ESTERIFICATION OF ACRYLIC ACID AND 2-ETHYL HEXANOL IN TUBULAR REACTOR FOR THE SYNTHESIS OF 2-ETHYLHEXYL ACRYLATE

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Thesis submitted in partial fulfilment of the requirements
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Bachelor of Chemical Engineering

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Dedicated to my beloved parents, uncle, aunty, siblings and friends.
Who gave me everlasting inspiration, never- ending encouragements and priceless support towards the success of my study.
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ABSTRACT

Acrylic ester is applied in paper treatment, polishes, leather, fibre, detergents, super-absorbent material plastic additives, textiles, sealant, adhesive and surface coatings (Xu et al., 2006). In recent years, the demand of acrylic esters has been increasing tremendously due to its multiples areas of application. It had a total demand of 3055KT globally in 2013. As the demand increases, the productions of acrylic ester 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 (Kiss, 2011) which resulting in expensive process. In the present study the effect of important operating parameters on the esterification of Acrylic Acid (AA) with 2-Ethyl Hexanol (2EH) for the production of 2-Ethyl Hexyl Acrylate (2EHA) in a tubular reactor was carried out. The reaction is catalysed by a heterogeneous catalyst, PK-208 and the reactants flow at constant flow rate which is 15.7 rpm. The important parameters includes, the range of catalyst weight which are varied from 5 to 15g, the range of molar ratio which are varied from 1:1 to 1:5, whereas the range of the reaction temperature is varied from 75^{o}C to 95^{o}C. Samples with individual volume of 0.5 ml are withdrawn at 1 hour intervals and were analysed using gas chromatography for the composition of 2EHA, AA and 2EH.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 results from GC are used to calculate the yield and conversion. The highest yield and conversion was obtained at the temperature of 95^{o}C, initial molar ratio of AA:2EH of 1:3 and catalyst loading of 5 g. The yield is relatively low, this is because the AA may be adsorbed by the resin and increase the loss of AA.

ABSTRAK

Ester akrilik digunakan dalam rawatan kertas, pengilat, kulit, gentian, bahan pencuci, super penyerap tambahan plastik bahan, tekstil, sealant, pelekat dan lapisan permukaan (Xu et al., 2006). Dalam tahun-tahun kebelakangan ini, permintaan ester akrilik telah meningkat dengan ketara kerana kawasan gandaannya permohonan. Ia mempunyai jumlah permintaan sebanyak 3055KT global pada tahun 2013. Seiring dengan peningkatan permintaan, pengeluaran daripada akrilik ester perlu sentiasa inovatif supaya ia boleh dihasilkan dalam harga yang lebih murah. Penggunaan pemangkin homogen dalam proses komersial menunjukkan bahawa pemangkin ini sukar untuk memisahkan dari medium tindak balas, oleh itu tidak dapat penggunaan semula pemangkin dan merumitkan proses pemisahan. Ia juga menggalakkan tindak balas sampingan (Kiss, 2011) yang mengakibatkan proses yang mahal. Dalam kajian ini kesan parameter operasi penting di pengesteran asid akrilik (AA) dengan 2-Ethyl Hexanol (2EH) untuk pengeluaran 2-Ethyl Hexyl Acrylate (2EHA) dalam reaktor tiub telah dijalankan. Tindakbalas ini memangkinkan dengan mangkin heterogen, PK-208 dan bahan tindak balas mengalir pada kadar aliran malar yang merupakan 15.7 rpm. Parameter penting termasuk, pelbagai berat pemangkin yang berbeza-beza dari 5 hingga 15g, pelbagai nisbah molar yang berbeza-beza dari 1: 1 hingga 1: 5, manakala julat suhu tindak balas adalah berbeza dari 75^{o}C kepada 95^{o}C. Sampel dengan jumlah individu 0.5 ml sedang ditarik balik pada 1 selang jam dan dianalisis dengan menggunakan kromatografi gas untuk komposisi 2EHA, AA dan 2EH. Keputusan daripada GC digunakan untuk mengira hasil dan penukaran. Hasil tertinggi dan penukaran telah diperolehi pada suhu 95^{o}C, nisbah molar awal AA: 2EH 1:3 dan pemangkin memuatkan 5 g. Hasil adalah rendah, ini adalah kerana AA boleh terserap oleh resin dan meningkat kehilangan AA.

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%	Percent
T	Temperature
V	Volume
^{o}C	Degree Celsius

LIST OF ABBREVIATIONS

2EH	2-Ethyl Hexanol
2EHA	2-Ethyl Hexyl Acrylate
AA	Acrylic acid
GC	Gas chromatography
FID	Flame ionization detector

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 (Nazriah & Hamdan , 2015). Homogeneous catalyst is used in the conventional method to accelerate the esterification reaction which takes days to achieve equilibrium (Ahmad et.al., 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 et al., 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 et al., 1999). Heterogeneous catalyst are insoluble, have good selectivity and specificity, can easily recovered and have good thermal stability (Farnetti et al., 1999). 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 (Sert et al., 2013).

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 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 high yield. This method is expected to reduce the occurrence of side effect and increase the yield of the desired product. Moreover, this method could lead to the production of 2EHA with cheaper price.

1.4 Objectives

In the present work, esterification of acrylic acid (AA) and 2-ethyl hexanol (2EH) in tubular reactor to produce 2-ethylhexyl acrylate (2-EHA) is studied with the objectives of to investigate the effect of important operating parameter for the esterification of AA with 2EH catalyst by PK-208 in a tubular reactor.

1.5 Scopes of Study

The scopes of study for the present work included the investigation of 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 (75^0C to 95^0C) and catalyst loading (5 to 15g).

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 Acrylic ester

There are several type of acrylic ester in the market which are ethyl acrylate, ethyl acrylate, butyl acrylate, and 2-EH acrylate (Rohan, 2016). 2-ethylhexyl acrylate (2EHA) is a clear colourless liquid with a pleasant odor , volatile liquid and slightly soluble in water and less dense than water and filly soluble in alcohol, ethers and most organic solvent (Komoń et at., 2013). It has very good film formation property for which it is used in paints, adhesives, and coating applications (Haloi and Singha, 2011). This ester are also used for the production of environmentally friendly solvents, flavors, pharmaceuticals, plasticizers, polymerization monomers and emulsifiers in the food, cosmetic and chemical industries (Liu et al., 2006). Table 2:2.1 shows the physical and chemical properties of 2EHA.

Table 2.2:1: Physical and Chemical properties of 2EHA

Properties	Value	Reference
Molecular weight	184.2753	(PubChem, 2004)
Melting point	-90°C	(ChemicalBook, 2016)
Boiling point	215-219 °C(lit.)	(ChemicalBook, 2016)
Density	0.885 g/mL at 25 °C(lit.)	(ChemicalBook, 2016)
Vapour pressure	0.15 mm Hg (20 °C)	(ChemicalBook, 2016)
Surface tension	26.4 dynes/cm at 25^{o}C	(DOW)
Water solubility	-0.01 % wt	(DOW)
Flash point	189 ^{o}F	(DOW)
Flammability	Combustible	(ILO-ICSC, 2003)
Explosive properties	Above 82^{o}C	(ILO-ICSC, 2003)

2-ethylhexyl acrylate is used in the production of homopolymers. It is also used in the production of co-polymers, for example acrylic acid and its salts, esters, amides, methacrylates, acrylonitrile, maleates, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene and unsaturated polyesters. 2-ethylhexyl acrylate is also used in pressure sensitive adhesives. It is applied in paper treatment, polishes, leather, fibre, detergents, super-absorbent material plastic additives, textiles, sealant, adhesive and surface coatings (Xu et al., 2006). The vast applications of 2EHA are ascribed to it versatile properties as shown in Table 2.1.

The worldwide 2-ethylhexyl acrylate marketplace, in conjunction with its give up merchandise, has witnessed a sizable growth inside the beyond few years and this increase is anticipated to increase in the coming years. 2-ethylhexyl acrylate is one of the fundamental natural chemical raw substances in particular used inside the production of coatings, adhesives, super absorbents, thickeners, plastic components, and so forth. The Asia-Pacific region accounted for 38% of the global demand in 2014 (Micromarketmonitor, 2015). It had a total demand of 3055KT globally in 2013.

The acrylates can be manufactured by a number of procedures. These include dehydration of the corresponding hydroxyalkanoic acid, saponification of the alkaline nitrile, catalytic hydration of acetylene and carbon monoxide, or the reaction of acetone with hydrocyanic acid and also esterification reaction (Bingham et al., 2001).

2.3 Type of catalysts for the esterification of AA

Esterification is the general name for the chemical process for the production of ester by the reaction of two reactants which is typically an alcohol and an acid and removal of water. Esters are compounds of the chemical structure R-COOR', where R and R' is either alkyl or aryl groups. The Figure 2.3:1 shows the esterification reaction mechanism. This reaction equation is:

$$RCOOH + ROH \rightarrow RCOOR' + H_2O$$

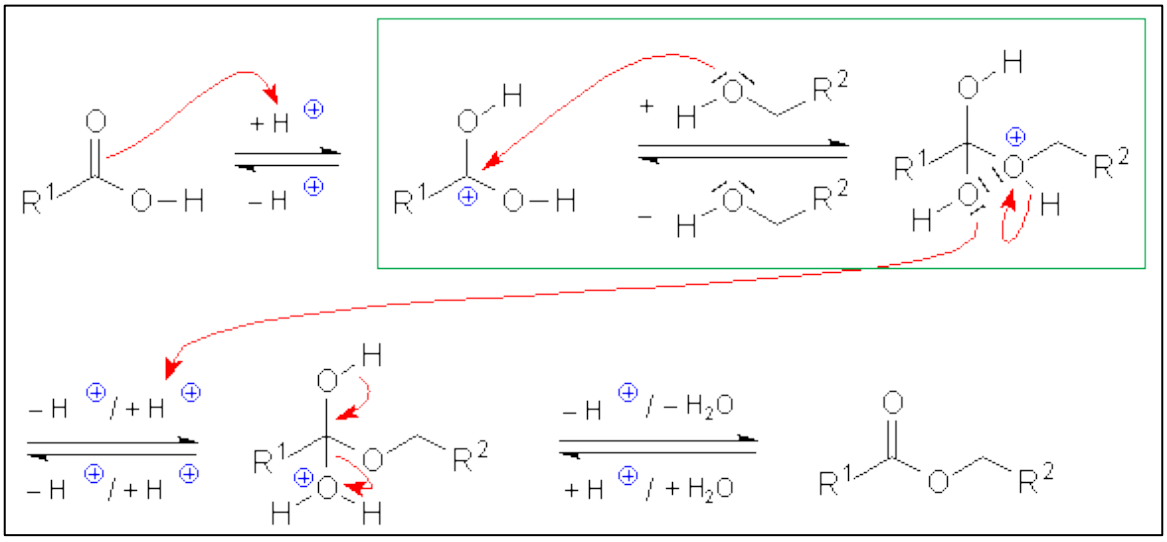


Figure 2.3:1: Esterification reaction mechanism

The esterification reaction is a liquid-phase process, where the limiting conversion of the reactants is determined by equilibrium. Typically esterification reactions are very slow; it requires several days to attain the equilibrium in the absence of catalyst. Therefore, the reaction is enhanced with an added catalyst(Lilja et al., 2002). Catalyst is needed for the esterification reaction to accelerate the process via lowering the activation energy. The common types of catalysts are homogeneous, heterogeneous and also enzymatic or more known as biological catalyst. These catalyst are Bronsted acid or Lewis acid catalyst type. The Bronsted acid catalysts are such as hydrochloric acid and sulphuric acid. The Lewis acid catalyst type is preferred to avoid

alcohol dehydration and create the situation that compatible with acid labile group (Hoydonckx et al., 2004).

Esterification can take place without adding catalysts but the reaction is extremely slow and requires several days to reach equilibrium at typical reaction conditions (Liu et al., 2006).

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 Brønsed acid catalysts and Lewis acid catalysts.

Homogeneous catalyst is soluble in reaction mixture and widely used in industrial because the economic consideration (Das & Parida, 2007). These catalysts include sulphuric acid, hydrochloric acid, hydrofluoric acid, para-toluenesulfonic acid, heteropolyacid, polyphosphoric acid and the mixtures of these catalysts. The advantages of homogeneous catalyst are it have strong catalytic effect and provide distinguish performance in the reaction rate.

Esterification of acrylic acid (AA) with an excess of cyclohexene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 2-octene at 333-383 K was carried out by using *p*-toluenesulfonic acid (p-TSA) as homogeneous acid catalyst, however the conversion was only 39.5%. The reaction was carried out in two different reactor which are batch and in distillation column reactor, this is to compare the conversion in both reactor (Saha & Sharma, 1996).

Esterification of AA with alcohol has commercially been performed by using liquid catalysts such as sulfuric acid, hydrofluoric acid, and *para*-toluenesulfonic acid, but these are toxic, corrosive and often hard to remove from the reaction solution (Chen et al., 1999; Sert et al., 2013).

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.

2.3.2 Biocatalyst

Similar to other catalysts, biocatalysts increase the speed in which a reaction takes place but do not affect the thermodynamics of the reaction.

Process using biocatalyst does not require subsequent wastewater treatment. It is environmental friendly and less energy-intensive (Raita et al., 2011). The most interesting part is its high selectivity. This is very important in chemical process synthesis as it may minimise the side reactions for easier separation.

Biocatalyst suffers from poor thermal and longer reaction time despite its low energy consumption and operating cost. Moreover, biocatalysts have limiting operating region (enzymes typically denatured at high temperature and can cause allergic reactions.

2.3.3 Heterogeneous catalyst

The use of heterogeneous catalyst could promote the advantages of reducing equipment corrosion and ease of product separation.

Esterification of AA with 2-EH was carried out using different type of heterogeneous catalyst such as Amberlyst-46, Amberlyst-70, Amberlyst-39 and Amberlyst-131. Amberlyst-70 has been identified to that give the best conversion and yield of 76 % and 71.6 % respectively after 6 hours (Komoń et al., 2013).

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.

Chin et al. (2015) studied the esterification of AA with 2-ethyl Hexanol catalysed by Amberlyst-15 was studied. Amberlyst-15 gave the best yield of 70 % in temperature at 388 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%.

Strohlein et al. (2006) studied the esterification of AA and methanol in a chromatographic reactor using Amberlyst 15 as stationary phase at 333K and reactant ratio 1:2 and 1:3. The conversion was 98% with complete separation of reaction products at low operating temperature.

Table 2.3:1 summarizes the type of heterogeneous catalysts used for esterification reaction.

Table 2.3:1: Heterogeneous catalysts used for esterification reaction.

Alcohol used	Temperature (K)	Molar Ratio (Acid to alcohol)	Catalyst	References
2-ethyl hexanol	333-373	7:1-1:7	Amberlyst-46, Amberlyst-70, Amberlyst-39 and Amberlyst-131	Komon *et al.* (2013)
Propylene glycol	333-358	1:1-4:1 1:1-1:3	Amberlyst-15	Altiokka & Odes (2009)
2-ethyl hexanol	388 K	1:3	Amberlyst-15	Chin et al. (2015)
Methanol	333	1:1	Amberlyst 15	Ströhlein *et al.* (2006)

2.4 Operating conditions of the esterification of AA with different alcohol

The operating conditions for the esterification of acrylic acid with different type of alcohols are given in the Table 2.4:1

Table 2.4:1: Different operating condition.

Reactant	Operating condition and reaction performance	Authors
2-Ethyl hexanol	1) Temperature = 338-388K 2) Molar ratio of reactant = 1:3 3) Catalyst loading = 10wt% 4) Reactor = batch system with total reflux (TR) and dean stark for continuously water removal (CWR). The best yield 70% at T=388K	(Ahmad et al., 2014; Chin et al., 2015)
n-amyl alcohol	1) Temperature = 323 to393 K 2) Molar ratio of reactant = 1:10 3) Catalyst loading = 0.26 mol H^+/L 4) Reactor = batch reactor The 50% conversion corresponding to the 85% of the equilibrium conversion of acetic acid, versus time	(Akbay & Altiokka, 2011)
Propylene glycol	1) Temperature = 353K 2) Molar ratio of reactant = 1:1 3) Catalyst loading = 5wt%	(Altiokka & Ödeş, 2009)

	4) Reactor = batch reactor The best conversion and yield is 0.45	
2-Ethylhexan-1-ol	1) Temperature = 353 to 393 K 2) Molar ratio of reactant = 1:1 3) Catalyst loading = 1-10wt% 4) Reactor = isothermal batch reactor The best conversion and yield is 71.6 %.	(Komoń et al., 2013)
N-Butanol	1) Temperature = 323 and 363K 2) Molar ratio of reactant = 3:1 3) Catalyst loading = - 4) Reactor = fixed-bed adsorptive reactor The best conversion is 38% higher than the equilibrium concentration.	(Constantino et al., 2015)
N-Butanol	1) Temperature = 338-358 K 2) Molar ratio of reactant = 1:1,1:2, and 1:3 3) Catalyst loading = 10,15 and 20 g/L 4) Reactor = Batch reactor The best conversion is 43.34%	(Sert et al., 2013)
Methanol	1) Temperature = 333-423 K 2) Molar ratio of reactant = 0.4 3) Catalyst loading = - 4) Reactor = batch chromatographic	(Strohlein et al., 2006)

	column The yielding that about 12 mol of methanol per mol of methyl acrylate are needed in order to obtain 98% conversion of acrylic acid	
Cyclohexane	1) Temperature = 373 K 2) Molar ratio of reactant = 4:1 3) Catalyst loading = 5wt% 4) Reactor = batch and distillation column reactors: The best conversion is 92 % by using Amberlyst-15 compare to p-toluene sulphonic acid (p-TSA) only 39.5% coversion	(Saha & Sharma, 1996)
Butanol	1) Temperature = 353K 2) Molar ratio of reactant = 1:1.35 3) Catalyst loading = 0.1wt% 4) Reactor = batch and flow conditions The best conversion is 93% using HPW/carbon as catalyst.	(Dupont et al., 1995)

2.5 Literature review summary

Typically esterification reactions are very slow; it requires several days to attain the equilibrium in the absence of catalyst. The heterogeneous catalyst is preferred because it can overcome the drawbacks of homogeneous catalyst and biocatalysts. Catalyst PK-208 has been chosen for present work which is for the esterification of Acrylic Acid and 2-Ethyl Hexanol in tubular reactor for the synthesis of 2-Ethylhexyl Acrylate. PK-208 is a heterogeneous catalyst which can be reused (up to 6 times) and it can be removed from mixture easily.

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 3.2:1 along with their respective uses and purity. All these chemicals were used without further purification.

Table 3.2:1: List of chemicals

Chemical/Reagent	Assay	Function
2-Ethyl Hexanol (2EH)	99.99%	As a reactant
Acrylic acid (AA)	99.9%	As a reactant and as standard for GC analaysis
n-Hexane	99.99%	As a solvent for GC analysis
2-ethyl hexyl acrylate (2EHA)	99.99%	As a standard for GC analysis
Nitrogen	99.99%	As a makeup gas for GC analysis
Compressed air	99.99%	To initiate flame
Hydrogen	99.99%	As an inert gas for GC analysis
Helium	99.99%	As a mobile phase and carrier gas for GC analysis
Hydroquinone monomethyl ether (MEHQ)	99.99%	As an inhibitor

The strong acidic ion-exchange resin, PK-208 was used as a catalyst without further purification. The properties of PK-208 are shown in Table 3.2:2.

Table 3.2:2: Properties of PK-208

Characteristic	Units	Form/Value
Mean Particle Size	μm	650
Particle Density	g/mL	1.18
Water Content	%	58 - 68
Particle Size Distribution on 1180 μm	%	5 max.
Particle Size Distribution thr. 300 μm	%	1 max.
Effective Size	mm	0.40 min.
Uniformity Coefficient	-	1.6 max
Maximum Operating Temperature	℃	120
Operating pH Range	-	0 - 14
Minimum Bed Depth	mm	800
Service Flow Rate	m/h	10 - 60

Source: Products of Mitsubishi Kasei Co.

3.3 Apparatus and Equipment

3.3.1 Esterification Reaction Studies

The esterification reaction was carried out in a tubular reactor. Figure 3.3.1 shows the experimental setup and Table 3.3.1 shows the function of each part in the set up. The setup comprises of reactor, heating oil storage tank, heat exchanger and centrifugal pump.

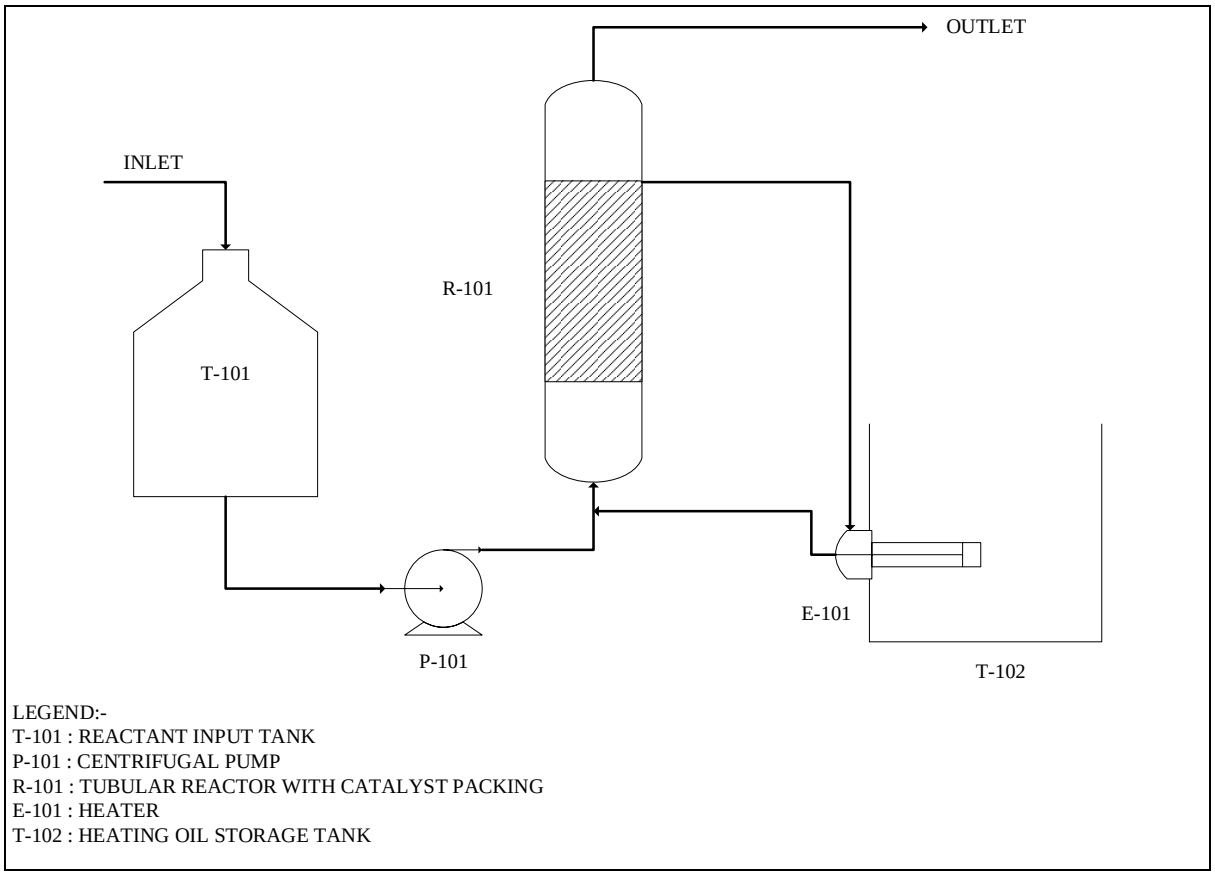


Figure 3.3:1: The experimental setup for esterification reaction studies

Table 3.3:1: List of main components in the experiment setup for the esterification reaction studies.

Component	**Description**
Heat exchanger (E-101)	It is a coil immersed in oil bath for heating up the inlet stream of the reactor.
Reactor (R-101)	As tubular reactor. The length of the reactor is 10 inch and the diameter of the reactor in 0.5 inch. Sample is withdrawn at the outlet of the reactor.
Centrifugal pump (P-101)	It is used to pump the reactant to the reactor system.
Reactant tank (T-101)	A stainless steel tank that is used to store the reactant.
Catalyst packing section (R-101)	The reactor contains catalyst packing section which is used to load the catalyst (PK-208)
Heating oil storage tank (T-102)	Storage of heating oil which is used to heat up the inlet stream of the reactor.

3.4 Experimental Studies

3.4.1 Esterification Reaction Studies

The experiment is carried out in a tubular reactor. The setup comprises a reactant tank which is made of stainless steel. The reactant tank is 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 is used to pump the reactants to the reactor system. The reactants flow at constant flow rate which is 15.7 rpm. Then, the product is 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.

3.4.2 Studies on the Effect of important Operating Variables

The parameters which are included in the investigation are the temperature, catalyst loading, and initial molar ratio of acid to alcohol as shown in Table 3.4:1. 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 3.4:1: Important operating parameter and its' range

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

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 0.25µm, 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°C at 10 K/min for 17 minutes. The carrier gas, helium flowed at a flow rate of 36.8 cm^3/s (Agilent, 2012). Figure 3.5:1 shows one of the chromatograms for acrylates analysis.

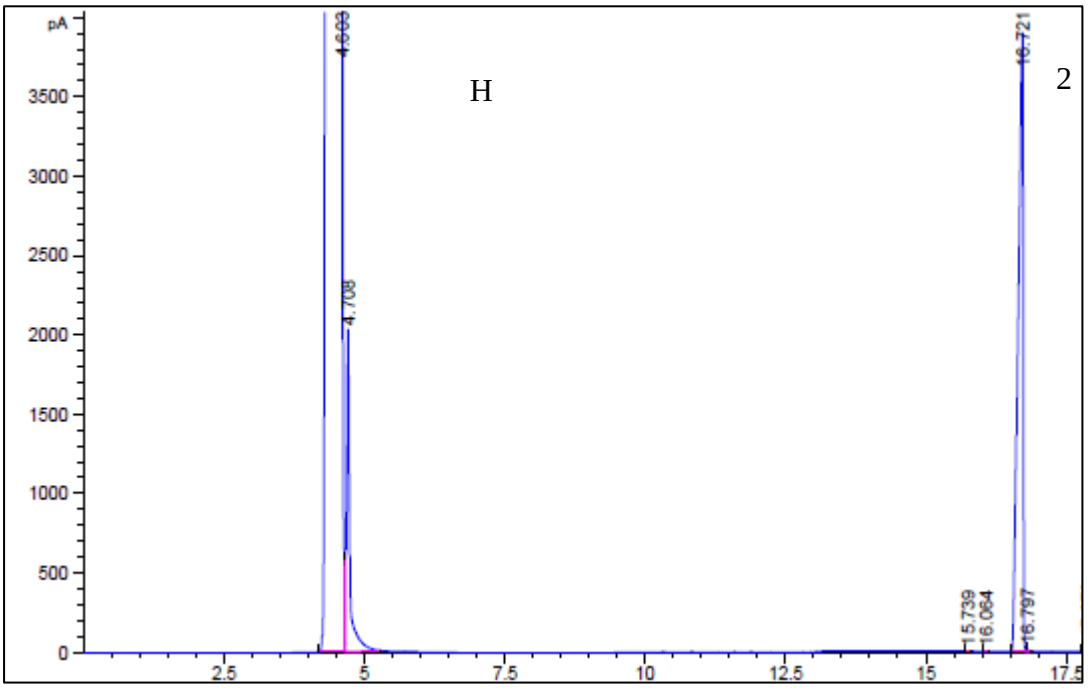


Figure 3.5:1: Chromatogram of 2EHA standard obtained from the GC analysis

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:

$$yield\ (\%) \ = \ \frac{C_{2EHA}}{C_{AA0}} \ \times \ 100\% \tag{3.1}$$

$$conversion\ (\%) \ = \ \frac{C_{AA0} - \ C_{AA}}{C_{AA0}} \ \times \ 100\% \tag{3.2}$$

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 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 (Ju *et al.*, 2010).

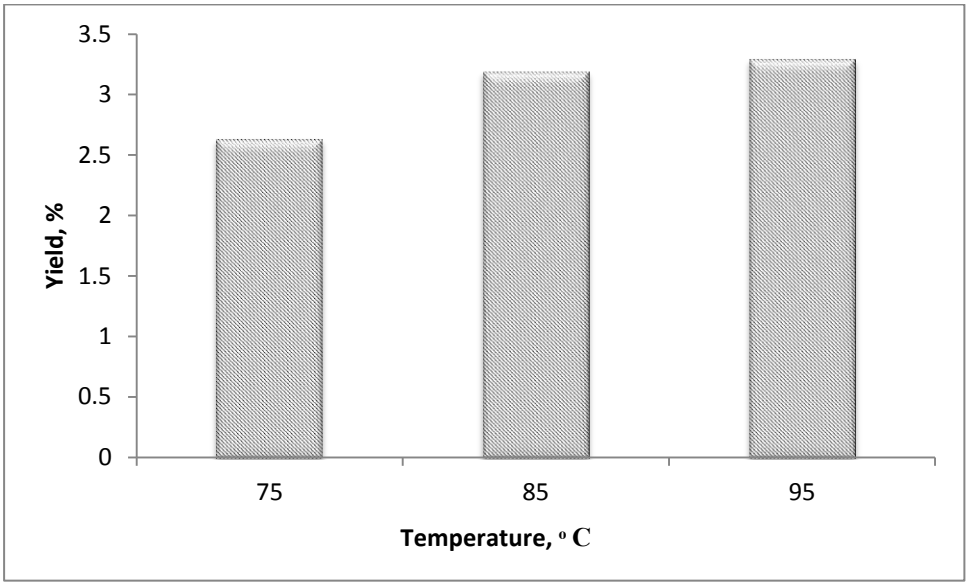
4.1.1 Effect of Temperature

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 4.1:1 (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.

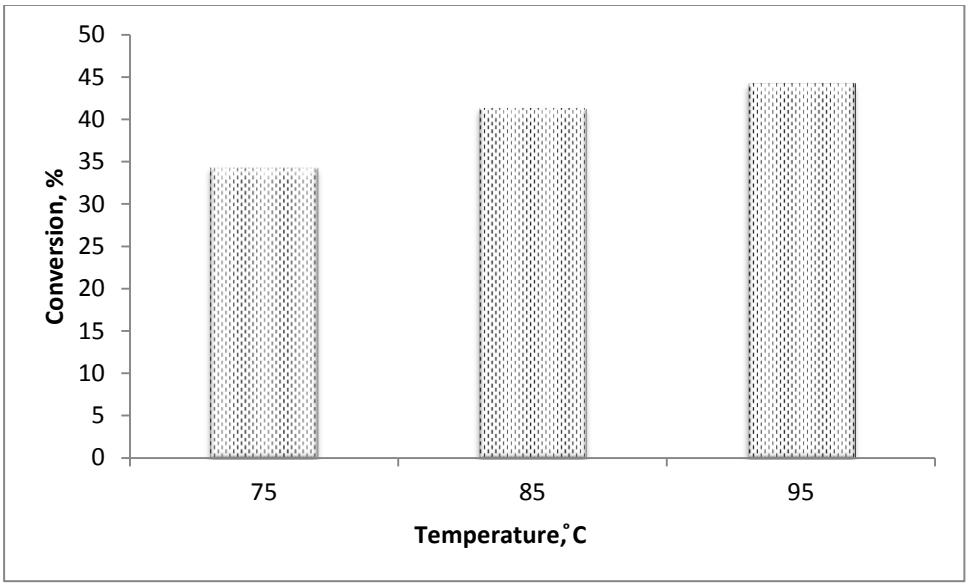
At the temperature increase, the conversion also increases. This is because increasing the reaction temperature would increase the kinetic energy of the reactant molecules and hence more of the reactant molecules would obtain the minimum amount of energy required to form products. The temperature rise 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.



(a)



(b)

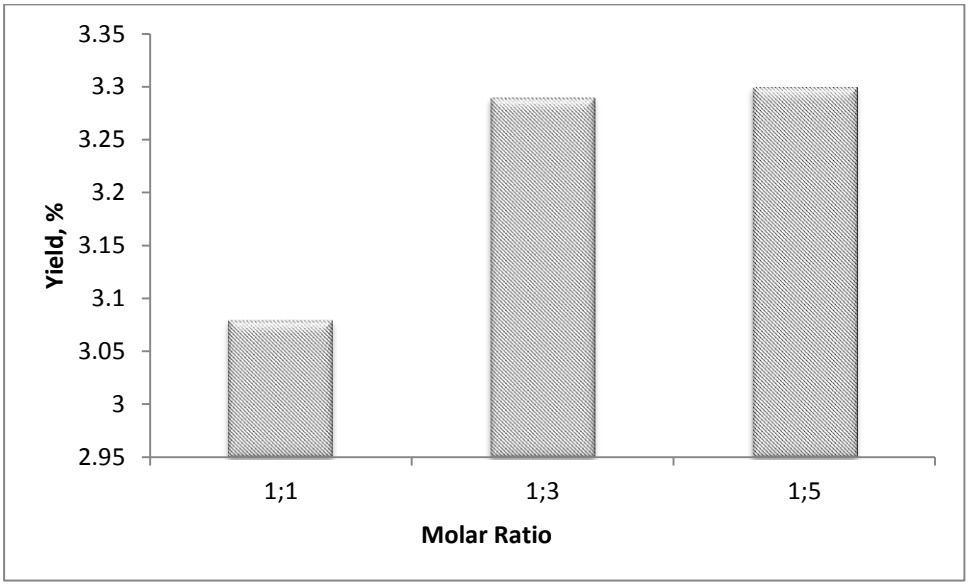
Figure 4.1:1: (a) Yield of 2EHA and (b) Conversion of AA for the reaction carried out at different temperatures. Reaction conditions: volume flow rate of 3 ml/min $M_{AA:2EH}$ of 1:3 and catalyst weight of 5g.

4.1.2 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 4.1:2 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 15.7 rpm.

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.

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.



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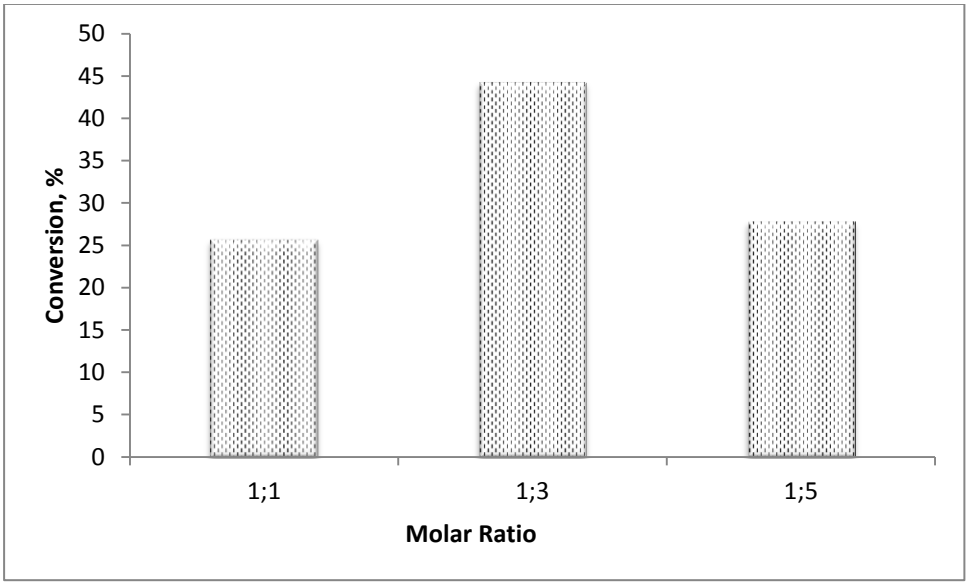
(a)



(b)

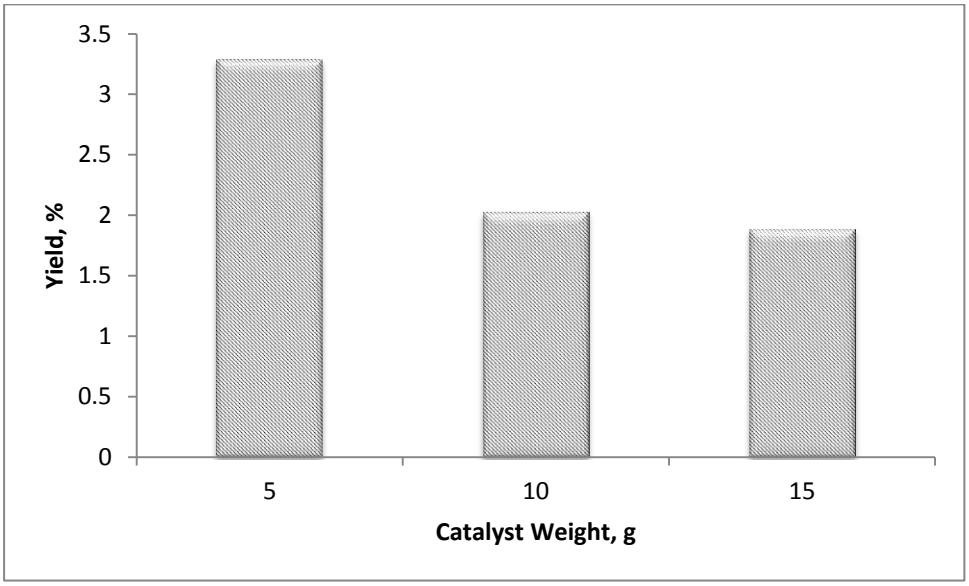
Figure 4.1:2: (a) Yield of 2EHA and (b) Conversion of AA for the reaction carried out at different molar ratio. Reaction conditions: volume flow rate of 3ml/min temperature of 95^{o}C and catalyst weight of 5g.

4.1.3 Effect of Initial catalyst loading

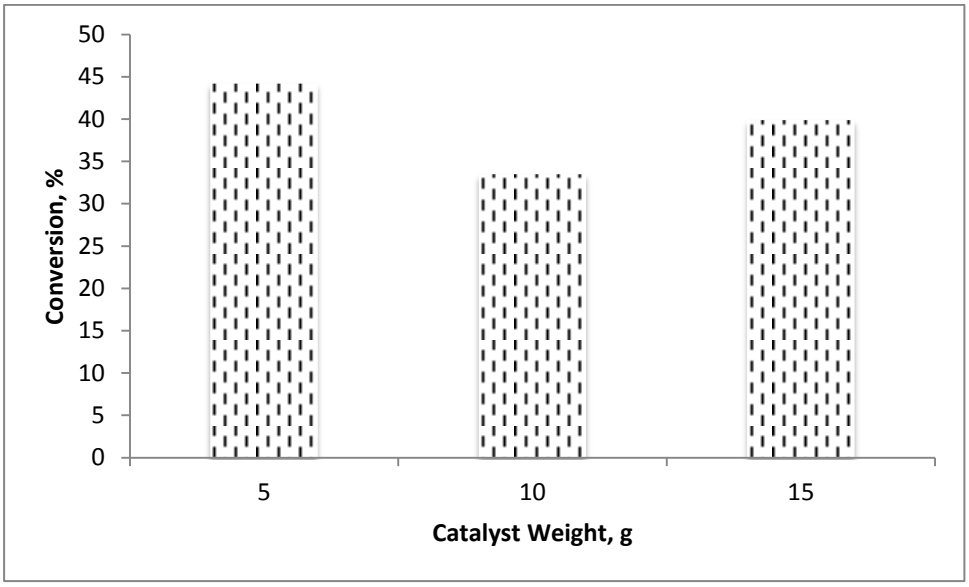
The effect of the amount of catalyst on the 2EHA yield was studied by varying the catalyst loading from 5-15g and keeping all other reaction parameters identical. Each reaction was carried out for 5 hours to obtain steady state. Based on the results illustrated in Figure 4.1:3, the increase in product 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 (Carsten Sievers, 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 4.1:3: (a) Yield of 2EHA and (b) Conversion of AA for the reaction carried out at different catalyst weight. Reaction conditions: volume flow rate of 3 ml/min, temperature of 95^{o}C and $M_{AA:2EH}$ of 1:3.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The PK-208 catalysed esterification of AA with 2EH at the temperature ranged from 75^{o}C to 95^{o}C, 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 95^{o}C, initial molar ratio of AA:2EH of 1:3 and catalyst loading of 5 g. The yield is relatively low because the AA may be adsorbed by the resin and increase the loss of AA.

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.

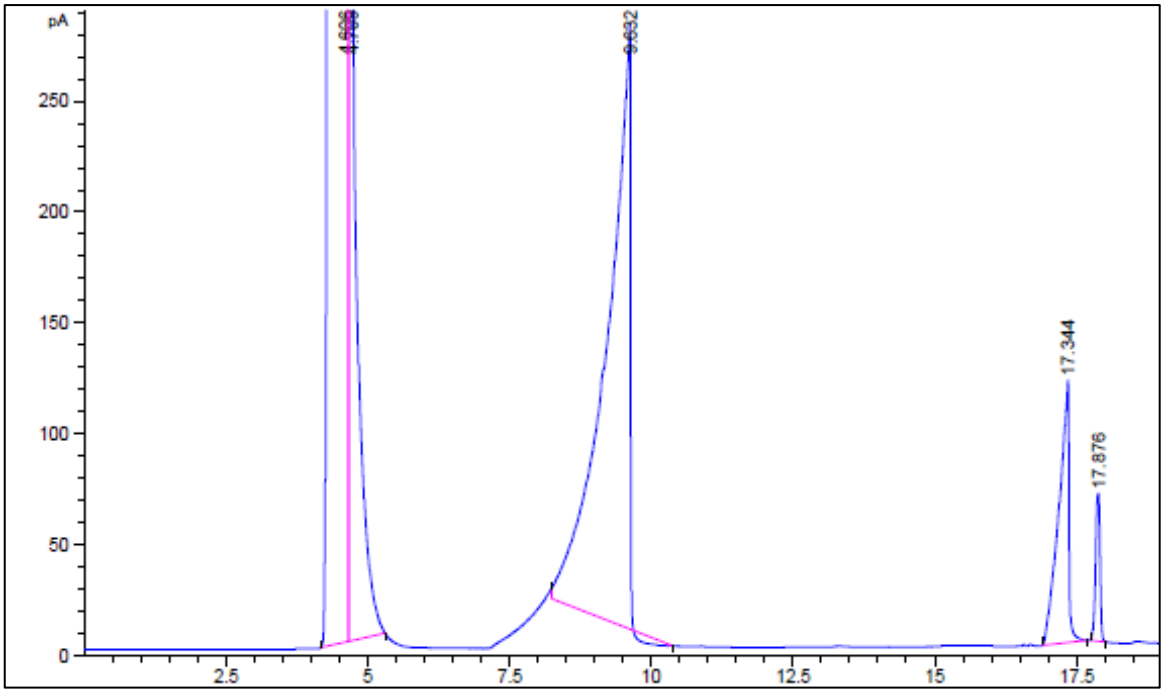

Figure A1: GC-FID spectrometry of 21019.9 ppm AA

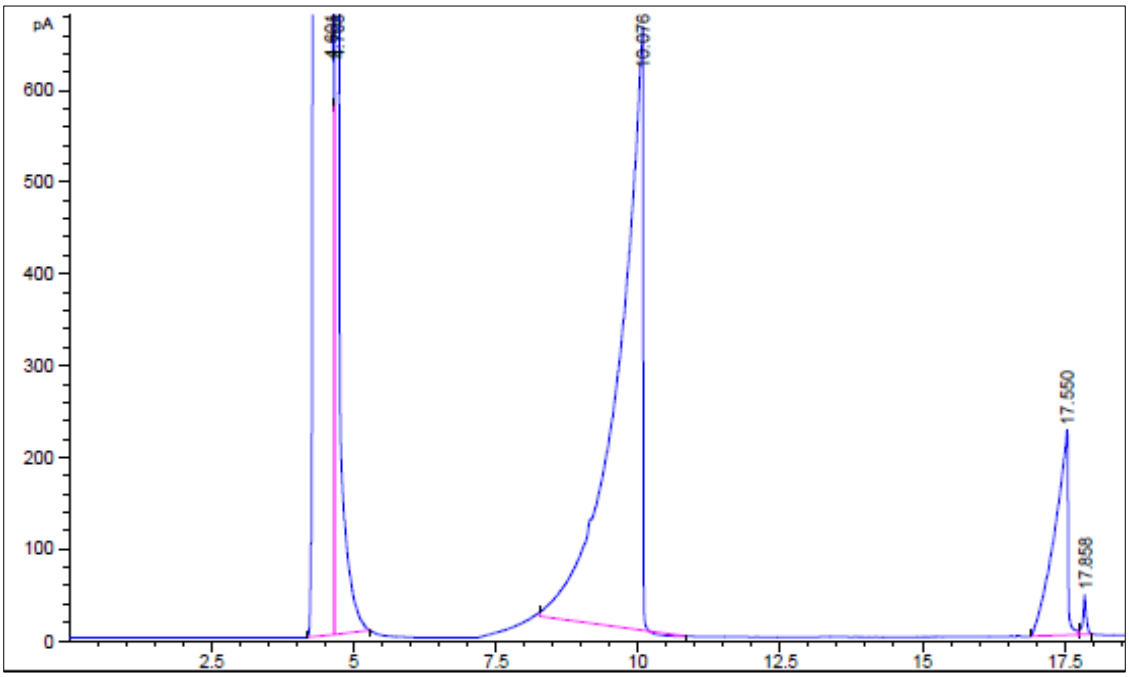

Figure A2: GC-FID spectrometry of 42039.8ppm AA

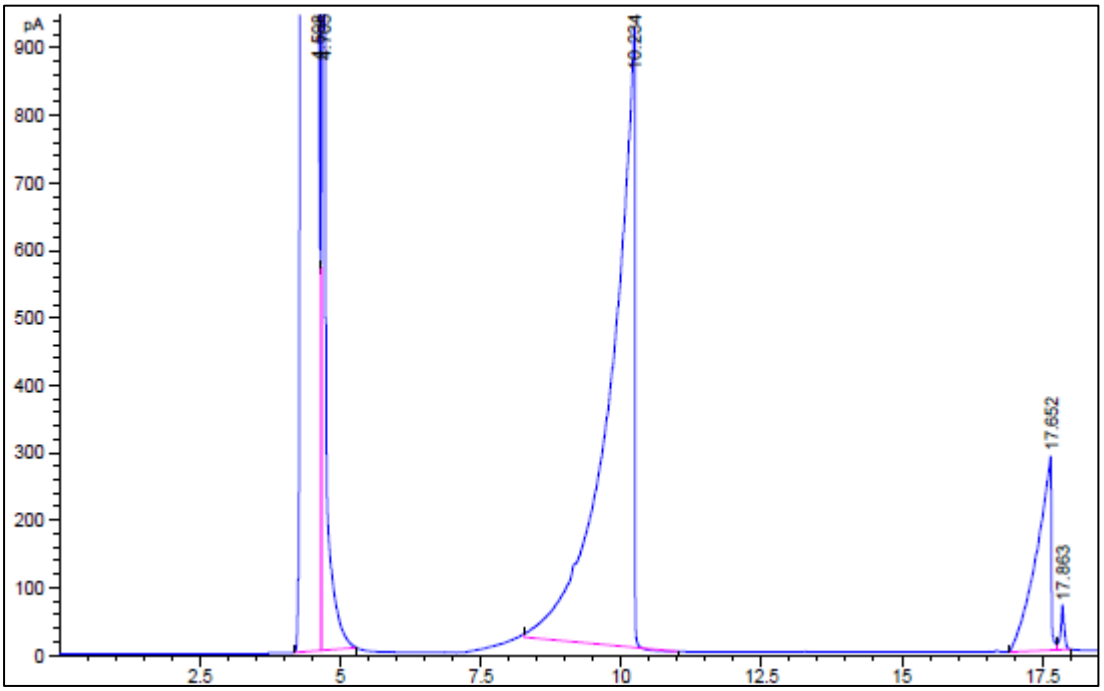

Figure A3 : GC-FID spectrometry of 63059.7 ppm AA

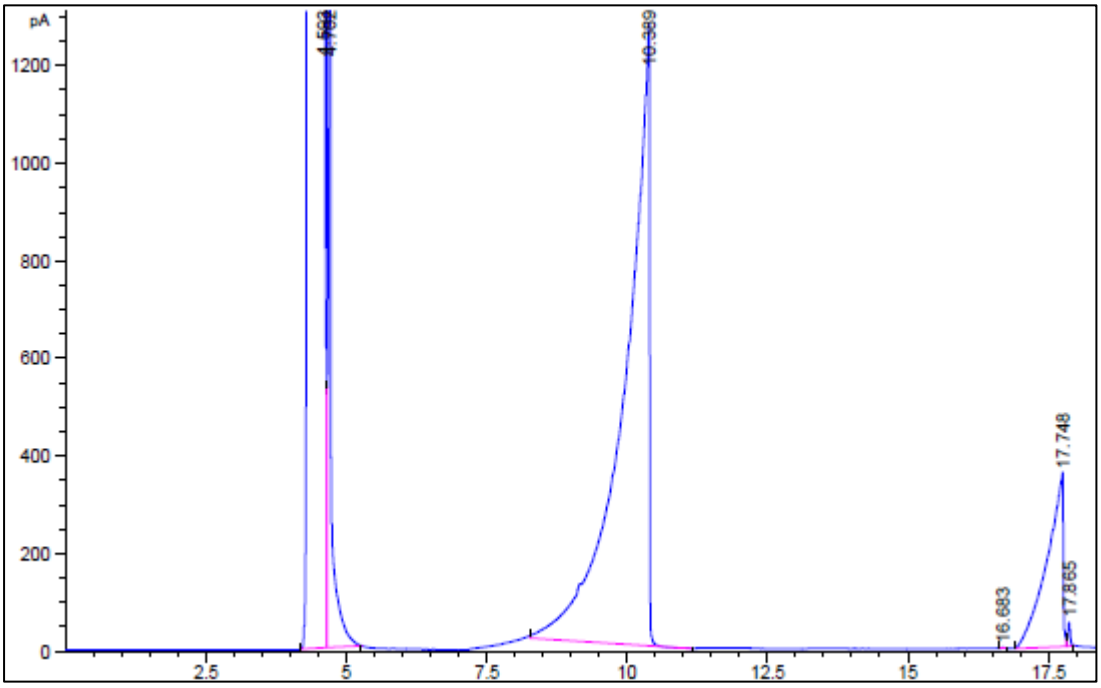

Figure A4 : GC-FID spectrometry of 84079.6 ppm AA

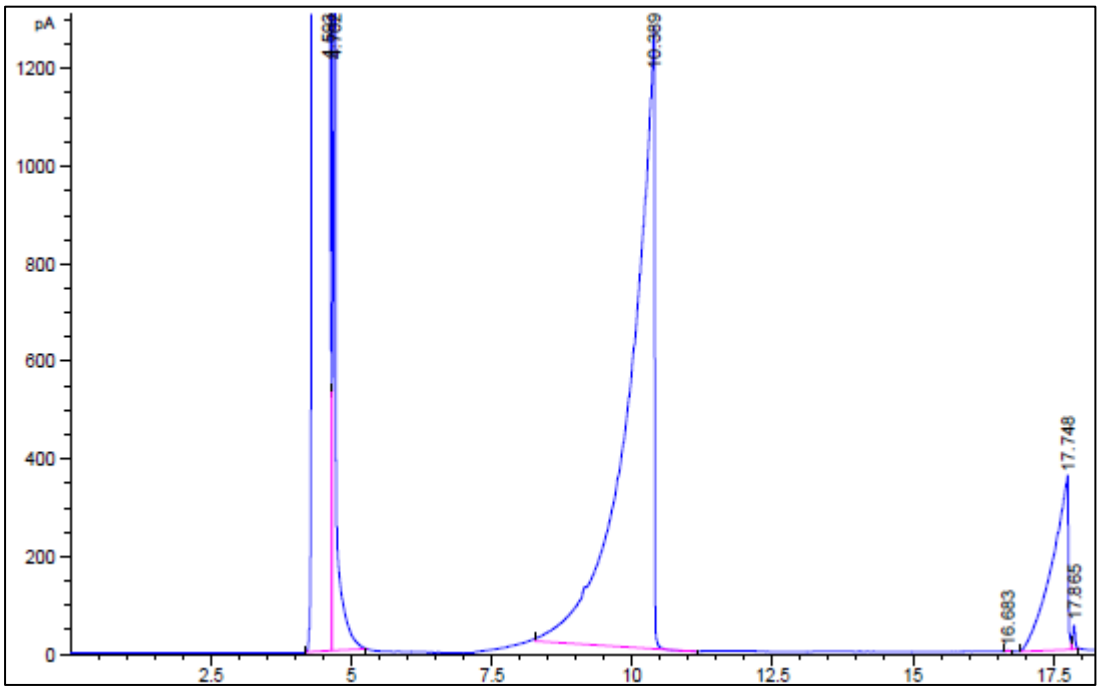

Figure A5 : GC-FID spectrometry of 51,146.19 ppm AA

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

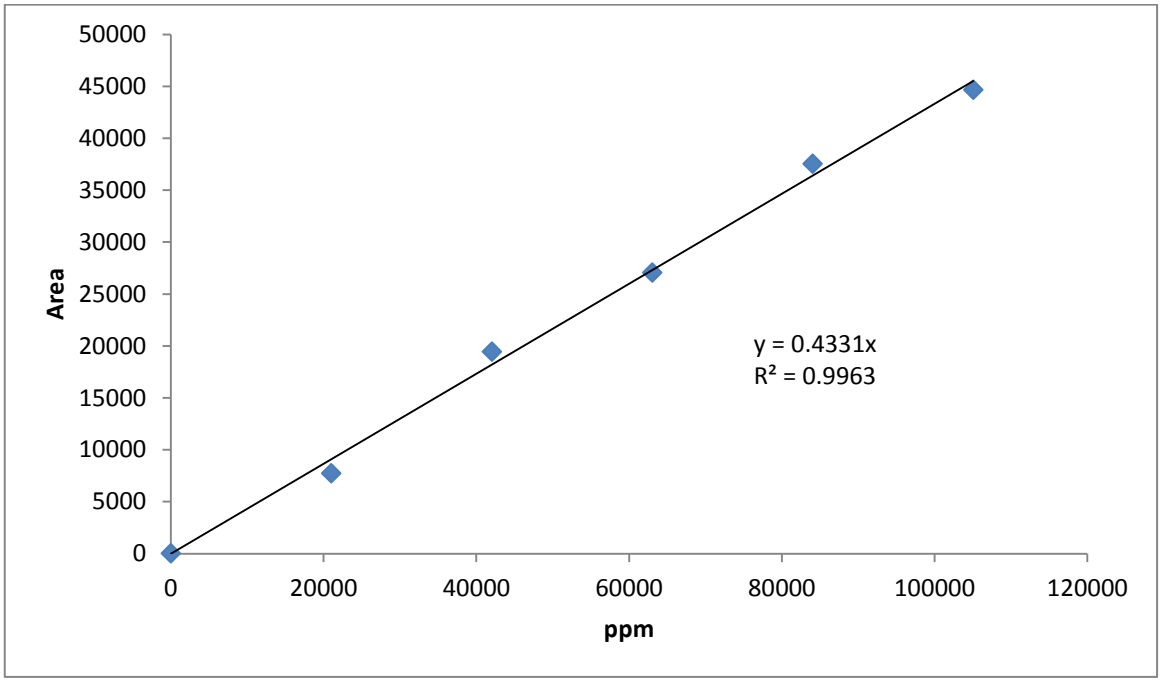

Figure A6: Calibration curve for AA using GC-FID

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:

$$ABS_{AA} = m\ x\ C_{AA} \quad \text{(A1)}$$

$$C_{AA} = \frac{ABS_{AA}}{m} \quad \text{(A2)}$$

$$C_{AA} = \frac{ABS_{AA}}{0.4331} \quad \text{(A3)}$$

$$C_{AA} = 2.3089\ x\ ABS_{AA} \quad \text{(A4)}$$

APPENDIX B

STANDARD CALIBRATION CURVE OF 2 ETHYL HEXYL ACRYLATE

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

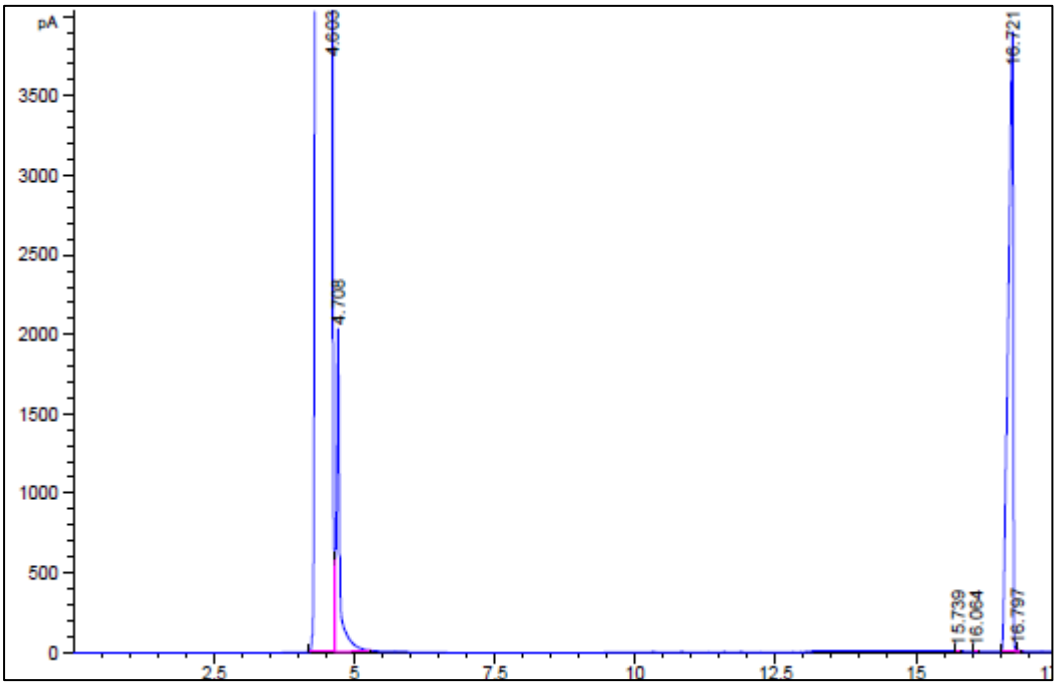

Figure B1 : GC-FID spectrometry of 3461.04 ppm 2EHA

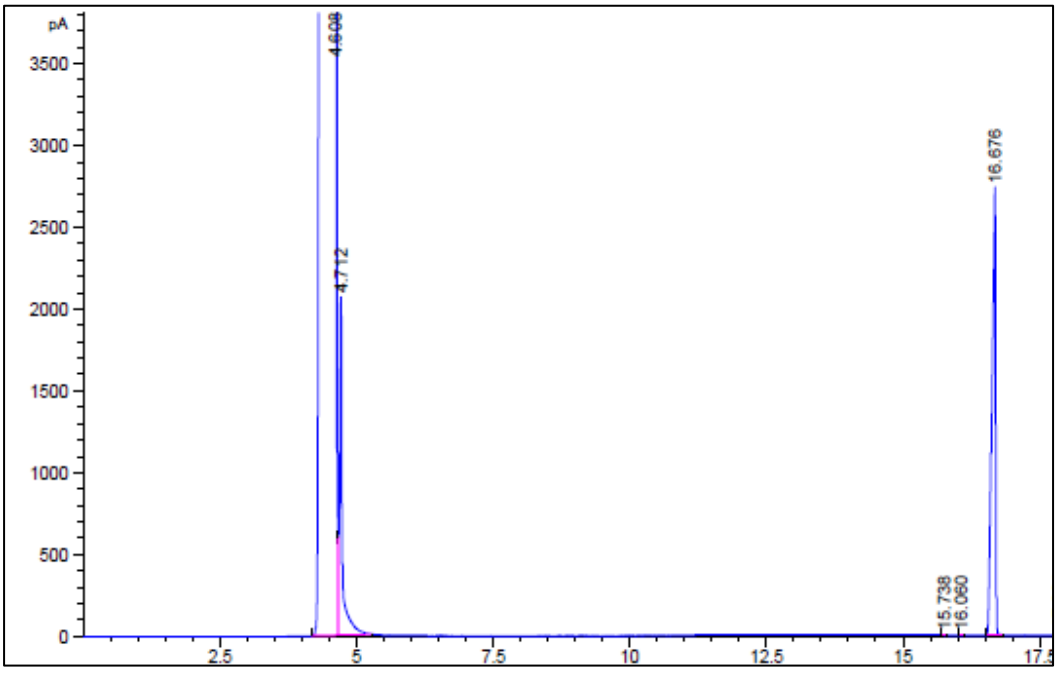

Figure B2 : GC-FID spectrometry of 6921.36 ppm 2EHA

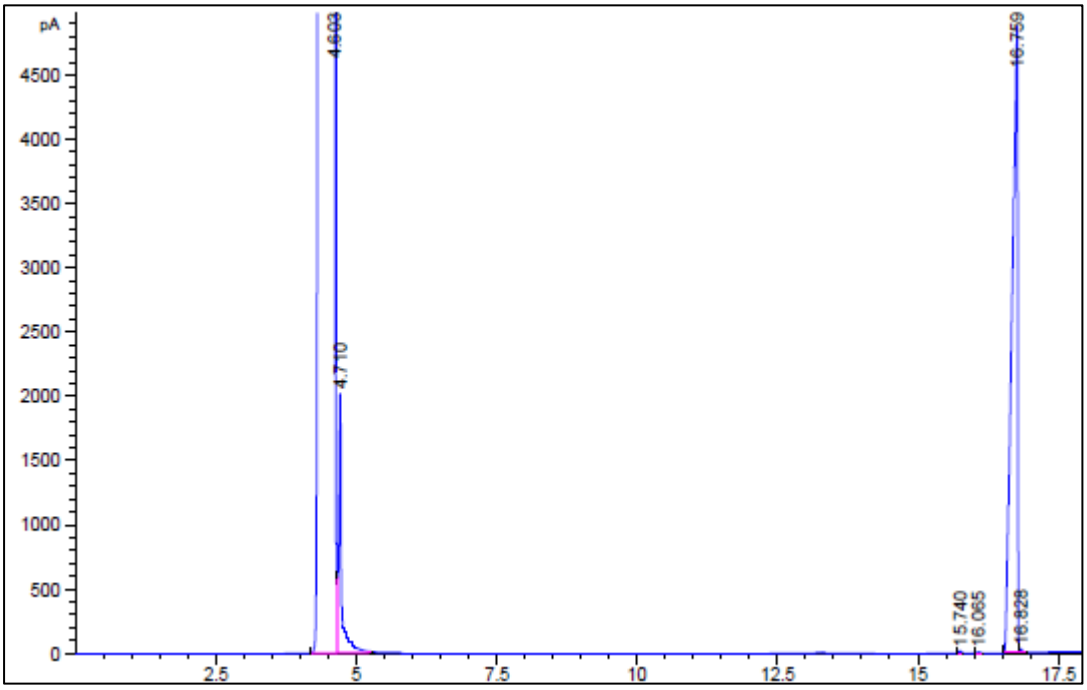

Figure B3 : GC-FID spectrometry of 10382.40 ppm 2EHA

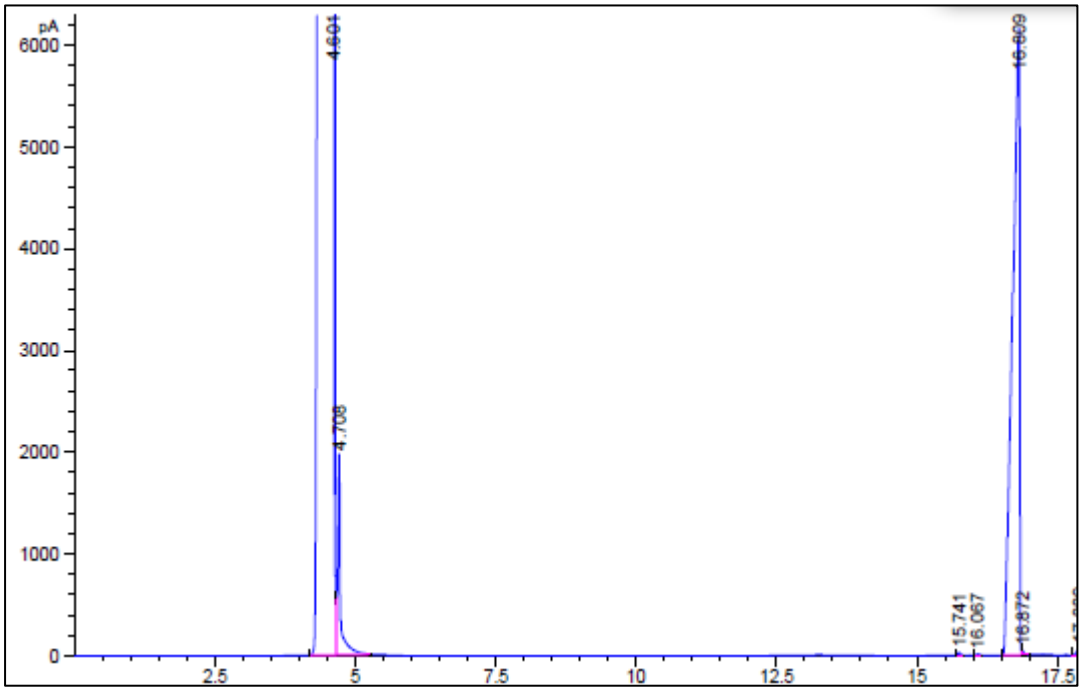

Figure B4 : GC-FID spectrometry of 13842.73 ppm 2EHA

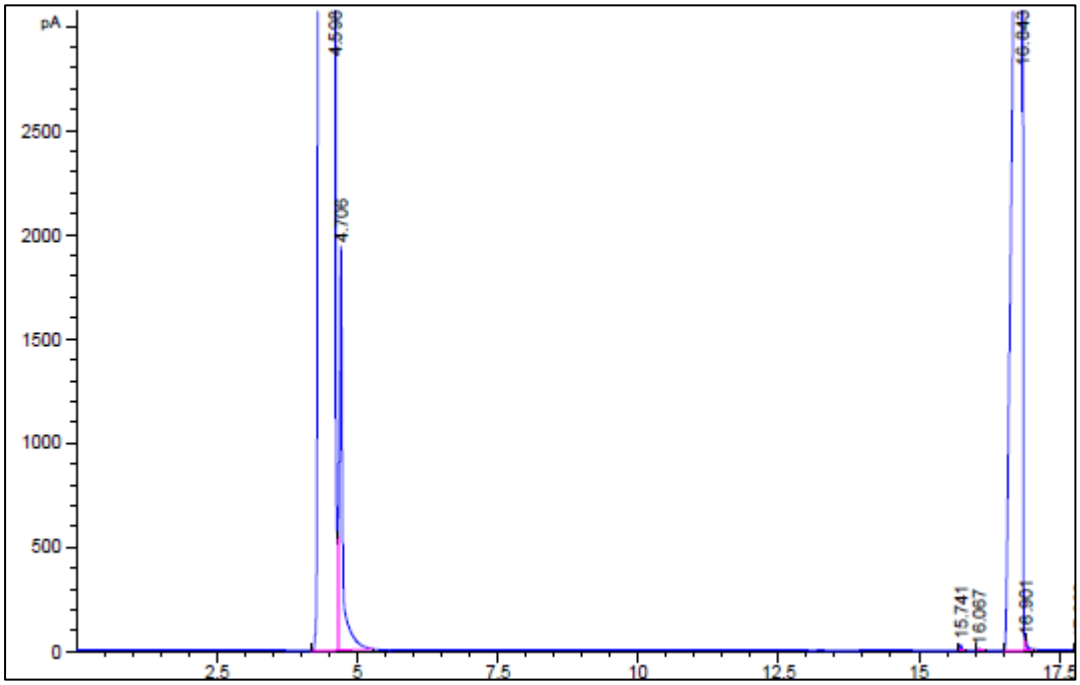

Figure B5 : GC-FID spectrometry of 17303.77 ppm 2EHA

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

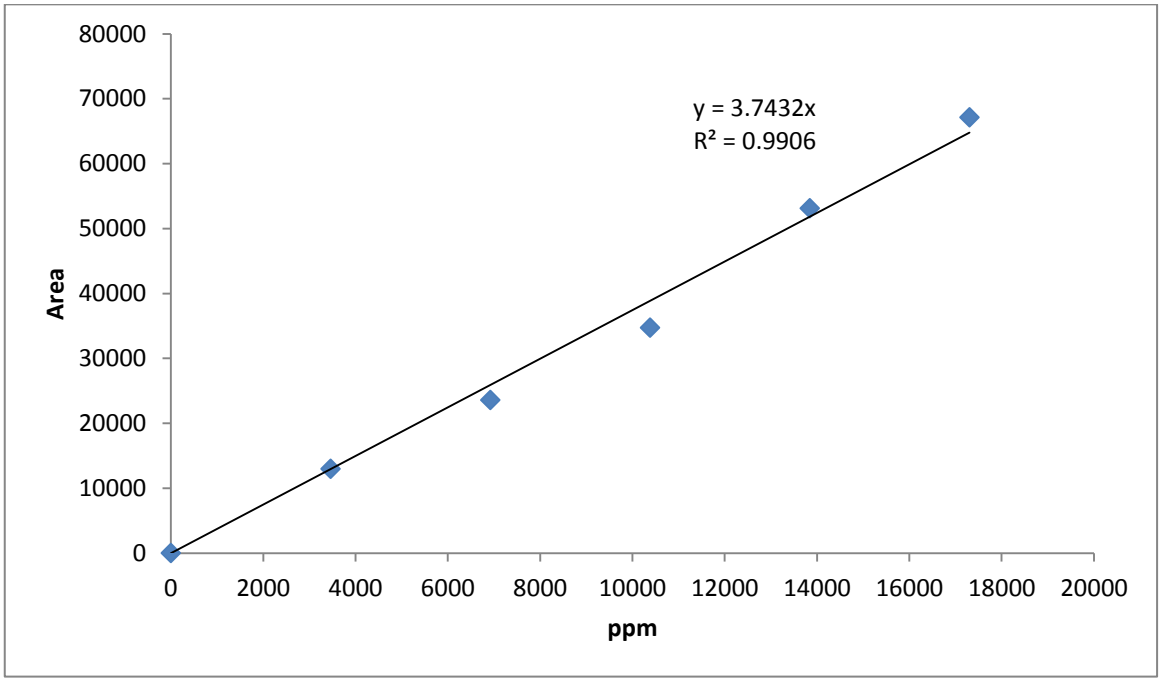

Figure B6: Calibration curve for 2EHA using GC-FID

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:

$$ABS_{2EHA} = m\ x\ C_{2EHA} \quad \text{(B1)}$$

$$C_{2EHA} = \frac{ABS_{2EHA}}{m} \quad \text{(B2)}$$

$$C_{2EHA} = \frac{ABS_{2EHA}}{3.7432} \quad \text{(B3)}$$

$$C_{2EHA} = 0.2672\ x\ ABS_{2EHA} \quad \text{(B4)}$$

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%