic acid and isomyl alcohol Catalyst : Purolite CT-175
0.12-0.65 mol H$^+$/L	N/A	333-358	8	Akbay & Altiokka (2011)	Reactant: Acetic acid and n-amyl alcohol Catalyst: Amberlyst-36
N/A	0.5-1.5	318-348	12	Izci & Bodur (2007)	Reactant: Acetic acid and isobutanol Catalyst: Dowex 50 Wx2 and Amberlite IR-120
0.01 kg cat/ kg soln	1:4 – 1:6	373 – 423	3	Pappu *et al.* (2013)	Reactant: Butyric acid and 2-ethylhexanol Catalyst: Amberlyst 70

Heterogeneous catalysts for the esterification of AA

The heteropoly compound $Cs_{2:5}H_{0:5}PW_{12}O(Cs_{2.5})$ is a strong acid heterogeneous catalyst, which is stable in water (Okuhara 2002). In the liquid-phase esterification of acrylic acid with 1-butanol, the following activity order was found (Hino and Arata, 1981):

$$\begin{gathered} Nb_2O_5 < \text{J-ZSM-5} < \text{Amberlyst 15} < Cs_{2.5} \\ \sim SO_4^{2-}/ZrO_2 \ll \text{H-Nafion} \end{gathered}$$

Chen *et al.* (1999) has compared the performance of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with $H_3PW_{12}O_{40}$ solid oxides and organic resins for the reaction of acrylic acid with 1-butanol. Organic acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) was more preferable compared to solid oxides as the conversion was higher and Amberlyst 15 showed the second highest conversion after Nafion-H. The activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was found to be retained after the addition of water, while the activities of the organic resins were greatly decreased. Thus, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was claimed to be water-tolerable due to the hydrophobic nature of the surface.

The esterification of acrylic acid with butanol catalysed by heteropolyacids ($H_3P_{12}W_{40}$) supported on activated carbon under batch and flow conditions were studied by Dupont *et al.* (1995). The supported heteropoly acids displayed a better activity per proton than the conventional catalysts such as sulfuric acid or resins like Amberlyst 15. The deactivation of the catalyst in flow system was found to be low due to the dissolution of the supported heteropoly acids in the reaction medium. In contrast, under batch conditions both polyanion dissolution and deposition of polymeric species resulted in deactivation of the catalyst (even in the presence of a polymerization inhibitor).

The heteropoly acids, phosphorous tungstic acid showed higher activities than the conventional acids in the esterification of methacrylic acid with tripropylene glycol (Shanmugam *et al.,* 2004). The mangan and ferum promoted sulfated zirconia was used to catalyse the reaction of acrylic acid esterification by 1-butene to sec-butyl acrylate at 343 K. It was found that Mn and Fe did not improve the catalytic activity and selectivity to sec-butyl acrylate compared with Amberlite resins or sulfuric acid. Nevertheless, the promoted sulphated zirconia strongly resisted deactivation (Essayem *et al.,* 2007).

Amberlyst 15 was used by Altıokka and Odes (2009) in their study of the esterification of acrylic acid with propylene glycol in a batch reactor at different temperature and initial reactant molar ratios. It was found that the selectivity of hydroxypropyl acrylate was significantly low at high AA conversion. Therefore, this process was recommended to operate at low conversion with a proper recycle of unreacted stream for industrial usage.

Amberlyst 15 also was used by Ströhlein *et al.* (2006) for the esterification of acrylic acid with methanol as a stationary phase in a chromatographic reactor. This process can be regarded as a possible competition for current technologies due to the low-operating temperature. Simulated-moving-bed reactor (SMBR) was claimed as a viable option to overcome the drawbacks of the conventional processes for the production of methyl acrylate. 12 moles of methanol per mole of methyl acrylate were required in order to obtain 98% conversion of acrylic acid. The separation of the reaction products could be completed at a relatively low operating temperature of 333 K.

Komon *et al.* (2013) found that Amberlyst 70 was the best among the other resin catalyst like Amberlyst 39, Amberlyst 46, and Amberlyst 131 in the esterification of acrylic acid with 2-ethylhexanol. The maximum conversion was approximately 80%.

Sert *et al.* (2013) has compared three different ion exchange resins, Amberlyst 15, Amberlyst 131 and Dowex 50Wx-400 for the esterification of acrylic acid and n-butanol. Amberlyst 131 was found to be more efficient catalyst giving the maximum conversion of acrylic acid with the conversion of 89%. The catalyst performances follow the sequence of Amberlyst 15<Dowex 50Wx-400<Amberlyst 131. The effects of temperature (338, 348 and 358 K), catalyst loading (10, 15 and 20 g/L), molar ratio of alcohol to acid (1:1, 2:1 and 3:1), and stirrer speed (600, 800, 1000 and 1200rpm) on the reaction rate were investigated. Absence of internal and external diffusion resistances was proven experimentally and theoretically by using Mears and Weisz Prater parameters.

Table 2.4 summarises the heterogeneously catalysed esterification of AA with different alcohol.

Table 2.4: The heterogeneously catalysed esterification of AA with different alcohol.

References	Catalyst and the loading	Molar Ratio (Acid to alcohol)	Temperature (K)	Reaction time (h)	Alcohol used
Altiokka & Odes (2009)	Amberlyst-15; 3.11-8.46 wt%	1:1-4:1 1:1-1:3	333-358	8.33	Propylene glycol
Chen *et al.* (1999)	Various catalyst (Amberlyst, Nafion, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$);0-2 g	N/A	N/A	5	1-butanol
Komon *et al.* (2013)	Amberlyst 70; 5% wt	7:1-1:7	333-373	6	2-ethyl hexanol
Ströhlein *et al.* (2006)	Amberlyst 15;	1:1	333	1	Methanol
Okuhara (1998)	$Cs_{2:5}H_{0:5}PW_{12}O(Cs_{2.5})$	N/A	N/A	N/A	1-butanol
Dupont *et al.* (1995)	$H_3P_{12}W_{40}$	1:1.35-1:3	353	4.5	Butanol
Shanmugam *et al.* (2004)	phosphorous tungstic acid	N/A	N/A	N/A	Tripropylene glycol
Essayem *et al.*, 2007	Amberlite resin	-	473	-	1-butene

2.3.3 Biocatalyst

Similar to other catalysts, biocatalysts increase the speed in which a reaction takes place but do not affect the thermodynamics of the reaction. However, it offers some unique characteristics over conventional catalysts as mentioned in Table 2.5. The most interesting part is the high selectivity. This is very important in chemical process synthesis as it may minimise the side reactions for easier separation.

Table 2.5: Advantages and disadvantages of biocatalyst in comparison with chemical catalyst.

Advantages	Disadvantages
Generally more efficient (lower concentration of enzyme needed)	Susceptible to substrate or product inhibition
Can be modified to increase selectivity, stability, and activity	Solvent usually water (high boiling point and heat of vaporisation)
More selectivity	Enzymes fount in nature in only one enantiomeric form
Milder reaction condition (typically in a pH range of 5 – 8 and temperature range of 20 - 40 ℃)	Limiting operating region (enzymes typically denatured at high temperature and pH)
Environmental friendly (completely degrade in the environment)	Enzymes can cause allergic reactions

Source : Faber, K. 2011

Biocatalysts for the esterification of other carboxylic acids

Among all types of biocatalyst, lipase catalysts are the most common biocatalyst for esterification process. Enzyme-catalysed esterification has acquired increasing attention in many applications, due to the significance of the derived products. The enzymatic esterification is widely used in biofuel production.

As shown in Table 2.6, most of the studies focus on the esterification of fatty acids. Garcia *et al. (*2000), Kraai *et al.* (2008), Abdul Rahman *et al* (2012) and Yin *et al.* (2013) studied the esterification of the fatty acid with cetyl alcohol, oleyl alcohol and 1-butanol catalysed by different types of lipase obtained from different sources of microbe. Garcia *et al* (2000) and Yin *et al* (2013) were using immobilized and silica supported lipase which attracted most research attention because of the ease of catalyst separation from the reaction mixture. Kraai *et al.* (2008) employed the homogeneous lipase. The conversion and selectivity were increased with the reduction in the energy requirement of the system. Abdul Rahman *et al.* (2012) have coated the lipase with ionic liquid in order to improve the lipase activity, selectivity and stability comparing to the uncoated lipase.

Table 2.6: The biocatalyst catalysed esterification of carboxylic acids other than AAwith alcohol.

References	Catalyst and the loading	Molar Ratio (Acid to alcohol)	Temperature (K)	Reaction time (h)	Reactant
Garcia *et al.* (2000)	Novozym 435 (Candida Antarctica immobilized lipase); 3-7 % wt	1:1-1:10	343-353	2	cetyl alcohol with oleic acid
Abdul Rahman *et al.* (2012)	Tetraethylammonium amino acid ionic liquids-coated Candida rugosa lipase	1:1	323	1	Various fatty acid with oleyl alcohol
Kraai *et al.* (2008)	Rhizomucor miehei lipase; 0.01–0.2g/L	10:1-1:10	304	1	oleic acid with 1-butanol
Yin *et al.* (2013)	lipase/organophosphonic acid-functionalized silica; 11-15%	1:1.1-1:1.3	293-303	N/A	oleic acid with ethanol

Biocatalysts for the esterification of AA

Biocatalyst/enzymatic catalyst consumed low energy and hence requiring low operating cost. However, the process required longer reaction time because of the poor thermal stability (about 323-328 K) of enzyme (Demirbas, 2008; Gerpen, 2005). Park *et al.* (2003) has performed the enzymatic esterification of β-methylglucoside with acrylic acid/methacrylic acid using Novozym 435 (lipase from *Candida antarctica*). The temperature was varied from 318-333K while the molar ratio was varied from 1:3-1:15. The maximum conversion achieved was 59.3% after 12 h.

Tsukamoto and Franco (2009) has esterified the AA with D-fructose using 0.7-2.1g of *Candida antarctica* lipase as catalyst. The reactions were carried out in the temperature ranged from 318-338 and molar ratio (acid to alcohol) ranged from 1:1-5:1.

2.4 Packed Bed Reactor (PBR)

Packed bed reactor is an assembly of randomly arranged particles that are bathed by the reactant fluid, which flows in random manner around the pellets. The catalyst pellets are held in place and do not move with respect to a fixed reference frame. Catalytic packed bed reactors find wide spread use in chemical industries (including oxidation of ethylene, naphthalene, vinyl acetate synthesis, esterification, transesterification and hydrogenation reactions).

2.4.1 Esterification in Packed Bed Reactor (PBR)

One of the most commonly example of PBR widely practice is in the production of biodiesel. Most of the recent research nowadays, adopting packed bed reactor system as a stepping stone to obtain kinetic behaviour before proceed with more advance or complex system like hybrid system (Tsai *et al.*, 2011; Smejkal *et al.*, 2009). Table 2.7 shows the applications of PBR for the esterification of carboxylic acid recently.

Table 2.7 : Applications of PBR for the esterification of carboxylic acid.

Reaction	Catalyst	Reference
Production of ethyl acetate from acetic acid and ethanol	Amberlyst 15	de la Iglesia *et al.* (2007)
Production of methyl acetate from methanol and acetic acid	Amberlyst 36	Tsai *et al.* (2011)
Pretreatment of free fatty acid with methanol	Relite CFS	Santacesaria *et al.* (2007)
Production of ethyl acetate from ethanol and acetic acid	Purolite CT151	Smejkal *et al.*, 2009

2.5 Reaction Kinetics For The Heterogeneously Catalysed Esterification Reaction

The reaction kinetics is important for reactor design. Kinetics is required in analysing the reactive process and controlling the reaction variables. It is used to simulate the process and predict the industrial potential of the catalyst (Shi *et al.*, 2011; Tsai *et al.*, 2011). The reaction mechanism can be elucidated using different type of kinetic model. The model must be fitted with the experimental data which gives positive activation energy (Teo and Saha, 2004).

The pseudohomogeneous (PH) model is widely used in esterification systems (Komon *et al.*, 2013; Pappu *et al.*, 2013). In the PH model, adsorption and desorption of all components are negligible. The PH model assumes complete swelling of the polymeric catalyst in contact with polar solvents, leading to an easy access of the reactants to the active sites. Eq. 2.1 shows the PH model.

$$-r_A = k_f \left(c_A c_{AL} - \frac{1}{K_{eq}} c_{ES} c_W \right) \qquad (2.1)$$

Where r_A, k_f, K_{eq}, denote for reaction rate of acid, forward reaction constant, and equilibrium constant respectively and c_A, c_{AL}, c_{ES}, and c_w denote for concentration of acid, alcohol, ester and water respectively.

On the other hand, the Eley−Rideal (ER) model can be applied when reaction between one adsorbed reactant and one non-adsorbed reactant from the bulk liquid phase is assumed to occur. Depending on which of the two reactants is adsorbed, for a single site surface reaction rate-controlling step, the reaction between an adsorbed and a non-adsorbed reactant molecule on the catalyst surface can be represented by the ER model as shown in Eq. 2.2 and Eq. 2.3.

$$-r_A = \frac{k_f \left(c_A c_{AL} - \frac{1}{K_{eq}} c_{ES} c_W \right)}{(1 + K_A c_A + K_W c_W)} \tag{2.2}$$

$$-r_A = \frac{k_f \left(c_A c_{AL} - \frac{1}{K_{eq}} c_{ES} c_W \right)}{(1 + K_{ES} c_{ES} + K_{AL} c_{AL})} \tag{2.3}$$

Where K_A, K_{AL}, K_{ES}, and K_w represent adsorption constant for acid, alcohol, ester and water respectively.

The Langmuir−Hinshelwood−Hougen−Watson (LHHW) model takes into account the adsorption of all components. Assuming that the process is controlled by the reaction on the catalyst surface, the LHHW model assumes that the reaction takes place between two adsorbed molecules (Sert and Atalay, 2012). Eq. 2.4 depicts the LHHW model.

$$-r_A = \frac{k_f \left(c_A c_{AL} - \frac{1}{K_{eq}} c_{ES} c_W \right)}{(1 + K_A c_A + K_{AL} c_{AL} + K_{ES} c_{ES} + K_W c_W)^2} \tag{2.4}$$

2.5.1 Reaction kinetics for the esterification of other carboxylic acids

Pseudo-homogeneous model was claimed to be well fitted with the kinetic experimental data of the esterification reaction catalysed by ion exchange resins. This conclusion was drawn by Yu *et al.* (2004) for the esterification of acetic acid with methanol catalysed by Amberlyst 15 and Pappu *et al.* (2013) for the esterification of butyric acid and hexanol catalysed by Amberlyst 70. Instead of using the concentration based PH model, Pappu *et al.*, (2013) has taken into account the non-ideality of the liquid phase by using the activity of the components. The activity coefficients were predicted using the UNIFAC group contribution method.

Kinetic studies for the esterification of lactic acid and acetic acid with methanol in batch reactor were carried out by Sanz *et al.* (2002) and Sert and Atalay (2012) respectively. The corresponding catalysts for these reactions were Amberlyst 15 and Amberlyst 131. Three kinetic models were compared and it was concluded that activity based LHHW model was well agreed with the experimental kinetic data.

Sert and Atalay (2012) and Yu *et al.* (2004) studied the kinetic of esterification of acetic acid with methanol and both employed ion exchange resin as their catalyst but using the different kinetic model that is LHHW activity based and PH concentration based. An identical activation energy was found. Adam *et al.* (2012) reacted acetic acid with ethanol and resulted a higher activation energy which employed the PH ideal kinetic modelling. This is in line with the study of Pappu *et al.* (2013).

The esterification of oleic acid with methanol and ethanol has been studied by Song *et al.* (2009) and Sarkar *et al.* (2010) respectively in a batch reactor system. Activation energy of approximately 40 kJ/mol was determined based on the pseudo homogeneous concentration base kinetic model. The other carboxylic acids such as myristic acid, lactic acid, and naphthenic acid which were studied by Rattanaphra *et al.* (2011) and Sanz *et al.* (2002) in the batch reactor exhibit the similar thermodynamic trend of exothermic also determined using pseudo homogeneous kinetic model.

2.5.2 Reaction Kinetics for The Esterification of AA

The kinetic modelling studies of the esterification of waste water containing acrylic acid with alcohol are scarce. To date, most of the kinetic studies for the esterification of AA with alcohol were using concentrated or pure acrylic acid.

Komon *et al.* (2013) has carried out the kinetic study for the esterification of AA with 2EHA. Activity based PH model was claimed to well describe the reaction. The non-ideality of the liquid phase was considered by the activity of the components where the activity coefficients were estimated using the UNIFAC method. The activation energy obtained was 50.1 kJ/mol.

Kinetic behaviour of the esterification of acrylic acid and n-butanol, leading to n-butyl acrylate and water catalysed by Amberlyst 131 was studied by Sert *et al.* (2013). The experiments were carried out in a batch reactor. The acrylic acid conversion increased with an increase in temperature, which confirmed that the reaction is intrinsically kinetically controlled. The experimental data were correlated by the LHHW model and the activation energy was found to be 57.4 kJ/mol.

LHHW model was also well fitted with the experimental reaction rate generated by Altıokka and Ödeş (2009) for the kinetic study of the esterification of acrylic acid with propylene glycol. The reaction catalysed by Amberlyst 15 was conducted in a batch reactor. The simultaneous dimerization/polymerization of acrylic acid and products, in addition to the reversible esterification reaction, was proposed as the reaction mechanism. Phenothiazine (0.3 wt%) was also used as an inhibitor to reduce the polymerization of acrylic acid and product. The activation energy was 80.37 kJ/mol. The kinetic studies reported in the preceding section were summarised in Table 2.8.

Table 2.8: Kinetic studies for the esterification reaction of acrylic acid and other carboxylic acids with different type of alcohols.

Esterification	**Thermodynamic**	**Catalyst**	**Activation Energy**	**Reference**
Lactic acid + methanol	Endothermic	Amberlyst 15	48.67 kJ/mol (PH activity base)	Sanz *et al.* (2002)
Acetic acid + methanol	Exothermic	Amberlyst 15	44.2 kJ/mol (PH concentration base)	Yu *et al.* (2004)
Oleic acid + methanol	Endothermic	Zinc acetate	32.46 kJ/mol (PH concentration base)	Song *et al.* (2010)
Oleic acid + ethanol	Endothermic	SnO_2/WO_3	39.5 kJ/mol (PH concentration base)	Sarkar *et al.* (2010)
Myristic acid + methanol	N/A	sulfated zirconia	22.51 kJ/mol (PH concentration base)	Rattanaphra *et al.* (2011)
Acetic acid + methanol	Endothermic	Amberlyst 131	37.8 kJ/mol (LHHW activity base)	Sert & Atalay (2012)
Butyric acid + hexanol	Exothermic	Amberlyst 70	41.7 ±2.3 kJ/mol (PH activity base)	Pappu *et al.* (2013)
Acrylic acid + n-butanol	Exothermic	Amberlyst 131	57.4 kJ/mol (LHHW activity base)	Sert *et al.* (2013)
Acetic acid + ethanol	N/A	L-(N-α-acetylphenylalanine)-ruthenium (III) complex (RHAPhe-Ru) immobilized on silica	343.92 kJ/mol (PH concentration base)	Adam *et al.* (2012)
Acrylic acid + 2-ethylhexanol	Endothermic	Amberlyst 70	52.3 ±1.9kJ/mol (PH conc. based) 50.1 ±3.1kJ/mol (PH activity based)	Komon *et al.* (2013)

2.6 Polymerisation Inhibitors

It is widely known that acrylic acid is easily polymerized on heating, but heating is more or less necessary in reaction and a device for inhibiting the polymerization is variously considered. Hydroquinone monomethyl ether (MEHQ), p-benzoquinone, and phenothiazine (PTZ) are examples of commercial inhibitors/stabilizers.

Polymerization of acrylic acid depends greatly upon the temperature employed and if the temperature exceeds the range of 60 to 70ºC, its polymerization velocity is increased exponentially with respect to the temperature. Table 2.9 summarizes the polymerisation inhibitors used in the research studies on the esterification of AA.

Table 2.9: Summary of polymerisation inhibitors used in the esterification of AA.

References	Polymerisation Inhibitor used	Range	Remark
Dupont *et al.* (1995)	MEHQ and phenothiazine	0.16-0.38 w/w % of AA	-
Vonner *et al.* (2015)	MEHQ	20-200 ppm	The existing MEHQ in AA purchased from supplier
Chin *et al.* (2015)	MEHQ	20-200 ppm	The existing MEHQ in AA purchased from supplier
Sert *et al.* (2013)	Phenothiazine	N/A	-

2.7 Summary

Resins have been identified as the potential heterogeneous catalyst for the esterification of AA with 2EH in producing 2EHA. Heterogeneously catalyzed esterification of AA with 2EH in a tubular packed bed reactor is purported to be a more economical feasible system for the mass production of 2EHA. To date, the study of the esterification of AA with 2EH in a tubular packed bed reactor employing resin as a catalyst is scarcely found in the open literature.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The present chapter includes the materials, apparatus and equipment used for the reaction studies and sample analysis throughout the esterification of the Acrylic Acid and 2-Ethyl Hexanol. All the experimental procedures and operating parameters adopted are also stated in this chapter.

3.2 Materials

The chemicals used in the experimental study for the purpose of the esterification reaction and the product analysis are given in Table 3.1 along with their respective uses and purity. All these chemicals were used without further purification.

The chemicals used in the experimental studies are listed in Table 3.1 with the purity, brand and function. All these chemicals were used without further purification.

Table 3.1: List of chemicals.

Chemical/Reagent	Assay	Brand	Function
DIAION resin	N.A	Mitsubishi, Japan	Catalyst
2-ethyl hexanol (2EH)	99.99%	Fluka	Reactant
Acrylic acid (AA)	99.9%	Sigma Aldrich	Reactant
n-Hexane	99.99%	Sigma Aldrich	Solvent for GC-FID analysis
Sodium chloride (NaCl)	99%	Rohm & Haas	Solvent for ion exchange capacity (IEC) analysis
Potasium Hydroxide (KOH)	99%	Rohm & Haas	Titrant for ion exchange capacity (IEC) analysis
2-ethyl hexyl acrylate (2EHA)	99.99%	Sigma Aldrich	Standard for GC-FID analysis
Butyl acrylate (BA)	99.99%	Sigma Aldrich	Internal standard for GC-FID analysis
Phenothiazine	98%	Sigma Aldrich	Polymerisation inhibitor in esterification reaction
4-Methoxyphenol (MEHQ)	99%	ReagentPlus	Polymerisation inhibitor in esterification reaction
Nitrogen	99.99%	Air Product	Makeup gas for GC-FID analysis
Compressed air	99.99%	Air Product	To initiate flame in FID
Hydrogen	99.99%	Air Product	Innert gas for GC-FID analysis
Helium	99.99%	Air Product	Mobile phase and carrier for GC-FID analysis

3.3 Apparatus and Equipment

3.3.1 Esterification Reaction Studies

The esterification reaction was carried out in a tubular packed bed reactor. Figure 3.1 shows the experimental setup and Table 3.2 shows the function of each part in the set up. The setup comprises of reactor, heating oil storage tank, heat exchanger and centrifugal pump.

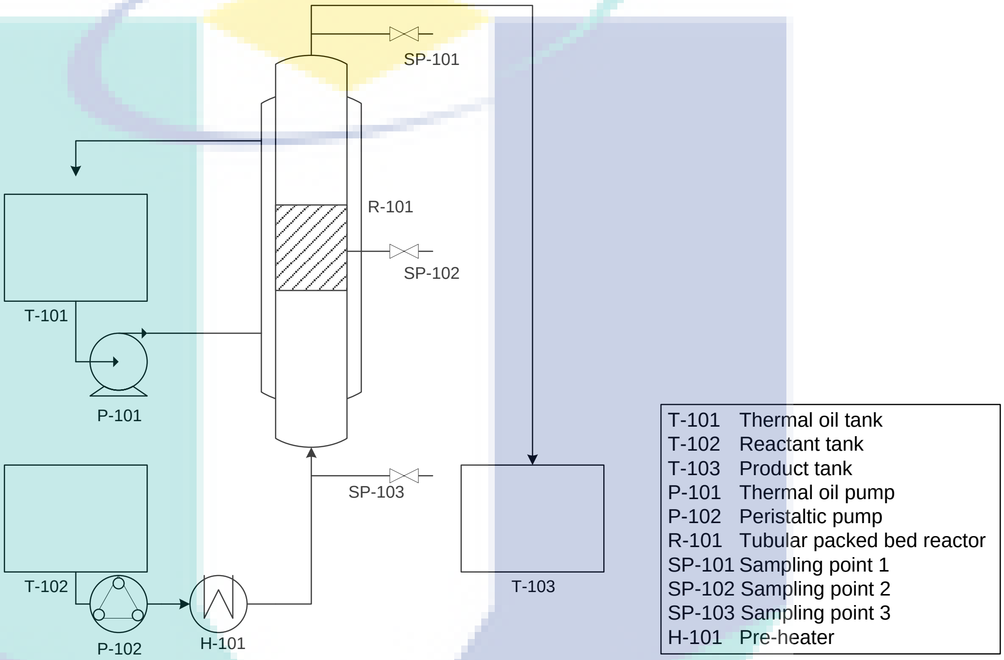


Figure 3.1: Packed bed reactor experimental apparatus.

Table 3.2: List of main components in the experimental setup for the PBR studies.

Component	Description	Function
Thermal oil tank	Vessel with 50 L capacity equiped with heating coil system. Stainless steel SS304	To hold and heat up thermal oil to desired temperature
Heater pump	Centrifugal pump (SS316) with heat resistance capability up to 673K	To flow the heated thermal oil to jacketed PBR
Packed bed reactor	Cylindrical jacketed tubular vessel with internal diameter of 1 inch and height of 11 inch	As the continuous reactor.
Reactant tank	5L vessel stainless steel SS304	As the container for reactant before flowing to PBR
Feed transferring pump	Peristaltic pump	To control the flow of reactant entering PBR.
Temperature probe	J-type thermocouple with the length of 10 cm.	To manipulate the process temperature during the reaction.
Sampling point	Gate valve	To control the process temperature during the reaction.

3.4 Experimental Studies

3.4.1 Residence Time Distribution Studies

The RTD was determined experimentally by injecting an inert chemical compound, that is Dextran, called a tracer, into the reactor to assess the performance of packed bed reactor, the knowledge of basic data, as residence time distribution and mass transfer parameter of the packed bed reactor, is crucial. For residence time distribution (RTD) studies, the tracer experiments were carried out by pulse injections of a Dextran solution (15 kg m^{-3}) in 2EH. Samples of 0.2 cm^3 were injected at different flow rates (5, 7.5, and 10 mL min^{-1}) using 2EH as eluent and the column outlet concentration was monitored using a UV–VIS detector at 300 nm. At least, three runs were performed for each flow rate to check the stoichiometric time reproducibility of the experimental curves.

3.4.2 Esterification Reaction Studies

The experiment was carried out in a tubular reactor. The setup comprises a reactant tank which is made of stainless steel. The reactant tank was connected to a heat exchanger, a coil immersed in oil bath for heating up the inlet stream of the reactor (feed solution) to desired temperature. A peristaltic pump was used to pump the reactants to the reactor system. The reactants flowed constantly with a rate 3 mL/min. Then, the product was collected in the outlet of the reactor. Samples with individual volume of 0.5 ml are withdrawn at 1 hour intervals and were analysed using gas chromatography for the composition of 2EHA, AA and 2EH.

The parameters varied were the temperature, catalyst loading, and initial molar ratio of acid to alcohol as shown in Table 3.3. The range of each variable was decided based on the literature review and also the limits of experimental setup and catalyst like the deactivation temperature of PK208 at 115˚C.

Table 3.3: Important operating parameter and its range.

Parameter	Range
Temperature	75 – 95^{o}C
Catalyst loading	5 – 15g
Initial molar ratio (in excess 2EH)	1:1 – 1:5

3.4.3 Kinetic Modelling Studies

Kinetic modelling studies using batch reactor

The best DIAION resin was chosen for kinetics study to obtain kinetic data at various temperatures (358, 368, 378, and 388 K). The others operating parameters were remained. The samples were withdrawn subsequently until equilibrium conversion had reached.

The conversion and yield profile generated from the study of the effect of temperature was used to develop the kinetic model of the esterification of AA with 2EH. Pseudohomogeneous (PH), Eley Rideal (ER) and Langmuir Hinshelwood Hougen-Watson (LHHW) reaction models were used to fit with the experimental kinetic data. The activity based model is used to account the non-ideal mixing of the bulk liquid phase. PH model is widely used in the esterification systems (Pappu *et al.*, 2013; Komoń *et al.*, 2013; Yu *et al.*,2004). In the PH model, adsorption and desorption of all components are negligible. The PH model assumes complete swelling of the polymeric catalyst in contact with polar solvents, leading to an easy access of the reactants to the active sites. LHHW and ER models are appropriate for heterogeneously catalyzed reactions. Both models are applicable whenever the rate of reaction is limited by surface reaction. LHHW model well describes the surface reaction between adsorbed molecules while ER model well represents the surface reaction takes place between one adsorbed species and one non-adsorbed reactant from the bulk liquid phase (Scott Fogler, 2011). In the present study, the activity based kinetic model was preferred due to the non-ideal mixing of the bulk liquid phase. The activity of component *i*, α_i can be related to its mole fraction, x_i using Eq. 3.1:

$$\alpha_i=\gamma_i x_i \tag{3.1}$$

Where γ_i is the liquid activity coefficient for component *I* and it can be calculated using UNIFAC group contribution method (Komoń *et al.*,2013). The UNIFAC model splits up the activity coefficient for each species in the system into two components; a combinatorial, $\gamma^c{}_i$ and a residual component, $\gamma^r{}_i$ as shown in Eq. 3.2 and it was calculated using a UNIFAC program written in Microsoft Excel:

$$ln\gamma_i= ln\ \gamma^c{}_i + ln\ \gamma^r{}_i \tag{3.2}$$

The PH, ER and LHHW models are as in Eqs. 3.3-3.5:

$$r_{2EHA} = k_f\left(\alpha_{AA}\alpha_{2EH} - \frac{1}{K_A}\alpha_{2EHA}\alpha_W\right) \tag{3.3}$$

$$r_{2EHA} = \frac{k_f(\alpha_{AA}\alpha_{2EH} - (1/K_A)\,\alpha_{2EHA}\alpha_W)}{(1 + K_{AA}\alpha_{AA} + K_W\alpha_W)} \tag{3.4}$$

$$r_{2EHA} = \frac{k_f(\alpha_{AA}\alpha_{2EH} - (1/K_A)\,\alpha_{2EHA}\alpha_W)}{(1 + K_{AA}\alpha_{AA} + K_{2EH}\alpha_{2EH} + K_{2EHA}\alpha_{2EHA} + K_W\alpha_W)^2} \tag{3.5}$$

Where K_a is the activity based equilibrium constant, K_i is the adsorption equilibrium constant for species *i* and k_f is the rate constant. The esterification of AA with 2EH occurs based on the chemical reaction as in Eq. 3.6:

$$\begin{array}{lllllll} CH_2CH & + & CH_3(CH_2)_3CH & \leftrightarrow & CH_2CHCOOCH_3 & + & H_2O \\ COOH & & (C_2H_5)CH_2OH & & (CH_2)_3CH(C_2H_5)CH_2 & & \\ \text{(AA)} & & \text{(2EH)} & & \text{(2EHA)} & & \text{(W)} \end{array} \quad (3.6)$$

This reaction is an acid-catalysed equilibrium limited esterification. The thermodynamic equilibrium constant of the reaction, K_a is shown in Eq. 3.7.

$$\begin{aligned} K_a &= exp\left(-\frac{\Delta G^0}{RT}\right) = \prod a_i^{v_i} = \prod_i (x_i\gamma_i)^{v_i} \\ &= \frac{x_{2EHA}x_W}{x_{AA}x_{2EH}}\frac{\gamma_{2EHA}\gamma_W}{\gamma_{AA}\gamma_{2EH}} \end{aligned} \quad (3.7)$$

k_f can be related to the temperature with Arrhenius equation as below:

$$k_f = k_{f0}\exp\left(-\frac{E_f}{RT}\right) \quad (3.8)$$

Where k_{f0} is the pre-exponential factors for the reactions, E_f denotes the activation energy of reactions, R is the gas constant and T is the temperature of the reaction. In the case of this batch-wise heterogeneously catalysed the reaction, r_{2EHA} was determined using Eq. 3.9 (Teo and Saha, 2004). The derivative (dC_{2EHA}/dt) was obtained by differentiating the concentration-time data,

$$r_{2EHA} = \frac{dC_{2EHA}}{dt} \quad (3.9)$$

Where C_{2EHA} is the concentration of 2EHA and *t* is the reaction time. *kf* and K_i were obtained simultaneously by fitting r_{2EHA} profile at different temperatures to the proposed kinetic models using L–M (Levenberg–Marquardt) method for non-linear regression analysis in POLYMATH6.10. k_{f0} and E_f were obtained by plotting the Arrhenius plot.

Kinetic modeling studies using packed bed reactor

The chemical concentration profile for different variation of temperature (75℃, 80℃, 85℃, 90℃, and 95℃) was used to develop the kinetic model of the esterification of AA with 2EH. The kinetic data were correlated with a mass-balance equation for acrylic acid around the entire packed-bed reactor through Eq. 3.10:

$$W/(10^3\ F_A) = \int_0^{X_A} \frac{dX_A}{-r_A} \qquad (3.10)$$

Where F_A (F x C_{A0}) is the molar flow rate of acrylic acid in the inlet stream. The rate expression $-r_{Ao}$ depends on the assumed reaction mechanism. Three types of rate expressions, including the pseudo homogeneous (PH) model, Eley-Rideal (E-R) model, Langmuir-Hinshelwood-Hogen-Watson (LHHW) model, were adopted to correlate the kinetic data for all experimental conditions as given previously in Chapter 2 (Gonzales and Fair, 1997). The activity based model is used to account the non-ideal mixing of the bulk liquid phase.

3.5 Analysis

The samples from esterification of acrylic acid (AA) with 2-ethyl hexanol (2EH) were analysed using gas chromatography. Agilent HP 1200 gas chromatography (GC) equipped with flame ionization detector (FID) and DB-200 column with length of 30 m, diameter of 0.32 mm and inner diameter of 0.25 µm, was used to analyse the chemical compounds involve in the esterification reaction of 2EH and AA catalysed by PK-208. The chemical compounds that were analysed are 2EHA and AA.

The samples dissolved in n-Hexane were analysed for the composition of 2EHA and AA using GC-FID with the injector and detector block temperatures at 503 K (with 1:10 split ratio) and 523 K respectively. The oven temperature is maintained at 308 K for 5 minutes then it is increased to 473 ℃ at 10 K/min for 17 minutes. The carrier gas, helium flowed at a flow rate of 36.8 cm^3/s. Figure 3.2 shows one of the chromatograms for acrylates analysis.

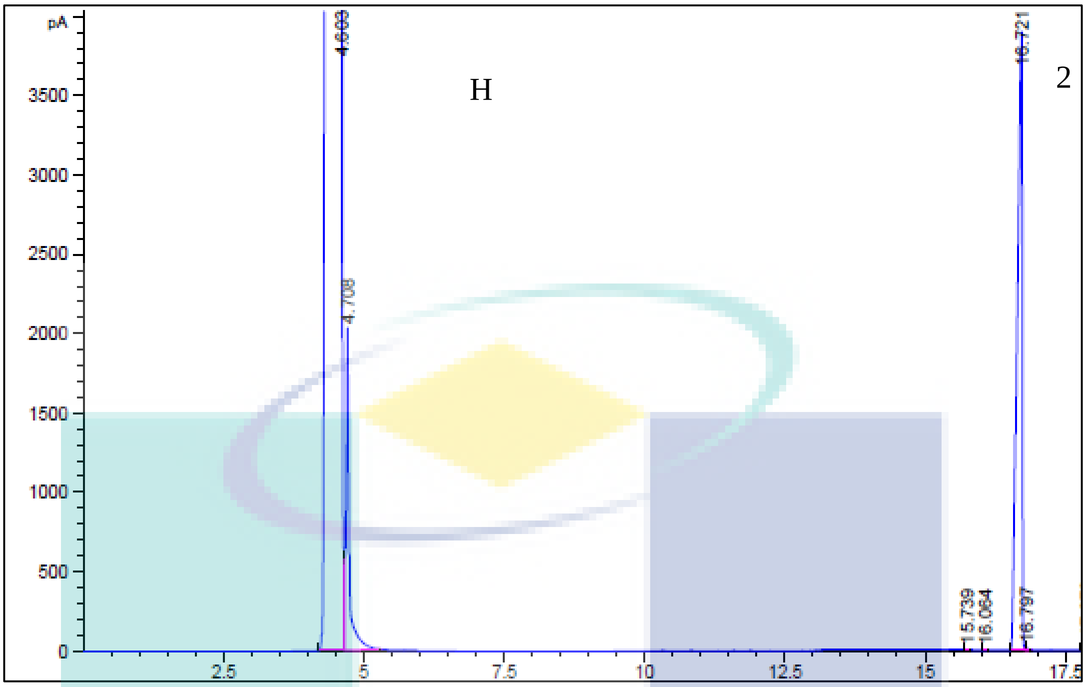


Figure 3.2: Chromatogram of 2EHA standard obtained from the GC analysis.

The calibration curves of 2EHA and AA from the GC analysis are required to obtain the concentration of these components in the sample. The GC standard of each components are used to generate the calibration curve., The concentration of the components in the samples can be determined using the calibration curve if the area under the peak of that particular component in the chromatogram is known. The concentrations for the working standard samples of AA are ranged from 21020 ppm to 105100 ppm with 21020 ppm interval for each point. While the respective concentrations for the working standard samples of 2EHA were ranged from 3461 ppm to 17304 ppm with 3461 ppm interval for each point. The area-concentration data for standard calibration curve for AA and 2EHA was represented respectively in Appendix A and B.

The following equation has been used to calculate yield of 2EHA and conversion of AA:

$$yield\ (\%) = \frac{C_{2EHA}}{C_{AA0}} \times 100\% \qquad (3.11)$$

$$conversion\ (\%) = \frac{C_{AA0} - C_{AA}}{C_{AA0}} \times 100\% \tag{3.12}$$

Where C_{2EHA} is the concentration of 2EHA, C_{AA} is the concentration of AA, and C_{AA0} is the initial concentration of AA. The sample calculation of yield and conversion are in Appendix C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst Screening

In general, three types of ion exchange resins were tested: highly macroporous (RCP145 and RCP160), macroporous (PK208, PK216, and PK228) and gelular (SK104 and SK1B). These catalysts are differ by their porous structure and physicochemical properties. The highly microporous resins possesses a higher cross-linking degree of divinyl benzene (>45%). The properties of the catalysts used in the present study are summarized in Table 4.1.

Table 4.1: Ion exchange capacity and leaching properties of the tested acidic ion exchange resins.

Catalyst	**Type**	**DVB CL%**	**Ion exchange capacity (meq/ml)**	**Leaching 2EH (%)**
SK104	Gelular	4	3.75	2.00
SK1B	Gelular	8	4.15	1.45
PK208	Macroporous	4	3.75	2.67
PK216	Macroporous	8	3.90	2.69
PK228	Macroporous	14	4.00	4.00
RCP145	Highly porous	45	3.00	4.17
RCP160	Highly porous	60	3.50	1.57

The ion exchange resins, SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160 have been tested for their catalytic performance in the esterification of AA with 2EH. The time courses of the reaction over various DIAION-type ion exchange resins are presented in Figure 4.1. It is noteworthy that, out of the studied resins, the highest yield of 2EHA, over the entire reaction duration is achieved by PK208, followed by the reactions catalysed by SK1B, RCP145, SK104, PK216, RCP160 and PK228. At 4 h, the yield of 2EHA obtained in the reaction catalysed by PK208 is 41%.

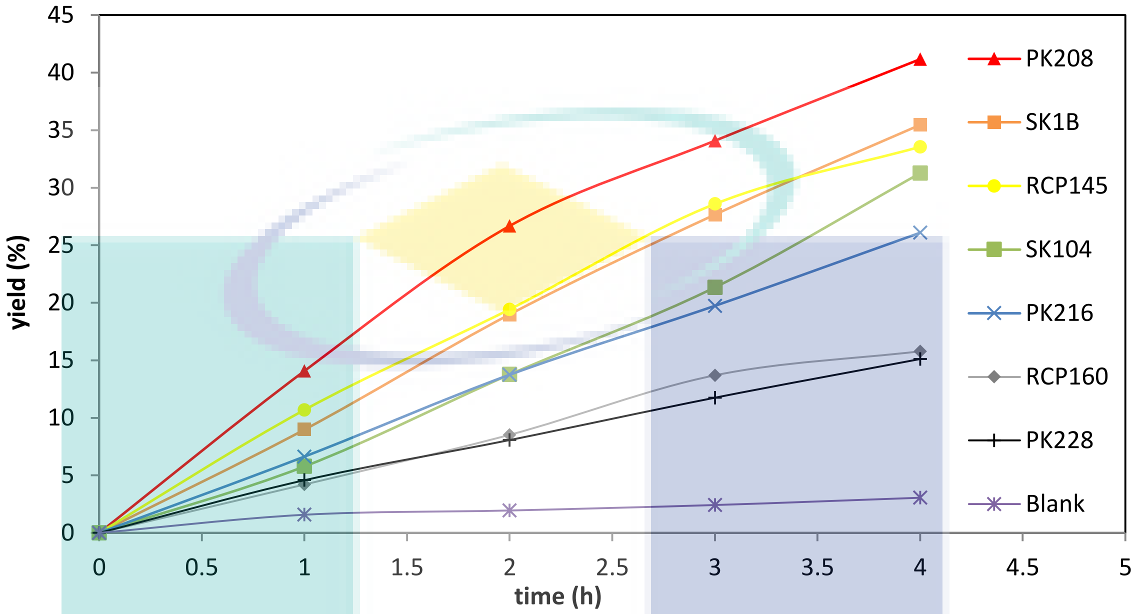


Figure 4.1: Yield of 2EHA for the reactions catalysed by different type resin catalysts for 4 h. Operating condition: Purity of AA: 99.9 % ; Temperature: 95 ℃; Catalyst loading of 10% w/w (catalyst/AA); molar ratio of AA:2EH is 1:3.

The catalytic performance of these catalysts is attributed by the ion exchange capacity (IEC) and percentage of crosslinkage (%CL) of the resins. The gel type resins like SK1B and SK104 perform better when its IEC increases. The %CL does not have much effect on the catalytic performance of these non-porous resins (Bhandari *et al.*, 2016). For the porous resins like PK208, PK216, PK228, RCP145 and RCP160, their catalytic performances are very much depending on %CL. The resins with lower %CL have shown higher 2EHA yield. The degree of crosslinkage of resins is closely related to its pore size. Resins with the lower degree of crosslinkage have a larger pore size. Reactants can easily diffuse and travel to the active sites due to its lower mass transfer resistances. Thus, a higher rate can be obtained for the reaction catalyzed by resins with a lower degree of crosslinkage (Bhandari *et al.*, 2016).

SK1B exhibits the highest IEC followed by PK228 and PK216. This indicates that the catalyst activity does not depend solely on IEC but other factors like the resin active sites accessibility. PK208, SK1B, and RCP145 have shown the best catalyst activity in the esterification of AA with 2EH. Similar to most of the cases, the macroporous type resin, PK208 outperforms SK1B, the gel type resin and RCP145, the highly porous type resin attributing to the higher degree of swelling. The gel type resin is a hard glassy transparent resin bead which consists of a homogeneous matrix on a microscopic scale without discontinuities (Chakrabarti & Sharma, 1993). It does not have permanent pore and hence possessing a very low surface area when it is dry (Ali, 2009). These resins swell when brought into contact with a solvent and swelling creates space or 'solvent porosity' inside the resin to enable the access of reactant molecules to the polymer network (Martinec et. al, 1978). On the other hand, the macroporous type resin is available as a hard opaque bead which has permanent pores and is relatively rigid. Hence, it exhibits a less pronounced swelling behaviour as comparing to a gel type resin. The swelling degree of the macroporous type resin is typically inversely related to its crosslinked density (Martinec et. al, 1978). The degree of crosslinking for each catalyst is shown in Table 3.1.

Ion exchange resins can be deactivated by the hydrolysis of the functional groups and/or blocking of the active sites. The hydrolysis can be attributed to the polymerization of products or polycondensation, depolymerisation, the release of oligomeric sulphonic acids due to oxygen sensitivity and desulfonation (Neier, 1991). It was reported that partial desulfonation occurred and the three-dimensional network shrinkage took place in Amberlyst 15 when the temperature was increased up to 413 K (Teo and Saha, 2004). In the present study, SK1B, PK208 and RCP145 were anticipated to remain its activity in the chemicals used such as 2EH and AA unless it was fouled by the poly acrylic acid formed through the polymerisation of AA at certain reaction temperature.

On top of this, leaching would also occur if the catalyst was used in the reaction study involving AA as a reactant. To validate the anticipation on the catalyst fouling due the polymerised AA, these resins were reused up to four times for 4 h at 368 K. Based on the results depicted in Figure 4.2, the yield of 2EHA obtained in the reaction catalysed by PK208 is higher as compared to RCP145 attributing to the lesser leached sulfonic acid from PK208 as stated previously. Despite the better leaching properties and higher ion exchange capacity of SK1B as compared to PK208, the reaction catalyzed by SK1B gave lower yield of 2EHA possibly due to limited access to active site per surface area. Both resins have shown a significant reduction of approximately 20% in the yield of 2EHA is observed after the catalyst is reused for the first time, attributing to the blockage of the active site by the components like water (Dixit and Yadav, 1996). Indeed, water molecules compete with the reactants for the active sites and strongly adsorb on the sulfonic acid groups. One water molecule attaches itself to four sulfonic groups leading to a reduction in the number of available active sites and thus a decrease of the reaction rate (Zundel, 1969). A gradual reduction of ≤10% is observed for the subsequent cycles. The evenly distributed yield reduction over the subsequent reusability runs implies the deactivation due to fouling. The catalysts may be fouled by poly acrylic acid, indicating the inhibitor insufficiency in the present study. Despite the loss of activity, the yield of 2EHA obtained in the reaction catalyzed by the spent resins is significantly higher than the blank test without catalyst. The recyclability tests of these resins demonstrate their high potential for the industrial application in the production of 2EHA through the esterification of pure AA with 2EH.

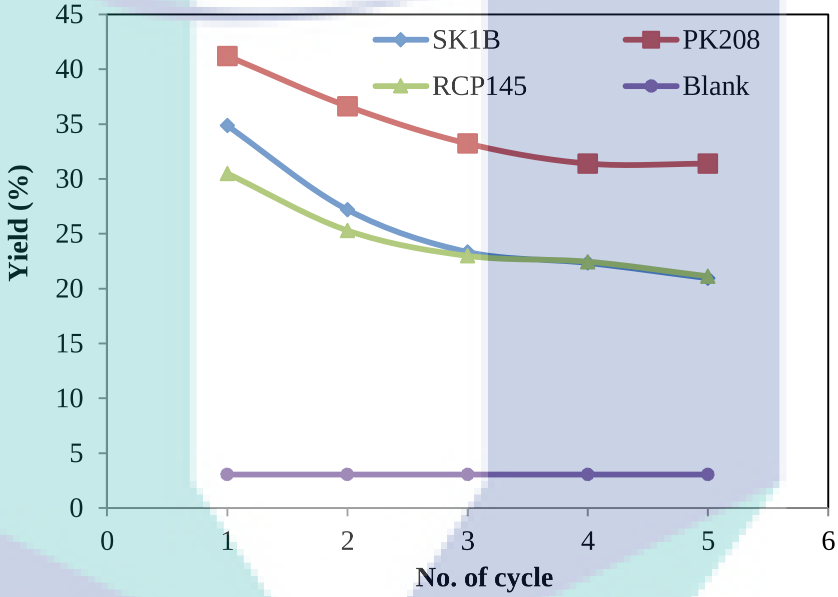


Figure 4.2: 2EHA yield (%) after 4 h of reaction for 5 cycles of reaction (temperature of 368 K and catalyst loading of 10 wt% with the initial molar ratio acid to alcohol of 1:3).

4.2 Residence Time Distribution Studies

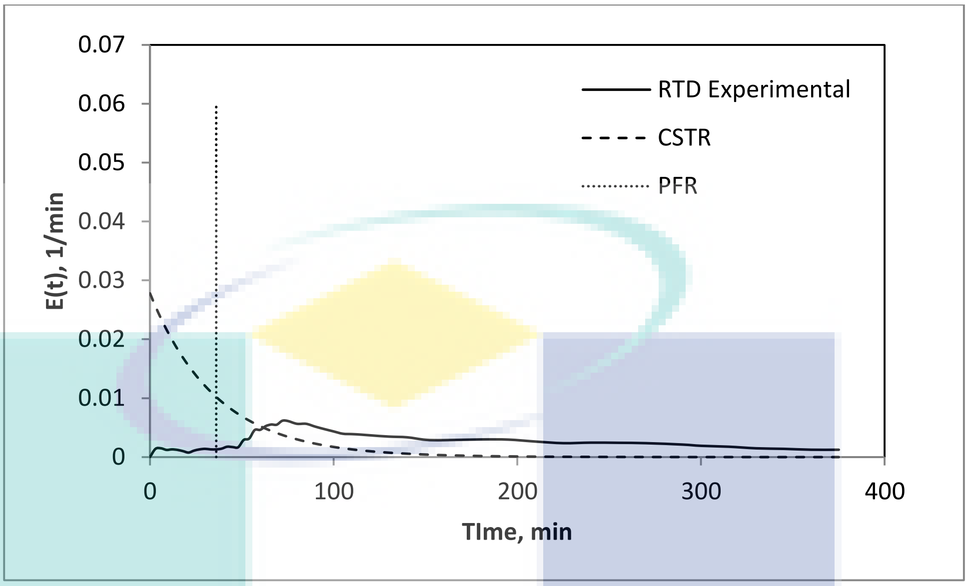


Figure 4.3: Graph showing variation of exit age distribution with time instant for packed bed reactor.

Figure 4.3 shows the variation of exit age distribution with time instant for the packed bed reactor. Comparing to the exit age distribution of the ideal CSTR, ideal plug flow reactor and laminar flow reactor, the exit age distribution of the packed bed reactor in the present study has inferring the occurrence of dispersion in the reactor. Therefore, the performance of this non-ideal tubular packed bed reactor should be simulated using Dispersion model. The variance (σ^{2_θ}, σ^2), mean residence time (τ_m) and Dispersion number of experimental Residence Time Distribution can be quantified and serve as the useful data for efficient operation design and system improvement.

4.3 Study of the Effect of Different Operating Variables on the Esterification of Pure AA with 2EH

The conversion and yield of esterification of AA and 2EH are affected by the parameters such as temperature, molar ratio of acid to alcohol and catalyst loading. A set of optimised parameters is required to develop an efficient process with high yield under the mild condition.

4.3.1 Effect of Temperature

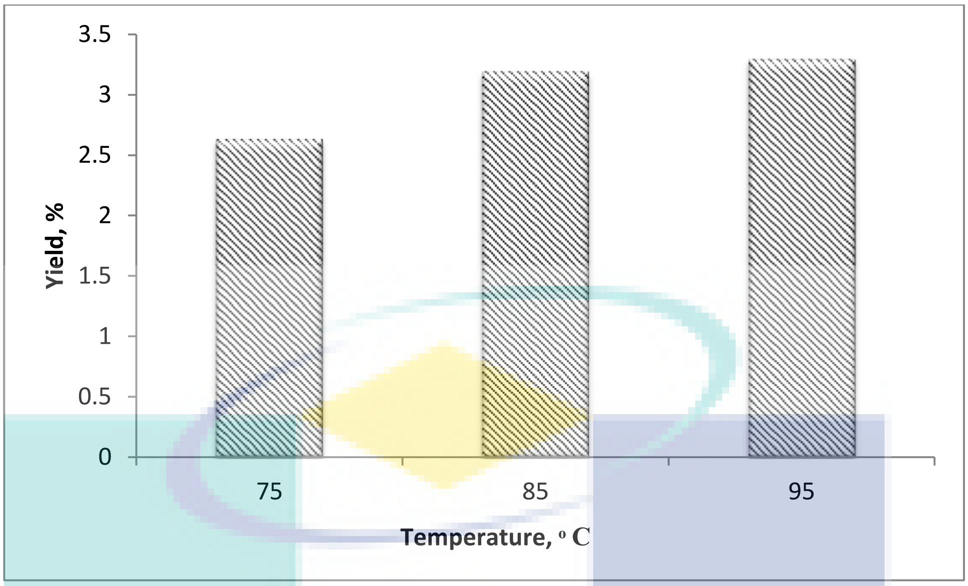
The effect of temperature was studied by varying the reaction temperature which is 75^{o}C, 85^{o}C and 95^{o}C. The molar ratio of AA to 2EH was fixed at 1:3 while the catalyst amount was fixed at 5g with 3ml/min volume flow rate. Figure 4.4 (a) and (b) illustrate the conversion and yield for the temperatures within the range of study. The experiment was carried out for 6 hours and it took 5 hours to obtain stead state.

At the temperature increase, the conversion also increases. This is because increasing the reaction temperature would increase the kinetic energy of the reactant molecules and hence more of the reactant molecules would obtain the minimum amount of energy required to form products. The temperature rise causes more often collision of the reactants which resulting more collision to break the bonds to form the ester (Ali *et al.*, 2007). However, the yield is relatively low. The significantly higher conversion may be due to the adsorbed AA on the resin (PK-208) that reducing the concentration of AA in the outlet stream. Dania *et al.* (2014) have studied about the adsorption using nonreactive binary mixtures, it was performed, at 323 and 363 K, to determine the adsorption parameters of the selected isotherm (multicomponent Langmuir isotherm) at this two temperatures.

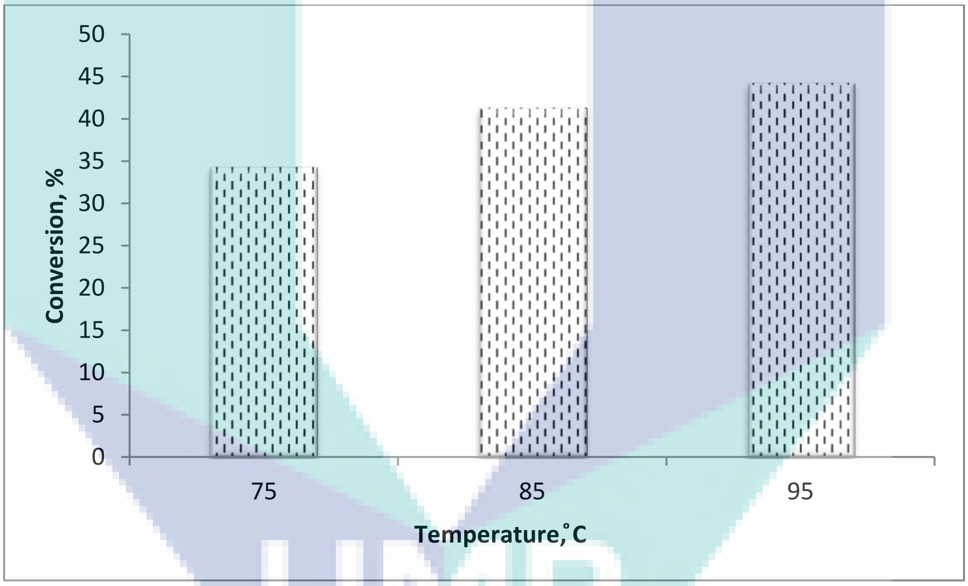
Temperature of 95^{o}C was chosen and used in the subsequent experimental studies as it has the highest conversion and yield.

4.3.2 Effect of Initial Molar Ratio

The usage of excess amount of alcohol can shift the reaction equilibrium towards ester production and shortens the time required to achieve equilibrium conversion. The excess of acid was reported to promote the side reaction of polymerisation and hence reducing the yield. The effect of initial molar ratio of AA to 2EH ($M_{AA/2EH}$) was investigated by varying the molar ratio of AA to 2EH in excess of alcohol (1:1, 1:3, and 1:5) to determine the best molar ratio. Figure 4.5 shows the effect of $M_{AA/2EH}$ on the product yield and conversion of AA with the catalyst amount of 5g and temperature fixed at 95^{o}C and volumetric flow rate of 5 mL/min.



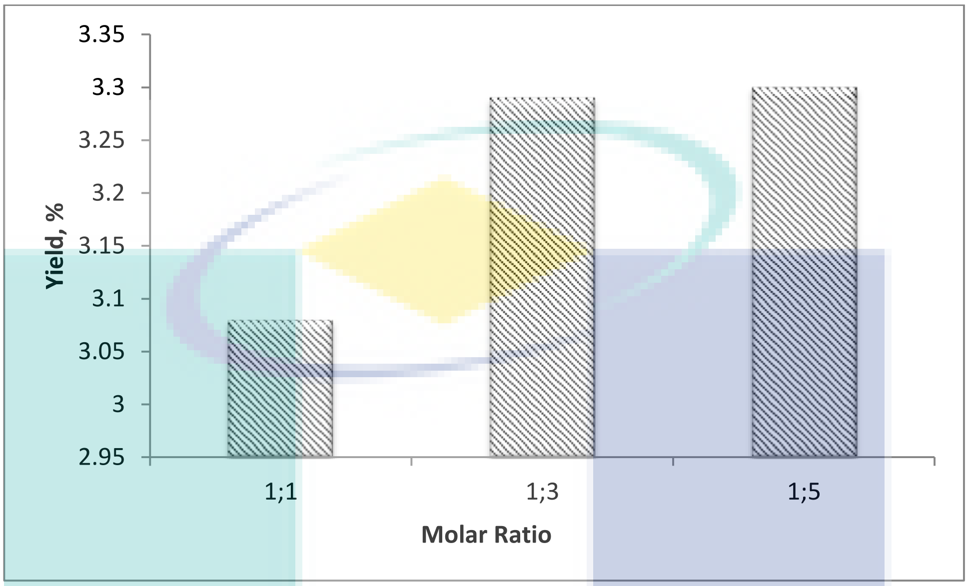
(a)



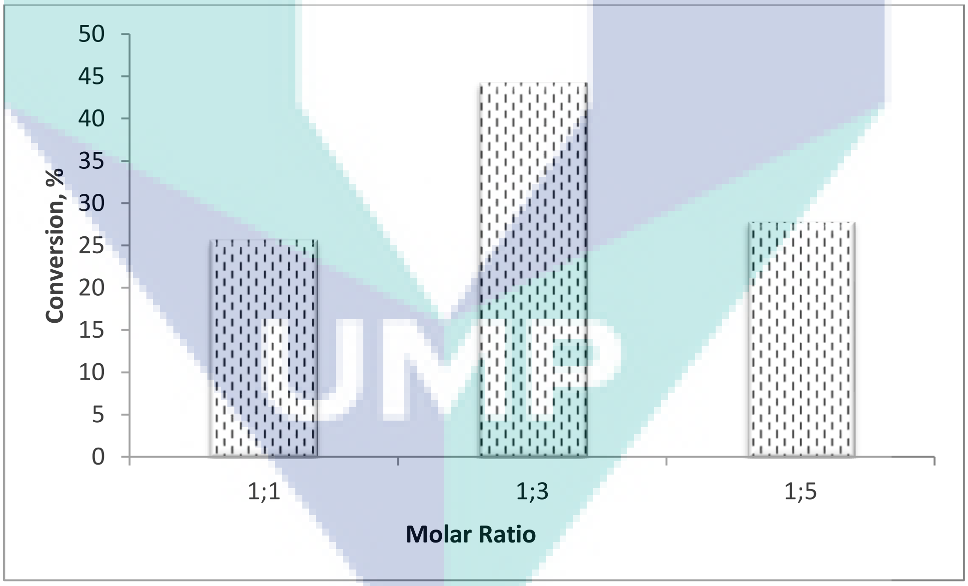
(b)

Figure 4.4: (a) Yield of 2EHA and (b) Conversion of AA for the reaction carried out at different temperatures. Reaction conditions: volume flow rate of 5 ml/min $M_{AA:2EH}$ of 1:3 and catalyst weight of 5g.

The highest conversion was observed at $M_{AA/2EH}$ of 1:3. The excess of 2EH could drive the reaction equilibrium to product side and hence shorten the time needed to achieve equilibrium conversion. Nevertheless, the conversion of AA at $M_{AA/2EH}$ of 1:5 was lower because the accessibility of molecules AA to the active site has been blocked by the excessive number of 2EH molecules. Furthermore, the excess of 2EH also could promote the side reactions which would lower the yield of 2EHA. For instance the excess of 2EH enhances the side reaction of etherification.



(a)



(b)

Figure 4.5: (a) Yield of 2EHA and (b) Conversion of AA for the reaction carried out at different molar ratio. Reaction conditions: volume flow rate of 5 mL/min temperature of 95°C and catalyst weight of 5g.

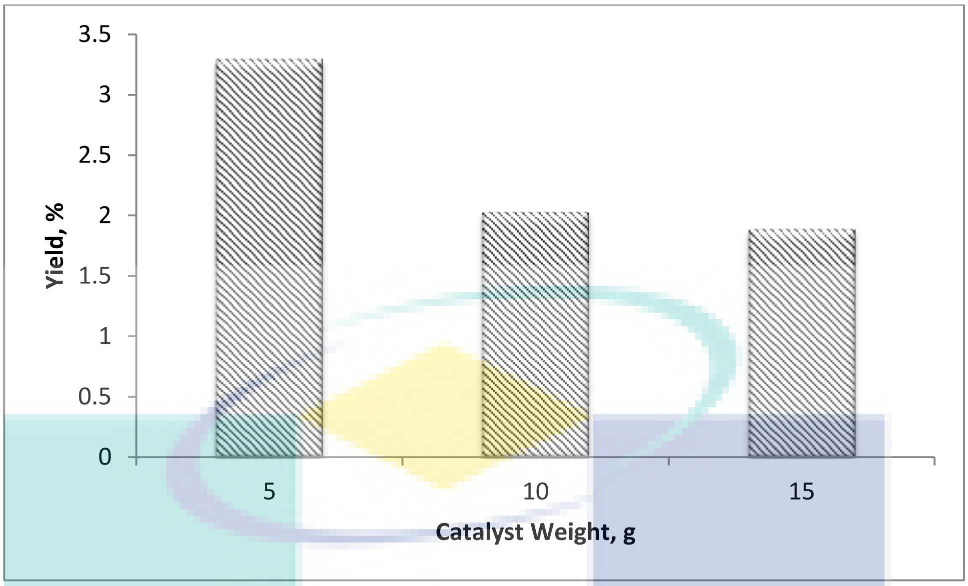
However, the yield is relatively low. The significantly higher conversion may be due to the adsorbed AA on the resin (PK-208) that reducing the concentration of AA in the outlet stream. Thus, the molar ratio 1:3 of AA:2EH was chosen as the best condition for esterification of AA with 2EHA.

4.3.3 Effect of Catalyst Loading

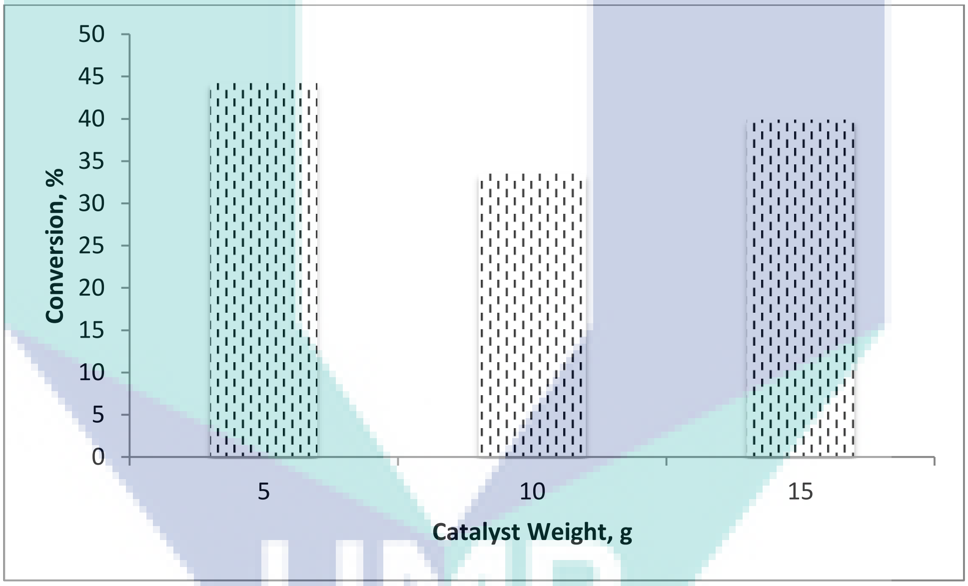
The effect of the amount of catalyst on the 2EHA yield was studied by varying the catalyst loading from 5-15 g and keeping all other reaction parameters identical. Each reaction was carried out for 5 hours to obtain steady state. Based on the results illustrated in Figure 4.6, the increase in product yield is significant when the catalyst amount is decreased from 15 to 5g. This can be attributed to the fact that AA may be adsorbed by the resin and increase the loss of AA.

The conversion decreased as the catalyst amount was increased from 5 to 15 g. The presence of a solvent can affect reactions at surfaces by competing with reactants and products for adsorption sites and solvating adsorbed species. Because many heterogeneous catalysts were designed to be stable under gas-phase reaction conditions, their operation in liquid reaction media at moderately elevated temperatures can result in unexpected structural changes. In some cases, components derived from the evolving catalyst contribute significantly to the catalytic activity (Sievers et al., 2016).

In additional, this has also proven that the process is economic feasible since the amount of catalyst used is only 5g (lower than 10%) (Teo and Saha, 2004). Therefore, the catalyst weight 5g was chosen as the best catalyst loading based on both conversion and yield.



(a)



(b)

Figure 4.6: (a) Yield of 2EHA and (b) Conversion of AA for the reaction carried out at different catalyst weight. Reaction conditions: volumetric flow rate of 5 mL/min, temperature of 95°C and $M_{AA:2EH}$ of 1:3.

4.4 Kinetic Modelling Studies

The reaction rate expression of the 2EHA formation depends on the mechanism of reagent adsorption on the heterogeneous catalyst. The PH, ER, and LHHW models are commonly applied for correlating the kinetic data of esterification reaction. The kinetic parameters obtained with the corresponding standard errors, σ are shown in Table 4.2 while the adsorption parameters are shown in Table 4.3. Since the residuals obtained from all the models were randomly distributed around the line of error=0 with zero means, it is to be noted that the ER model gave the best correlation between the three models adopted because the coefficient of determination (R^2) is closest to one. The parity plot for the experimental and predicted rate of reaction is shown in Figure 4.9.

Table 4.2: Kinetic parameters for the model used to fit the experimental data.

Model	**Kinetic Parameter**				
	k_{f0} (σ k_{f0}) (mol/L/min)	**E_f (σ E_f) (J/mol)**	**K_{A0} (σ K_{A0})**	**G_r (σ G_r)**	**R^2**
PH	1.989 x 10^4 (9.160 x 10^2)	39,990 (141.2464)	5.40 x 10^{10} (3.965 x 10^{10})	65,270 (1,915.62)	0.86
ER	3.164 x 10^4 (1.289 x 10^3)	34,061 (0.0393146)	1.51 x 10^8 (9.008 x 10^7)	48,882 (576.284)	0.94
LWWH	1.499 x 10^6 (5.034 x 10^4)	34,777 (105.0921)	1.43 x 10^9 (3.598 x 10^8)	54,542 (701.087)	0.92

Table 4.3: Adsorption parameters for the model used to fit the experimental data.

Model	**Adsorption parameter**				
	K_{AA}	K_{2EH}	K_{2EHA}	K_W	**R^2**
PH	-	-	-	-	0.86
ER	109.5 (5.078)	-	-	5.5 (1.086)	0.94
LWWH	175.2 (0.044)	2.2 (0.401)	0.1 (2.609)	18.2 (0.003)	0.92

The apparent activation energy for the esterification reaction was 34.06 kJ/mol. The activation energy of the esterification of AA with 2EH catalysed by DIAION PK208 was lower than the activation energy for the resins catalysed esterification of AA with the various types of alcohols as reported by Chin *et al.*, (2015), Komoń *et al.* (2013), Sert *et al.*(2013), Akbay and Altıokka (2011), and Fomin *et al.*(1991). This shows that PK208 is a better catalyst in reducing the energy barrier that surmounted by the AA and 2EH for an esterification reaction to occur.

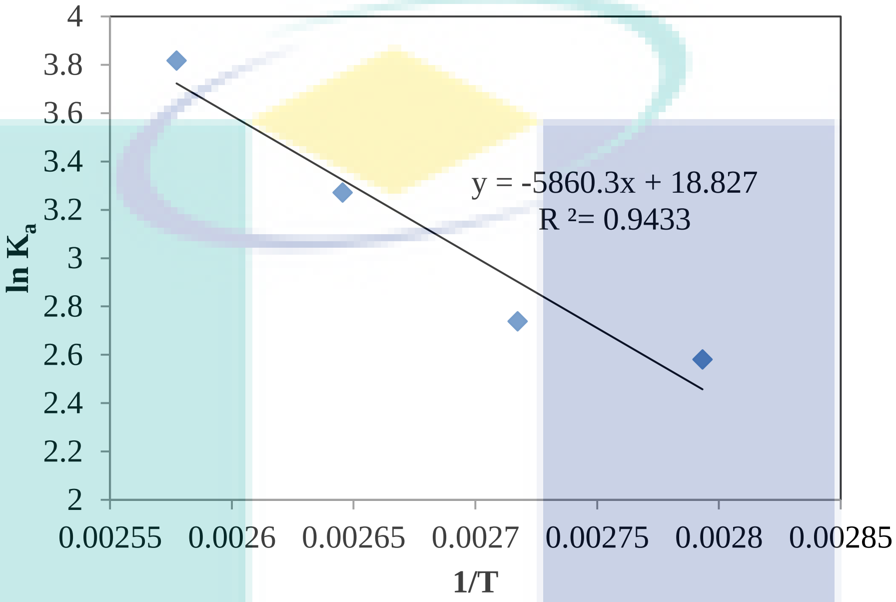


Figure 4.7 : ln K_a vs 1/T for ER model.

Figure 4.7 shows the increase of the equilibrium constant and equilibrium conversion with the temperature, indicating that the esterification of AA with 2EH is an endothermic reaction.

The good agreement between the experimental data with ER model has shown that the reaction is controlled by surface reaction (Sert and Atalay, 2012). Based on the ER model, it is proposed that the AA molecule adsorbs on the catalyst site and forms an oxonium ion intermediate, which is simultaneously attacked by the 2EH in the bulk liquid. During this exchange reaction, and the water molecule is formed in adsorbed state while 2EHA molecule is formed and desorbed immediately to the bulk liquid. All the adsorbed molecules then desorb and give rise to a vacant catalyst site in all cases. Fig. 4.8 shows parity plot of experimental reaction rate with calculated reaction rate for all temperature. This figure concluded that ER is best fitting with less error compared with another model fitting.

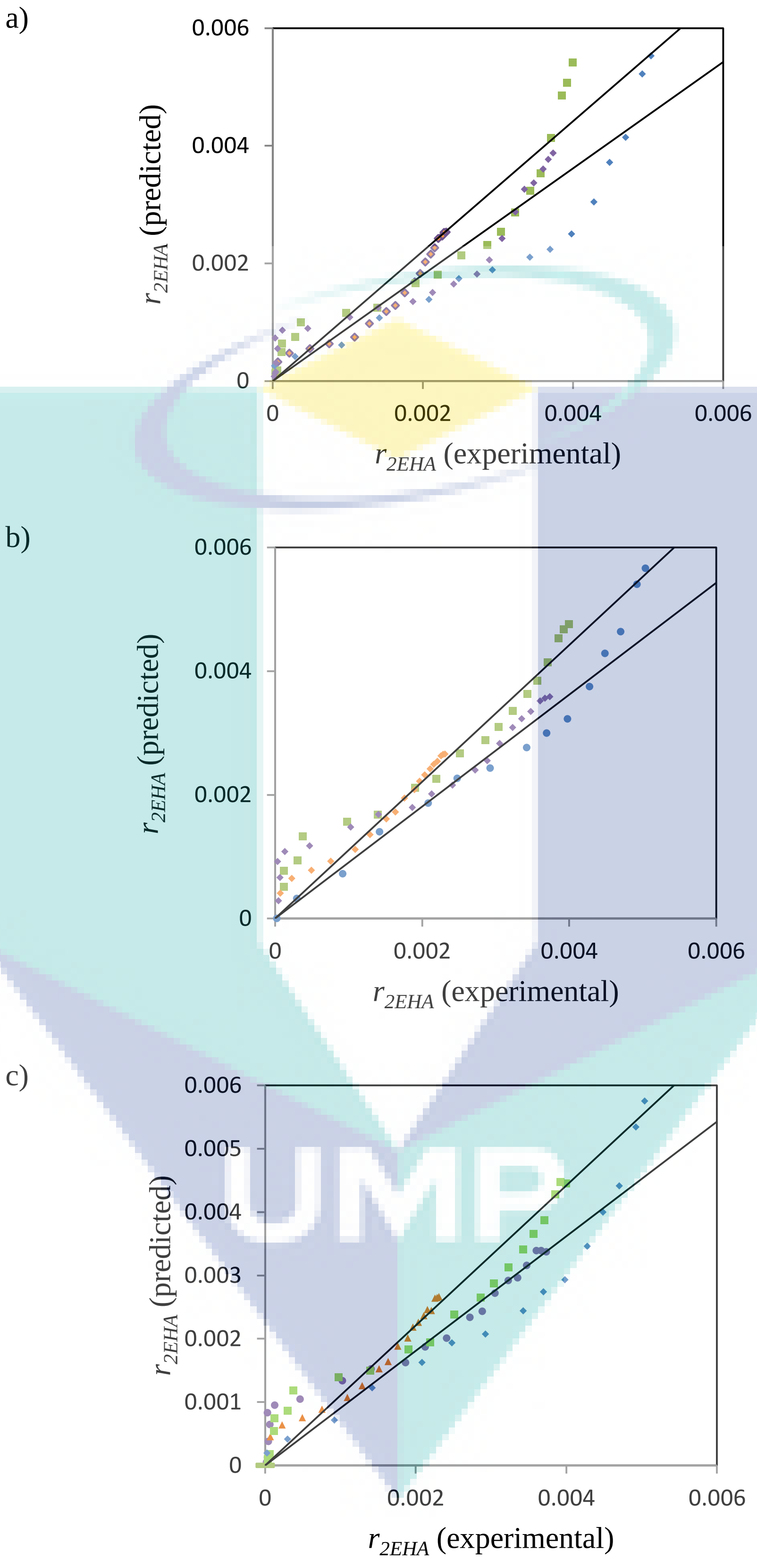


Figure 4.8: Parity plot for the experimental and predicted rate of reaction of (a) PH; (b) ER and (c) LWWH (blue=388 K; green=378 K; purple=368 K; orange=358 K).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Among the DIAION ion exchange resins, PK208 shows the highest reaction performance due to its enhanced degree of swelling and comparable fairly good ion exchange capacity. RTD studies has proven that the tubular packed bed reactor was non ideal in mixing. The PK-208 catalysed esterification of AA with 2EH at the temperature ranged from 75ºC to 95ºC, initial molar ratios of AA:2EH ranged from 1:1 to 1:3 and catalyst loading ranged from 5 to 15 g was investigated experimentally. It was carried out in a tubular reactor under the reaction conditions with constant volumetric flow rate which is 3 ml/min. Among the important operating parameters, reaction temperature has significantly affected the conversion of AA and the yield of 2EHA. The highest yield which is 3.29% and highest conversion which is 44.3 % was obtained at the temperature of 95ºC, initial molar ratio of AA:2EH of 1:3 and catalyst loading of 5 g. The yield is relatively low due the AA adsorbed by the resin and hence increasing the loss of AA. Eley-Rideal (ER) was the best kinetic model to predict the conversion of AA and yield of 2EHA.

5.2 Recommendation

The present study has shown that the conversion of the esterification of AA with 2EH is high but the yield is relatively very low. This is might be attributed to the polymerisation of AA. Optimisation study for the amount of the polymerization inhibitor used especially in the diluted AA system should be taken into account in the future.

In future, adsorption studies can also be carried out to examine the significance of the adsorption of catalyst by varying the weight of the catalyst. The yield is relatively low in present study, this might be because of the high volumetric flow rate. In future, the reaction should run in low flow rate so that the reactants have enough time to react with the catalyst.

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APPENDIX A

STANDARD CALIBRATION CURVE OF ACRYLIC ACID

Figure A1-A5 shows the chromatogram of standard AA with various concentrations.

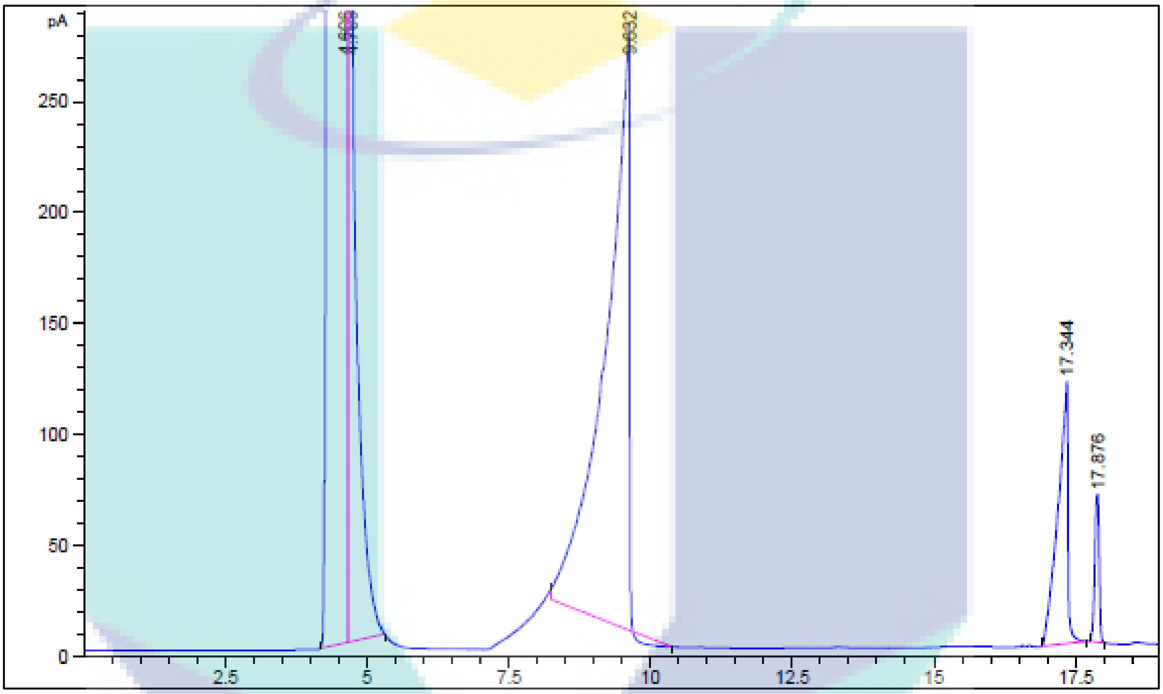

Figure A1: GC-FID spectrometry of 21019.9 ppm AA

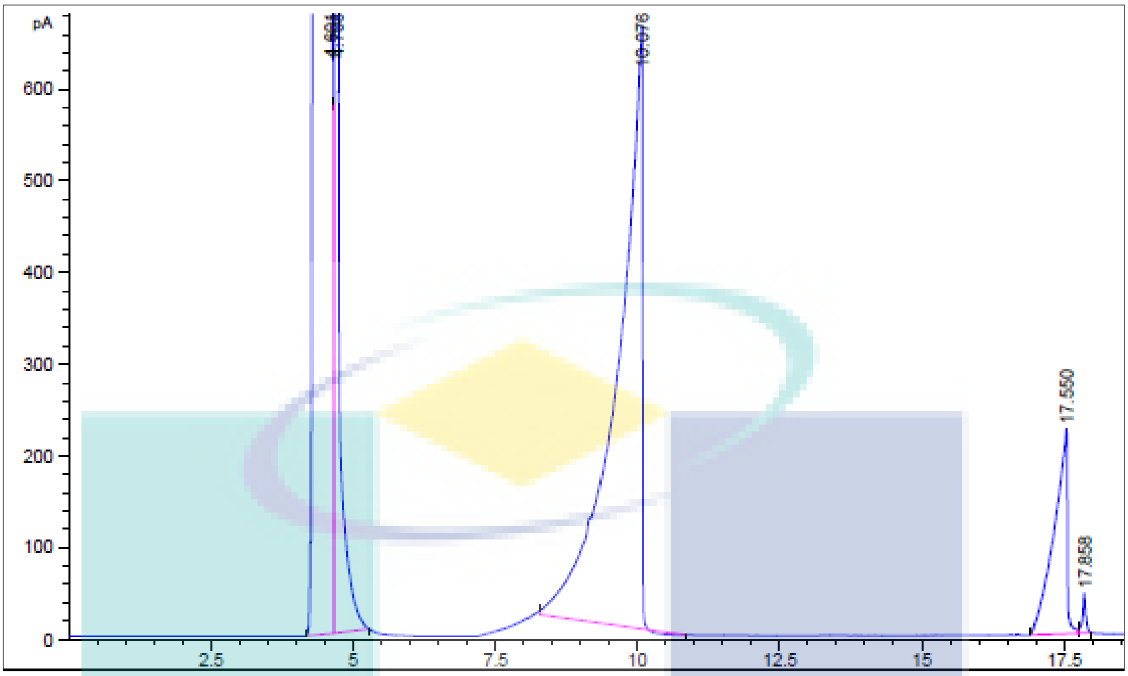

Figure A2: GC-FID spectrometry of 42039.8ppm AA

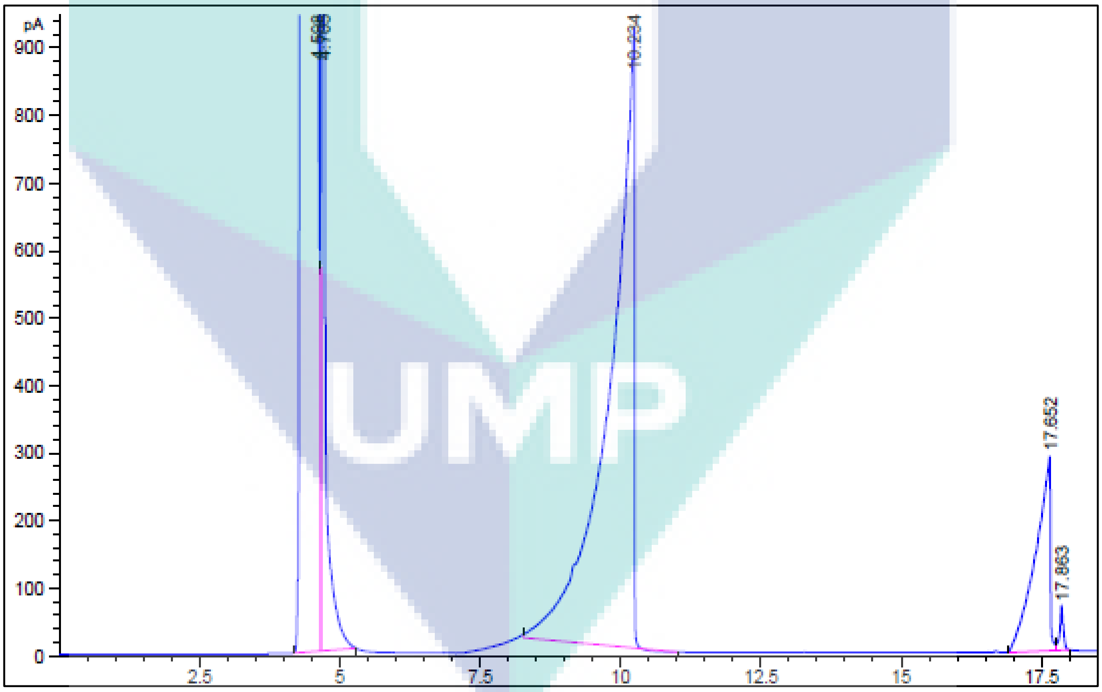

Figure A3 : GC-FID spectrometry of 63059.7 ppm AA

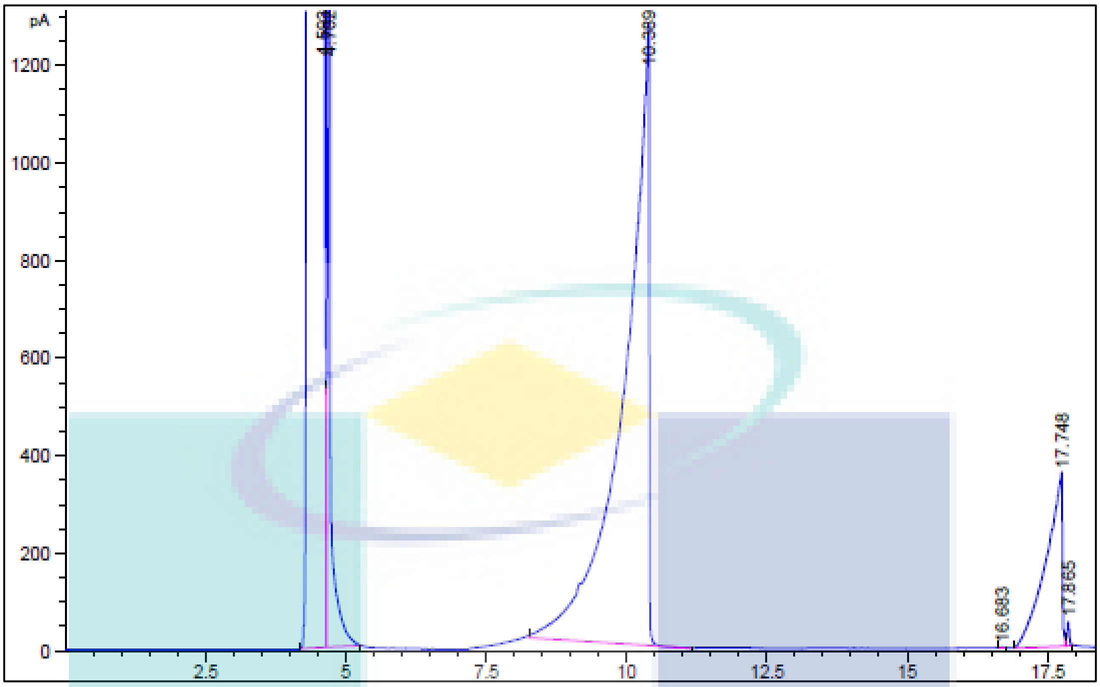

Figure A4 : GC-FID spectrometry of 84079.6 ppm AA

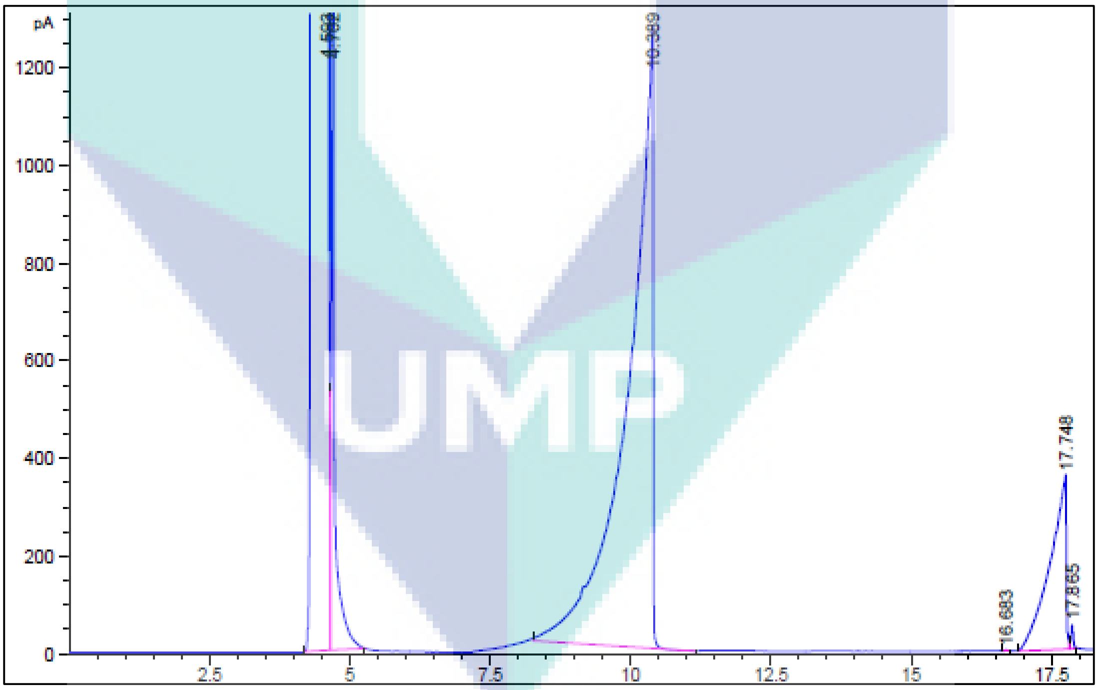

Figure A5 : GC-FID spectrometry of 51,146.19 ppm AA

The retention time for AA was detected at 10 min. The ABS-concentration data of standard calibration curve was included in table A1 and plotted in Figure A6.

Table A1: Concentration versus ABS for standard calibration curve plot of AA.

concentration (ppm)	ABS (pA*s)
0.00	0.000
21019.9	7693.7979
42039.8	19409.8000
63059.7	27035.7000
84079.6	37503.6000
105099.5	44621.6000

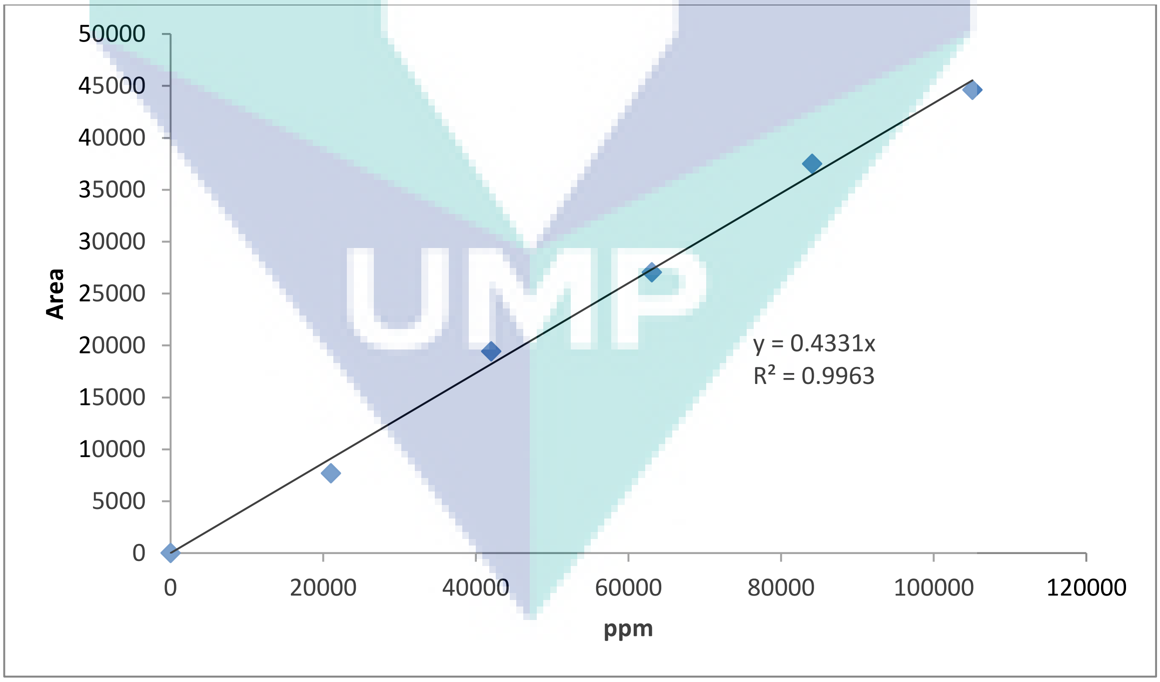

Figure A6: Calibration curve for AA using GC-FID

From the Figure A6, the following equation was developed to calculate the unknown concentration of AA for each sample using the absorbance given by GC-FID analysis:

$$ABS_{AA} = m\ x\ C_{AA} \tag{A1}$$

$$C_{AA} = \frac{ABS_{AA}}{m} \tag{A2}$$

$$C_{AA} = \frac{ABS_{AA}}{0.4331} \tag{A3}$$

$$C_{AA} = 2.3089\ x\ ABS_{AA} \tag{A4}$$

APPENDIX B

STANDARD CALIBRATION CURVE OF 2 ETHYL HEXYL ACRYLATE

Figure B1-B5 shows the chromatogram of standard 2EHA with various concentrations.

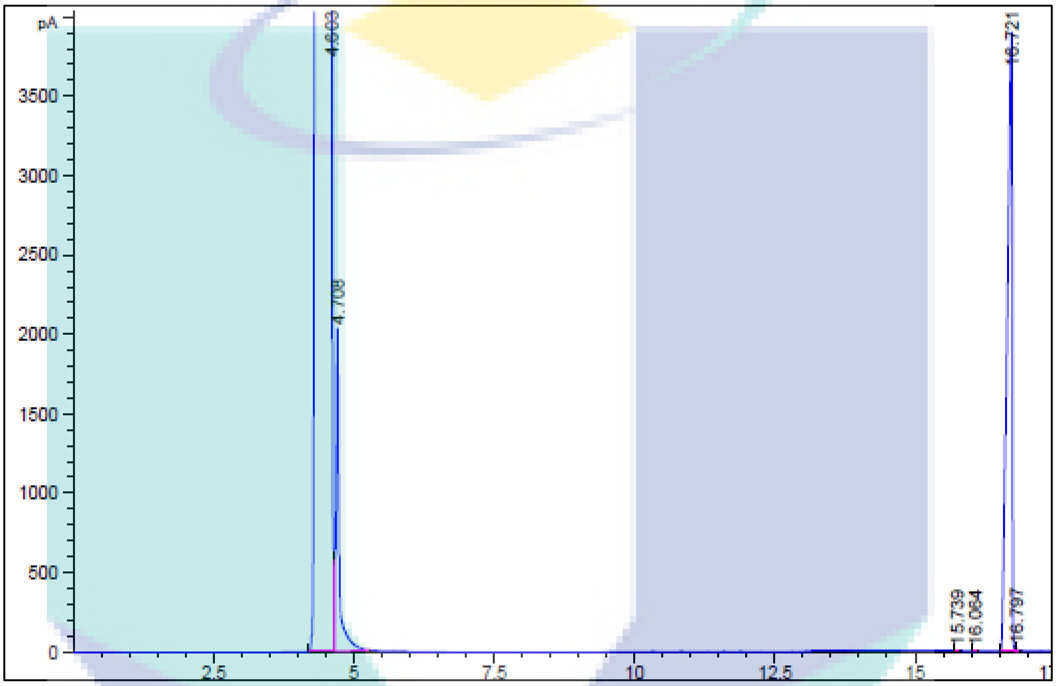

Figure B1 : GC-FID spectrometry of 3461.04 ppm 2EHA

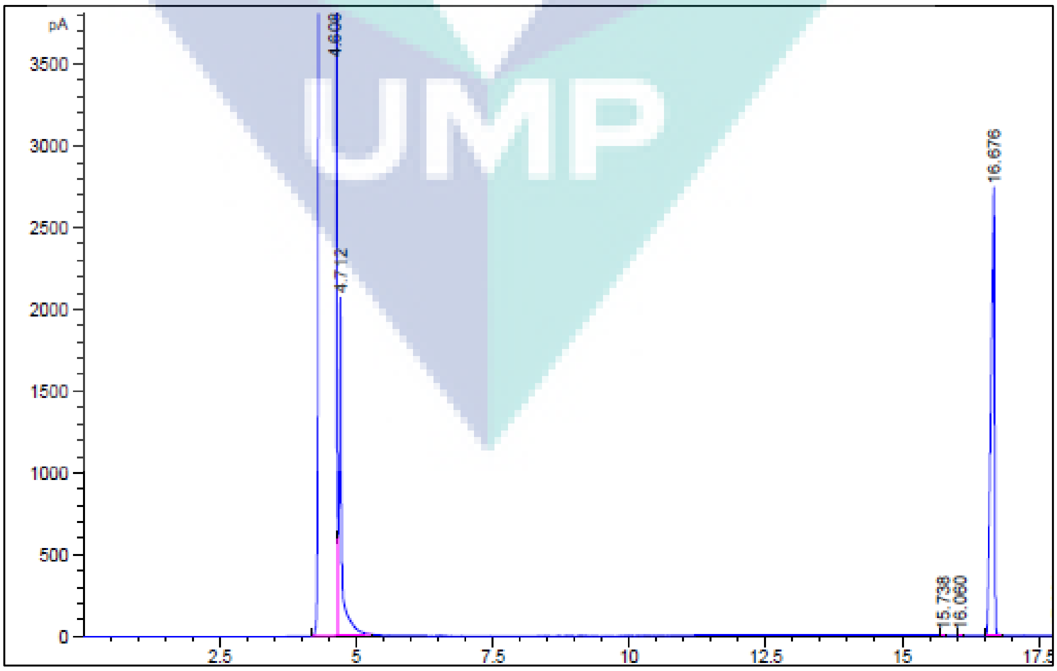

Figure B2 : GC-FID spectrometry of 6921.36 ppm 2EHA

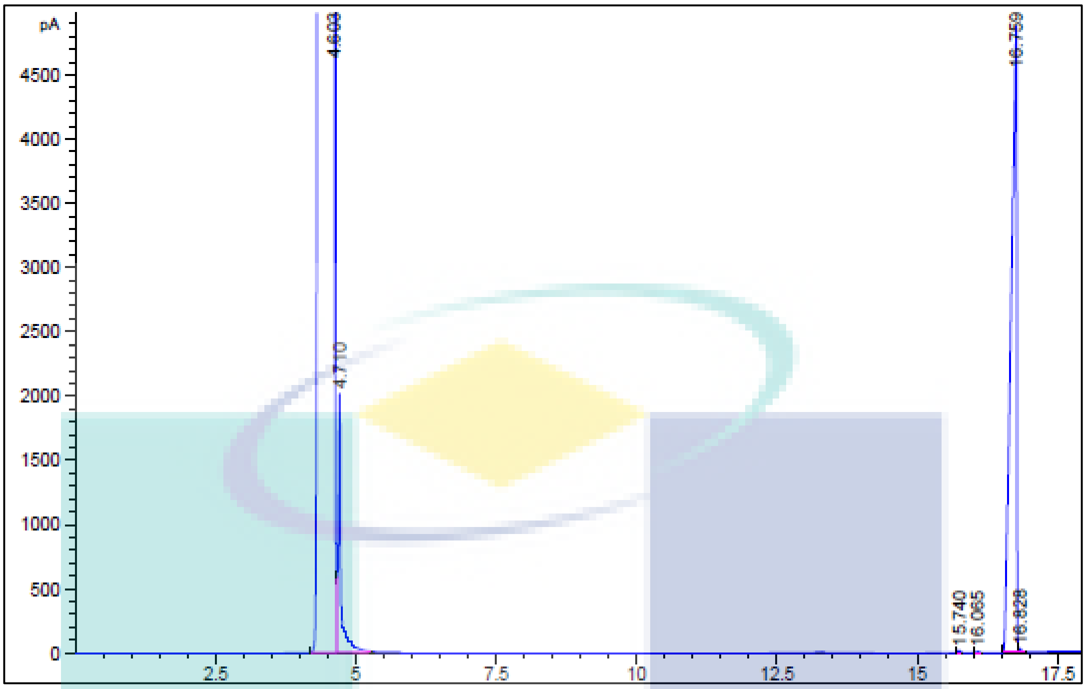

Figure B3 : GC-FID spectrometry of 10382.40 ppm 2EHA

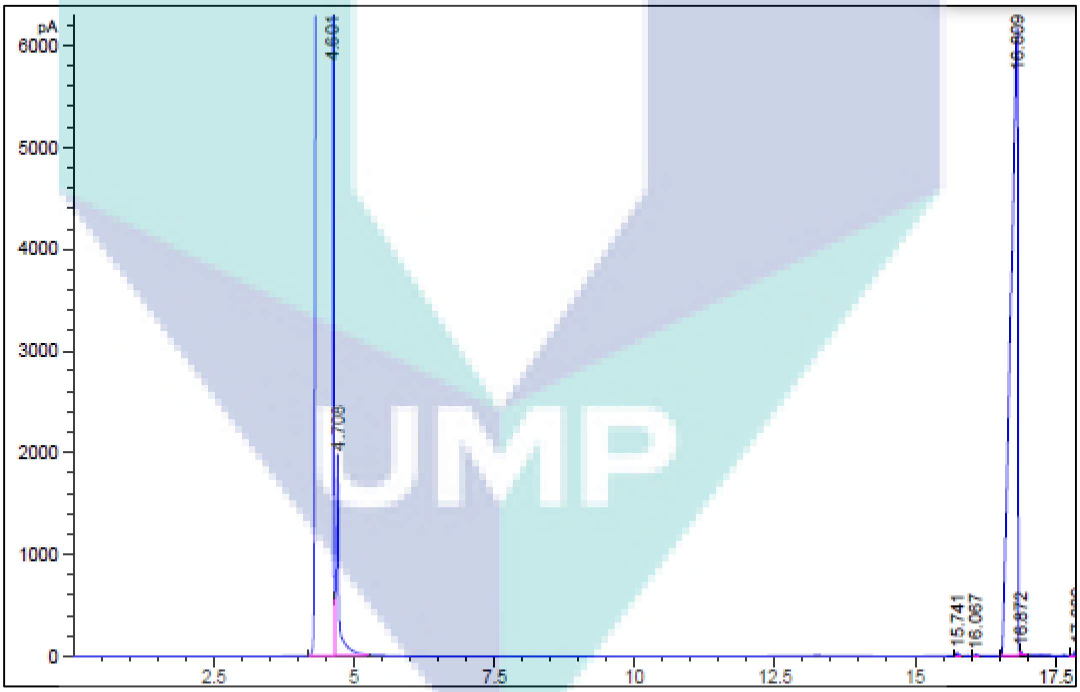

Figure B4 : GC-FID spectrometry of 13842.73 ppm 2EHA

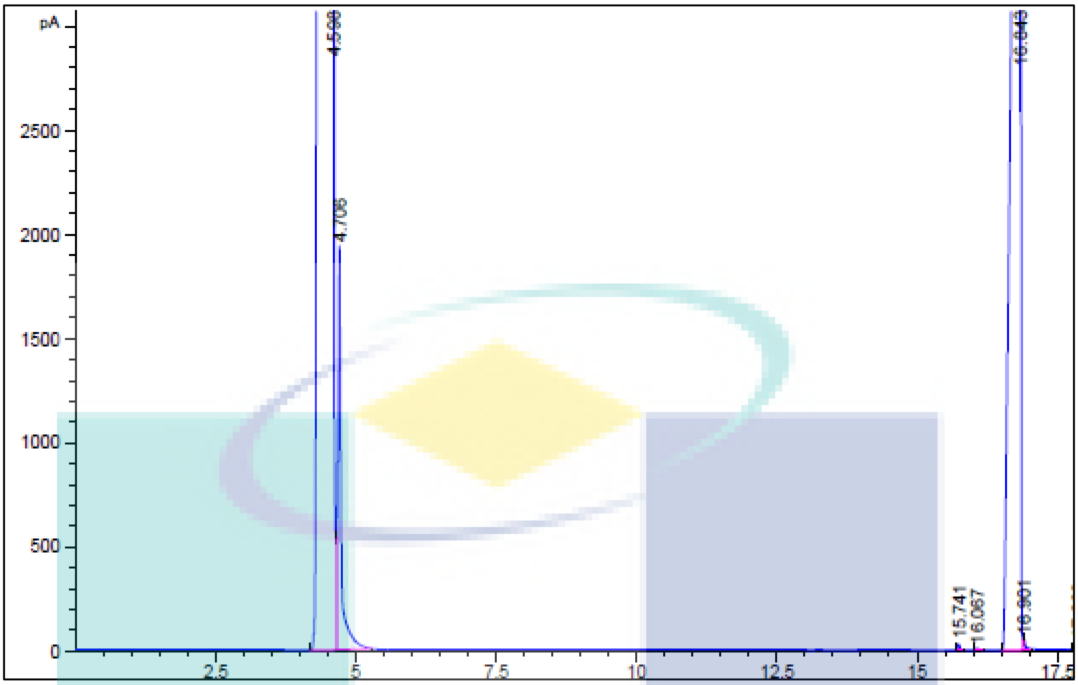

Figure B5 : GC-FID spectrometry of 17303.77 ppm 2EHA

The retention time for 2EHA was detected at 16.7 min. The ABS-concentration data of standard calibration curve was included in Table B1 and plotted in Figure B6.

Table B1: Concentration versus ABS for standard calibration curve plot of 2EHA

concentration (ppm)	ABS (pA*s)
0	0.000
3461.04	12968.6000
6921.36	23595.7000
10382.40	34731.9000
13842.73	53140.4000
17303.77	67112.7000

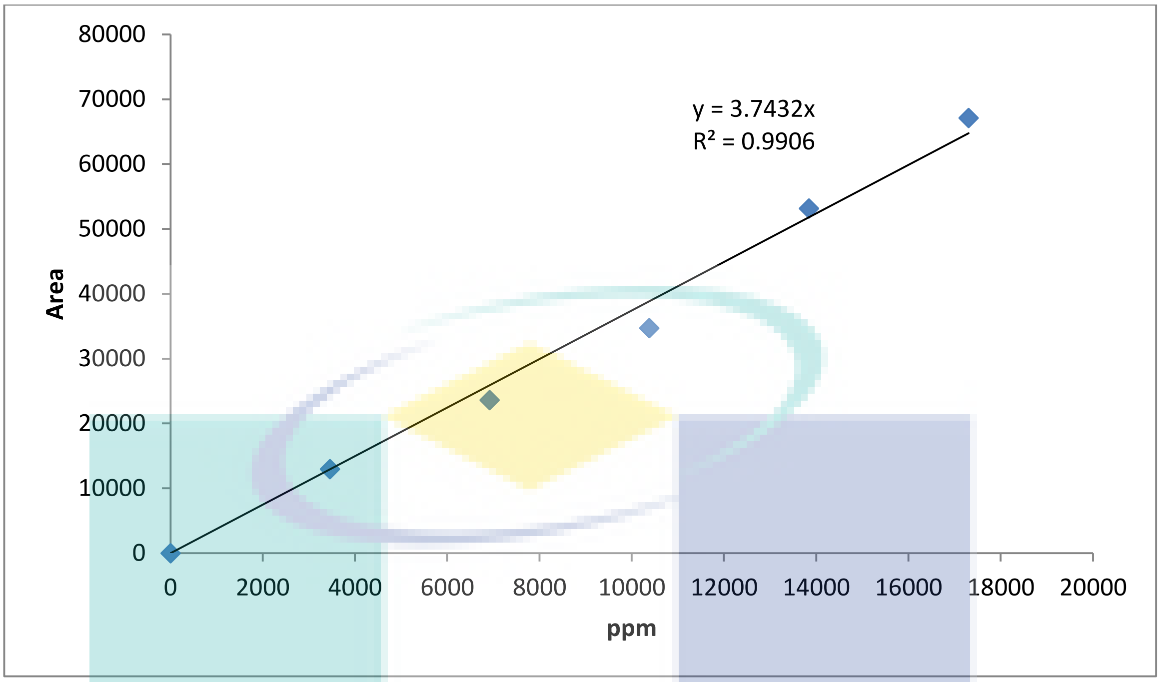

Figure B6: Calibration curve for 2EHA using GC-FID

From the Figure B6, the following equation was developed to calculate the unknown concentration of 2HA for each sample using the absorbance given by GC-FID analysis:

$$ABS_{2EHA} = m \, x \, C_{2EHA} \tag{B1}$$

$$C_{2EHA} = \frac{ABS_{2EHA}}{m} \tag{B2}$$

$$C_{2EHA} = \frac{ABS_{2EHA}}{3.7432} \tag{B3}$$

$$C_{2EHA} = 0.2672 \, x \, ABS_{2EHA} \tag{B4}$$

APPENDIX C

CALCULATION OF YIELD AND CONVERSION

Yield

From GC chromatogram, gives the area under the graph is 555.1445 pA*s (Temperature =75^{o}C, molar ratio=1:3 and catalyst weight = 5g). So, yield of 2EHA are calculated as follow:

$$yield\ (\%) = \frac{C_{2EHA}}{C_{AA0}} \times 100\%$$

1. Standard curve
    a) Y=$0.2672\ x\ ABS_{2EHA}$
    Where Y is the concentration of 2EHA in mg/L and ABS_{2EHA} is the area of 2EHA under the graph of GC chromatogram.
2. Molecular weight of 2EHA is 184.279 g/mol.
3. Initial concentration of AA is 1.8669 mol/L.

Concentration of 2EHA = Area x 0.2672 x dilution factor
= 555.1445 x 0.2672 x 10
= 1483.3461 mg/L

Unit conversion = 1483.3461 mg/L ÷ molecular weight ÷1000(1g=1000mg)
= 1483.3461 ÷187.279÷1000
= 0.0079205

Yield = (0.0079205/1.8669) x 100
= 0.42%

Conversion

From GC chromatogram, gives the area under the graph is 7960 pA*s (Temperature =75^{o}C, molar ratio=1:3 and catalyst weight = 5g). So, conversion of AA are calculated as follow:

$$Conversion\ (\%) = \frac{C_{AAO} - C_{AA}}{C_{AA0}} \times 100\%$$

4. Standard curve
    b) Y=2.3089 $x\ ABS_{AA}$
    Where Y is the concentration of AA in mg/L and ABS_{AA} is the area of AA under the graph of GC chromatogram.
5. Molecular weight of AA is 72.06 g/mol.
6. Initial concentration of AA is 1.8669 mol/L.

Concentration of 2EHA = Area x 2.3089x dilution factor
= 7960 x 2.3089 x 10
= 183788.44 mg/L

Unit conversion = 183788.44 mg/L ÷molecular weight ÷1000(1g=1000mg)
= 183788.44 ÷72.06÷1000
= 2.5510 mol/L

Yield = (1.8669-2.5510/1.8669) x 100
= -36.6%