ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL OVER SULFATED FERUM PROMOTED ZIRCONIA

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SUPERVISOR’S DECLARATION

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

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I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ABSTRACT

Acrylate polymer belongs to a group of polymers which could be generally referred as plastics. 2-ethyl hexyl acrylate, in which when it is polymerized, it becomes an ingredient in paints, coatings, textiles, adhesives, plastics and many other applications. Homogeneous acid commonly used as reaction catalysts are toxic, corrosive and difficult to be removed from the reaction medium while solid catalysts are easier to be removed and recycled from the reaction products. This will make the reaction process longer and reduce the waste production which gives environment and economic value to nature and industry respectively. The research objective is to determine the effectiveness of heterogeneous catalyst, sulfated ferum promoted zirconia (ZFS) in catalyzing esterification of acrylic acid with 2-ethyl hexanol to produce 2- ethyl hexyl acrylate (2EHA). The research needs to determine the maximum reaction condition for 2EHA esterification reaction and catalyst characterization using XRD, TGA and FTIR. Sulfated Ferum Promoted Zirconia shows the presence of tetragonal phase shape from XRD analysis which is a crystal shape and proved that the catalyst produces is ZFS. Thermal stability studies using TPD shows that the catalyst is stable to catalyze the reaction up until 570°C with total decomposition of 11.89 % (1.081mg). FTIR analysis show the presence of component of S=O region which is known as pyrosulfates group and OH group where the reaction conversion depends on the presence of these group. From the reaction analysis, the best reaction condition for esterification of 2-Ethyl Hexyl Acrylate using Sulfated Ferum Promoted Zirconia catalyst is 90ºC for 8 hours with 1:3 acrylic acids to 2 ethyl hexanol molar ratio using 1.5wt% catalyst loading. The reaction conversion from this reaction condition is 77.22%.

ABSTRAK

Polimer acrylate adalah sebahagian dari kumpulam polimer yang kebiasaaanya dirujuk sebagai plastik. 2 ethyl hexyl acrylate (2EHA) apabila dibentuk kepada bentuk polimer, menjadi bahan utama dalam pembuatan cat, lapisan pelindung, bahan tekstil, bahan kimia pelekat dan plastik. Asid homogenus yang biasa digunakan dalam pemangkin industri sangat toksik dan mengakis malah sukar dipisahkan dari bahan reaksi tindak balas semasa proses, juga sukar untuk digunakan semula. Ini menyebabkan kesan terhadap alam sekitar dan memanjangkan masa proses penghasilan sesuatu produk dalam industri, malah menyebabkan kerugian dari segi ekonomi dan penghasilan hasil buangan yang berbahaya. Objektif penyelidikan ini adalah bertujuan untuk mencari titik optimum keadaan tindakbalas untuk menghasilkan ester 2EHA seperti suhu,masa tindak balas, peratus berat pemangkin dan nisbah molar serta menganalisa karekter pemangkin menggunakan analisa analitikal seperti *X-Ray Diffraction* (XRD), *Thermogravimetry Analysis* (TGA) dan *Fourier Transform Infrared* (FTIR). Keputusan analisa mendapati, pemangkin yang dihasilkan adalah dalam keadaan kristal dan mempunyai fasa tetragonal yang mana membuktikan pemnagkin yang dihasilkan ialah Sulfated Ferum Promoted Zirconia (ZFS) seperti yang dirujuk di kenyataan literatur. Kestabilan therma dapat dilihat dan keputusan menunjukkan pemangkin dapat bertindak denagn stabil sehingga suhu mencecah 570°C dengan kehilangan peratusan sebanyak 11.89% (1.081mg). Ujian FTIR menunjukkan kehadiran kumpulan *polysulfates* S=O dan OH yang mana kumpulan ini berperanan dalam memangkinkan tindak balas kimia. Hasil dari ujian pengesteran, kondisi terbaik untuk menjalankan esterifikasi dari kajian ini ialah pada suhu 90°C selama 8 jam, 1:3 nisbah asid kepada alcohol dan 1.5% berat pemangkin digunakan. Kadar peratusan penghasilan ester dari kondisi terbaik itu ialah 77.22 %.

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LIST OF SYMBOLS

%	percentage
T_m	melting temperature
rpm	rotation per minute
μL	Micro litre
g	gram
mL	millilitre
˚C	degree celcius
Ppm	part per million

LIST OF ABBREVIATIONS

2EHA	2-Ethyl Hexyl Acrylate
ZFS	Sulfated Ferum Promoted Zirconia
FTIR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatoghraphy
TGA	Thermogravimetry Analysis
TFA	Trifluoroacetic Acid
WZ	Tungsted Zirconia
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the decade, polymer remains in production industry due to extraordinary range of properties of polymeric materials. This role ranges from natural biopolymers to familiar synthetic plastics and elastomers. Polymer plays an essential and ubiquitous role in everyday life. Wide applications of the polymer make the polymer still relevant with the world demand, which initiates the development and improvement of polymer. Acrylate polymer belongs to a group of polymers which could be generally referred as plastics. Acrylate ester monomer is commonly used in the production of copolymer and homopolymer.

Ester are widely used in industry such as polymer production and derived from reaction of an oxoacid with a hydroxyl compound such as an alcohol or phenol. Low molecular weight of ester is commonly used as fragrances. Ester chemical formulas typically written in the format of RCO_2R' where R and R' are the organic parts of the carboxylic acid and alcohol respectively.

Acrylic acid has served for more than 30 years as an essential component in the production of some of most commonly used industrial and consumer products, where two-thirds of the acrylic acid manufactured in the United State is used to produce acrylic ester such as methyl acrylate, butyl acrylate, ethyl acrylate and 2-ethyl hexyl acrylate, in which when it is polymerized, it becomes an ingredient in paints, coatings, textiles, adhesives, plastics and many other applications (Gerlinde*et al*., 2007). 2-Ethyl Hexyl Acrylate is one of the acrylate produced through the reaction of acrylic acid with 2- Ethylhexanol and is a highly demand acrylate by industry due to multiple uses in polymer production.

In several applications, for example pressure-sensitive adhesives, Poly (2-Ethyl Hexyl Acrylate) (P2EHA) is used, because of its low T_g value of 50ºC, good oil resistance and adhesion to various substrates. Moreover, it is polar compared to elastomers based on hydrocarbons (Kris *et al*., 2006). T_g is glass transition temperature that is a transition of liquid to solid like state may occur with either cooling or compression and always lower than the melting temperature, T_m. Other example of 2-Ethyl Hexyl Acrylate are pharmacological product, industrial coatings, agricultural coatings, graphic paper, acrylic fibers for floor covering and clothing, flocculants, dispersants, anti-scalants and acrylates binder.

1.2 Problem Statement

A conventional production of ester usually uses strong basic or acidic solution such as NaOH, KOH and H_2SO_4 as catalyst. These are homogeneous catalysts. The homogeneous catalysts widely are used in industry for decades, are strong mineral acid or basic and the reaction proceeds in liquid phase at moderate temperature and at moderate pressure.

However, these homogeneous acid catalysts are toxic and corrosive. Moreover, they are difficult to be removed from the reaction medium. The challenge is actually to replace them by other acid catalysts due to these considerations and pollution problems, and solid catalysts are easier to be removed from the reaction products and to recycle (DuPont *et al.,* 1996).

To have an easier separation of the products and a more facile regeneration of used catalysts, replacement of soluble acids by solid catalysts such as acidic resins Amberlysts or acidic salts of $H_3PW_{12}O_{40}$ was a quite attractive alternative (Essayem *et al.,* 2007). Therefore, heterogeneous solid acid catalyst is more frequently used since it is easier to be handled and easy to be separated from products. Solid heterogeneous catalyst does not only reduce the overall production costs but also environmental-friendly. The implementation of environmental-friendly heterogeneous solid catalysts is preferable to eliminate the drawbacks being associated with homogeneous catalysts such as corrosiveness, production of waste and energy intensive separation operations.

The shortcoming in the production of 2-ethyl hexyl acrylate is the use of homogeneous catalyst; sulphuric acid which is commonly used in industry is toxic, corrosive and difficult to be removed from the reaction medium. In this study, heterogeneous solid acid catalyst; sulphated zirconia are used to convert the raw material into 2-ethl hexyl acrylate (2EHA). The raw materials used are Acrylic Acid and 2- Ethylhexanol. The sulfated zirconia with promoted ferum is used in this study based on the previous study which mentioned that this catalyst can be avoided from the fast deactivation of catalyst.

1.3 Statement Of Objective

The objective that needs to be achieved in this research is:

- To determine the effectiveness of heterogeneous catalyst, sulfated ferum promoted zirconia (ZFS) in catalyzing esterification of acrylic acid with 2-ethyl hexanol.

1.4 Research Scopes

A scope is proposed for this study in order to achieve the objective. The scope of research is listed as below:

- To study the effect of catalyst loading, molar ratio, reaction temperature and reaction time for sulfated ferum promoted zirconia (ZFS) in esterification of acrylic acid with 2-ethylhexanol.
- To study the sulfated ferum promoted zirconia thermal stability.
- To determine the catalyst produced is sulfated ferum promoted zirconia (ZFS) by using XRD that use in esterification of acrylic acid with 2-ethylhexanol.
- To determine the active group by using FTIR analysis.

1.5 Rational and Significant of Study

The advantages of 2- Ethylhexyl Acrylate polymer are its flexibility, weather ability, adhesion, internal plasticization, resistance to abrasion and oils or greases and range of hardness.

To fulfil the demand of 2-Ethylhexyl Acrylate, this ester must be able to be produced in high quantity with high quality at a short range of time but at a low cost as possible and apply the awareness of environment pollution. As explained, production of 2-Ethylhexyl Acrylate will commonly use sulphuric acid as catalyst in esterification process, but it is toxic, corrosive and hard to be removed from the reaction medium. Then, sulphated ferum promoted zirconia is introduced for this esterification process as heterogeneous catalyst to improve the production performance. Solid catalyst is easier to be removed from the reaction products and to be recycled. Fe is introduced as promoter to sulfated zirconia and the research has shown that improvement in its resistance to deactivation.

Heterogeneous catalysis affects the environment by increasing the efficiency of industrial processes. Heterogeneous catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated, as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. Heterogeneous solid catalysts are preferable to eliminate the drawbacks being associated with homogeneous catalysts such as corrosiveness. Besides, separation of the catalyst from the reaction product will reduce the total production time and this will give huge impact in the economic value to the industry due to the increasing of the 2EHA annually production amount.

According to Laura et al., (2009), Sulfated Zirconia can be recycled several times without significant loss of activity and it is highly stable which could open the possibility for an environmental friendly catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Acrylic acid and esters are perhaps the most versatile series of monomers for providing performance characteristics to thousands of polymer formulations. Their performance characteristics which impart varying degrees of tackiness, durability, hardness and glass transition temperatures promote consumption in many end-use applications. Major markets for acrylate esters include surface coatings, textiles, paper coatings, adhesives and sealants, and plastics and many more variety of products produced from this acrylate ester polymerization make it a highly and worldwide demand. Global demand for crude acrylic acid is forecasted to grow at 4.8% annually during 2010–2015, driven by growth in superabsorbent polymers (SAPs) at 5.6% and acrylate esters at 4.3%.

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2.2 Esterification

Esterification is the chemical process for making esters, which are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. Esters can also be formed by other reactions such as reaction of an alcohol with an acid chloride (R-CO-Cl) or an anhydride (R-CO-O-COR'). Common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing the water that is formed. In this research, 2- Ethylhexyl Acrylate is produced by reaction of acrylic acid that is simplest unsaturated carboxylic acid with 2- Ethylhexanol or isoethanol, a fatty alcohol. Esterification of acrylic acids is a fundamental step in producing 2-Ethylhexyl Acrylate, an ester that is used in the production of homopolymer and copolymer. Figure 2.1 shows the reaction equation for esterification process of acrylic acid with 2-ethyl hexanol.

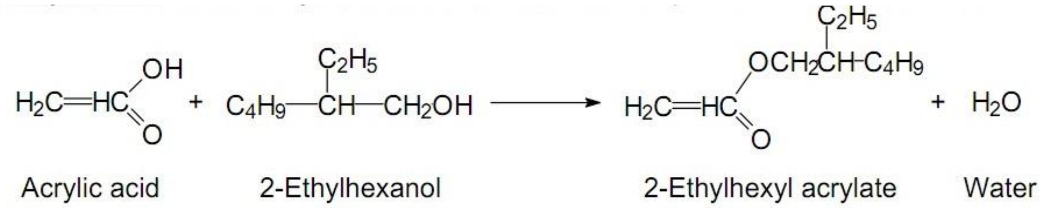


Figure 2.1 Esterification of Acrylic Acid with 2-ethyl hexanol

Early studies into the chemical mechanism of esterification, concluded that the ester product (R-CO-OR') is the union of the acyl group (R-C=O-) from the acid, RCO-OH, with the alkoxide group (R'O-) from the alcohol, R’-OH rather than other possible combinations.

Esterification of secondary alcohol is much more difficult to be achieved compared to primary alcohol. Lower nucleophilicity of oxygen atom and steric effect of these substrates hinder the formation of the corresponding ester. Slow reaction rates and reversible reaction may limit the conversion. (Bhorodwaj*et al.* 2010)

According to Kuriakose et al. (2004), in the presence of aromatic alcohol, selective esterification of bifunctional carboxylic is a useful organic synthesis reaction. The esters obtained are utilized to prepare fine chemicals used in the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, solvents, perfumes and cosmetics.

Esterification is a reversible reaction that therefore, the reactions are equilibrium reactions and needed to be driven to completion according to Le Chatelier’s principle. Esterifications are among the simplest and most often performed organic transformation. According to Kuriakose et al. (2004); esterification of acrylic acid with but-1-ene over sulfated Fe and Mn promoted zirconia, Mn and Fe did not improve the catalytic properties of sulfated zirconia as far as activity and selectivity to sec-butyl acrylate (90–95%) are concerned but strongly improved its resistance to deactivation.

2.3 Catalyst

Catalyst is used in the esterification process to enhance or accelerate chemical reaction process. Catalysts can be divided into two types, homogeneous catalysts such as such as sulphuric acids (H_2SO_4), sodium hydroxide (NaOH) and hydrochloric acids (HCl), heterogeneous catalyst such as solid acid catalysts sulfated zirconia (ZS), zeolites, alumina and resins.

There is other type of catalyst, autocatalysis that only occurs when a single chemical reaction whose reaction product is itself the catalyst for the reaction. Autocatalysis reactions' reaction velocity is much compliance to be influenced by the reaction temperature, in other words, the pressure plays a proportion role to the effect of temperature of equipment.

Reactions involving heterogeneous catalytic reaction commonly occur at the interface between the solid catalyst and the fluid or gas phase. The overall reactions can be broken down into the sequence of individual steps shown in Figure 2.2.

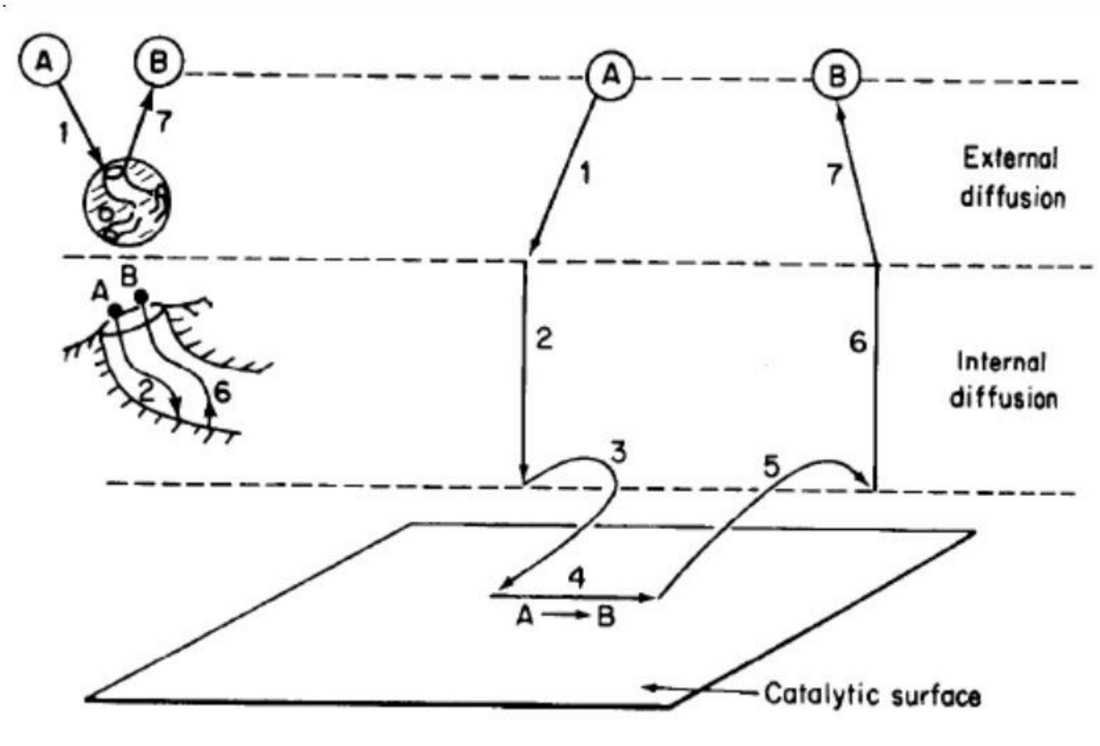


Figure 2.2 Steps in a heterogeneous catalytic reaction

The reactions are catalyzed in the steps involving external diffusion, internal diffusion, desorption and adsorption. The reactant from the bulk fluid will diffuse (mass transfer) to the surface of the catalyst. Then, the reactants will diffuse from the pore mouth, through the catalyst pores, to the immediate vicinity of internal catalytic surface. The adsorption happens to the reactant on the catalyst surface followed by reaction process. After the reaction takes place, the product will be removed from the catalyst surface in desorption process and further diffuse through the interior of the catalyst to the pore mouth at the external surface. The mass transfer of the reactant occurs from the external surface back into the bulk fluid. These processes explain about the steps in Figure 2.2.

2.3.1 Homogeneous Catalyst

Homogeneous catalysis is a chemistry term describing a catalyst which is in the same phase (solid, liquid or gas) as the reactants. According to Lotero et al (2005), currently, homogeneous catalyst is most used because it is cheaper as compared to the solid catalyst. Homogeneous catalysts can be categorized into two types which are acid catalyst and base catalyzed. Most people prefer to use homogeneous acid catalyst since it is faster (4000 times) than homogeneous base catalyst.

These are the example of acid catalyst and base catalyst:

Base catalysts:

Sodium hydroxide (NaOH), potassium hydroxide (KOH

Acid catalysts:

Sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), calcium carbonate ($CaCO_3$)

Performance comparison between various homogeneous acid catalysts such as sulfuric acid, methanesulfonic acid, phosphoric acid and trichloroacetic acid is done by Donato et al. (2007). Sulfuric acid and methanesulfonic acid have the conversion rate over 80%. Comparing sulfuric acid to the methanesulfonic acid in term of price and availability, sulfuric acid is more preferable. However, some concerns about these catalysts are they might be harmful to the environment if not treated carefully. Besides, homogeneous catalysts are hard to be separated since the product has to undergo separation process because the product and the catalyst are mix together. Although effective, the homogeneous catalysts suffer from several drawbacks, such as the existence of side reaction with reactant, corrosive nature.

Commonly, heterogeneous catalysts are more preferred than homogeneous catalyst. Heterogeneous catalyst is preferred and beneficial as the catalyst can be regenerated thus reduces the catalyst cost, utilization of lower quantity feed stocks for acrylate production, simplification of separation process thus reduces capital cost, as well as the decrease in wastewater which develops environmental friendly process.

2.3.2 Heterogeneous Catalyst

Fundamentally, heterogeneous catalysis is basically a catalyst in a different phase to the reactants. Separation of catalyst and products is easy, but the reaction is often less selective, because the catalyst material is not homogeneous.

From previous studies by KuYu *et al*., (2009), the esterification is done using ethanol and acetic acid over rare earth oxide and alumina promoted sulfated zirconia (SZ). In their findings, both surface area and pore diameter of the SZ catalysts after being promoted with rare earth oxide and alumina were significantly enhanced. Only tetragonal ZrO_2 (zirconia) crystal phase was formed for all samples. While the synthesis process of ethyl acetate by the esterification of ethanol and acetic acid occurs, the catalytic activity of the SZ catalyst could not be promoted by only doping with rare earth oxides, including La_2O_3, Ce_2O_3 and Yb_2O_3. However, double promotion with Yb_2O_3 and Al_2O_3 could greatly enhance the catalytic activity and stability of the SZ catalysts. Their work shows that changes in catalyst activity were in close correlation with variations of the amount of moderately strong and super strong Lewis acidity. The loss of sulphur species by solvation and coking during the reaction led to the catalyst deactivation. Solvation is the process of attraction and association of molecules of a solvent with molecules or ions of a solute.

Previous research about the esterification of free fatty acid, caprylic acid with ethanol is about to determine the effect of three different solid acid catalysts in esterification process. Three different solid acid catalysts that have been used are sulfated zirconia, tungstated zirconia and titania zirconia. The study shows that sulfated zirconia catalyst was found to be the most active for this reaction. However, its activity was not easily regenerated. Meanwhile, titania zirconia and tungstated zirconia have greater activity in esterification and it is easier to regenerate compared to sulfated zirconia by recalcination in air. Thus, tungstated zirconia catalyst is a most suitable catalyst in esterification process of free fatty acid (Lopez *et al*. 2008). But, there is no previous study about esterification of acrylate using sulphated zirconia.

According to Essayem *et al*. (2007), sulfated Zirconia that is used in this esterification research between acrylic acid with 2- ethyl hexanol, presents a potential interest due to its characteristics which are strong acidity, active as resins, besides, it is more selective. However, previous studies observe that sulphated zirconia deactivate rapidly, which preludes its use to replace Amberlyst resin. Study complemented with theoretical calculations allowed us to suggest that sulfated zirconia is as a very strong acid such as 100% sulfuric acid that make it able to compete with sulphuric acid which is a popular catalyst. Sulfation of other oxides such as iron oxide or alumina was also found to deeply increase their acidic strength but to a much lesser extent from the previous study. The found out that Mn particularly and Mn–Fe are active promoters not in the sense ofbetter activity but in the sense of a better resistance to poisoning and deactivation. Addition of promoters to sulphated zirconia did not increase the acid strength of the zirconia.

Previous research about Effect of Mn and Fe on the Reactivity of Sulfated Zirconia explained that, as a consequence of the foreign ions in the lattice, the unit cell size shrinks, and due to the lower valence of Mn or Fe in comparison with Zirconia, oxygen defects are generated in the bulk. The sulfate may become more reactive because of the change in support structure, or near-surface vacancies may act as a catalyst in the reduction process because they can accept negative charges. Electrons may also intermittently be localized at the more easily reducible promoter ions (Klose *et al.,* 2005). Definitely, the promoters enhance the oxidation potential of sulfate.

Table 2.1 shows the summaries from the previous studies that relate to the solid catalyst research.

Table 2.1 Summary from previous studies that relate to solid catalyst research and esterification research.

REACTION/ RESEARCH	CATALYST	FINDING	AUTHOR
Effect of Mn and Fe on the Reactivity of Sulfated Zirconia toward H2 and n-Butane	Sulfated Zirconia (SZ)	Manganese or irons do not enhance the Brønsted acid strength of SZ.Promotersthus do not improve the hydride abstraction or protonationability of the catalyst	Klose *et al* (2005)
Esterification of acrylic acid with but-1-ene	Sulfated Fe and Mn Promoted Zirconia	Mn and Fe did not improve the catalytic properties of sulfated zirconia, but strongly improved its resistance to deactivation	Essayem *et al.*, (2007)
Esterification and transesterification on tungstated zirconia	Tungstated Zirconia (WZ)	Tungstated Zirconia exhibited optimum catalytic activity after being calcined at T= 800ºC.	Lopez *et al*.,(2007)
Esterification of dodecanoic acid with 2-ethylhexanol	Sulfated Zirconia (SZ)	SZ catalyst is not deactivated by leaching of sulphate groups when trace amounts of water is present in the organic phase and easily hydrolysed in free water.	Omota *et al*., (2003)
Esterification of ethanol and acetic acid	Rare earth oxide and alumina promoted sulfated zirconia	Both surface area and pore diameter of the sulphated zirconia catalysts after promoted with rare earth oxide and alumina were significantly enhanced	KuYu*et al*., (2009)

Esterification of acrylic acid with 1-butanol	Solid Oxides:$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (I), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (II),WO_3ZrO_2,TiOSiO,$SiO_2Al_2O_3$; Organic Resin: Amberlyst 15 , Amberlite 200C,Nafion-H, Nafion-SiO2; Liquid Catalyst:$H_3PW_{12}O_{40}$,$H_4SiW_{12}O_{40}$,H_2SO_4	Amberlyst and mordenite gave lower values of the rate constant. The higher activities per unit proton of $Cs_{2.5}$ and Nafion are probably due to the superacidity. Besides acidity, the specific reaction rate may depend on the acid sites such as hydrophobicity	Chen *et al.*,(1999)
Esterification of Acrylic Acid and Methacrylic Acid with Olefin Oxides Catalyzed	Nitroxyl mono or poly-radical	Nitroxyl radical are effective and selective catalyst and also are inhibitors of polymerization of the starting materials and final product.	Radugina *et al.*, (1988)
Esterification of propanoic acid by butanol and 2-ethylhexanol	Carbon supported heteropolyacids and heteropolyacids pure	The recycling of these catalysts has shown that a deactivation occurs, due to the redissolution of the polyanion in the reaction medium.	DuPont and Lefebvre (1996)
Esterification of phthalic anhydride with 2-ethylhexanol	Sulfated zirconia and supported Heteropolyacids	The superacidicsulphated zirconia and supported HPAs were found to be efficient catalysts for the present esterification reaction	Thorat *et al.*, (1992)
Esterification of butyl hexanol with acrylic acid	Sulfated zirconia & Zirconia Phosphate	Crystallin phase catalyst have good thermal and chemical resistivity. Sulfated Zirconia	Patel et al.,(2008)

		is very good solid catalyst and it is easily deactivated by losing sulphate ions.	

CHAPTER 3

METHODOLOGY

3.1 Introduction

This research will focus on the effect of catalyst loading, reaction temperature, reaction time and molar ratio to the effectiveness of the esterification process.The experimental details such as raw material and chemical substances, apparatus and equipment used in the experiment, experimental procedure, sample preparation, thermal stability and analysis with high performance liquid chromatoghraphy (HPLC) will be explained in this chapter. Basically, the research activities include the preparation of sulphated ferum promoted zirconia using the method used in Asseyem *et al.,* (2006), followed by study about the optimum parameter for 2 - Ethylhexyl Acrylate esterification that are reaction temperature, reaction time, molar ratio and catalyst loading. The catalyst used in this study was characterized by using X Ray Diffraction (XRD) and Thermogravimetri (TGA). HPLC was used to determine the amount of unreacted acrylic acid in the esterification process. The amount of acrylic acid remained is represent the conversion rate of the ester by using sulphated ferum promoted zirconia (ZFS) catalyst.

3.1.1 General Flow of the Methodology

Flow chart below indicates the general process of esterification of acrylic acid with 2 - Ethylhexyl Acrylate over sulphatedferum promoted zirconia.

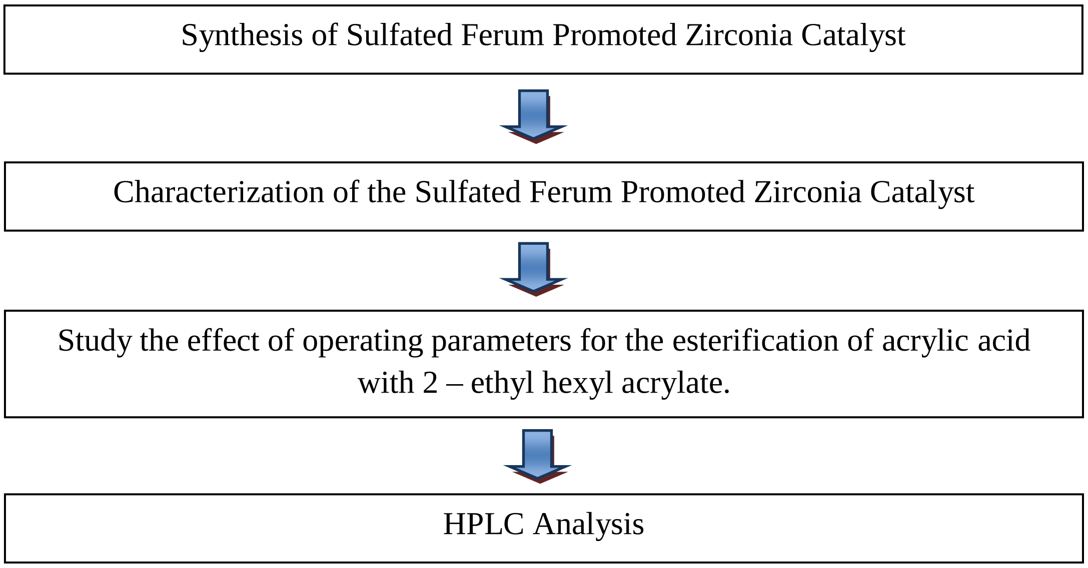


Figure 3.1 Methodology General Flow

3.2 Raw Material and Chemical Substances

Raw materials and chemical substances are shown in Table 3.1 below:

Table 3.1 List of raw materials and chemical substances.

NO	RAW MATERIAL/ CHEMICAL SUBSTANCE	FUNCTION
1	Acrylic Acid	Reactant of Process
2	2- Ethylhexanol	
3	Sulfuric Acid (100%)	Catalyst Preparation
4	Iron (III) Nitrate Nanohydrate	
5	Zirconium (IV) Hydroxide	
6	HPLC Grade Methanol	HPLC Mobile Phase
7	Trifluoroacetic Acid	
8	2- Ethylhexyl Acrylate	Product
9	Ultrapure Water	HPLC Dilution Water

3.2.1 Acrylic Acid

The estimated world capacity for crude acrylic acid was 4,676 metric kilotons (10.3 billion pounds) in 2006. Acrylic acid has served, for more than 30 years, as an essential building block in the production of some of our most commonly used industrial and consumer product. Acrylic acid is the simplest unsaturated carboxylic acid, consisting of a vinyl group connected directly to a carboxylic acid terminus. Major markets for the end product of acrylic acid include surface coatings, textiles, adhesives and plastics. Polyacrylic acid or copolymers find applications in superabsorbents, detergents, dispersants, flocculants and thickeners. Acrylic acid is produced from propene which is a byproduct of ethylene and gasoline production.

$$CH_2{=}CHCH_3 + 1.5\ O_2 \rightarrow CH_2{=}CHCO_2H + H_2O$$

Figure 3.2 Synthesis of Acrylic Acid by Propene

The structure of acrylic acid is shown in Figure 3.3 below

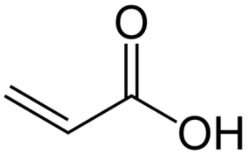


Figure 3.3 Acrylic Acid Structure, $C_3H_4O_2$

Acrylic acid chemical properties are shown in Table 3.2 below:

Table 3.2 Acrylic Acid Chemical Properties

PRODUCT IDENTIFICATION	
Synonyms	2-Propenoic acid, Acroleic acid
CAS Number	79-10-7
Molecular Weight	72.06 g/mol
Chemical Formula	CH =CHCOOH$_2$

PHYSICAL AND CHEMICAL PROPERTIES	
Appearance	clear, colorless liquid
Flash Point	54 °C
Solubility	1000 g/l (25 °C)
Boiling Point	141 °C (1013 hPa)
Melting Point	13 °C
Vapor Pressure	4 hPa (20 °C)
Density	1.05 g/cm³ (20 °C)
pH Value	2.1 (72.06 g/l, H_2O, 20 °C)

3.2.2 2-Ethyl Hexanol

2-Ethylhexanol (2-EH), or isooctanol, is a fatty alcohol, a branched, eight-carbon alcohol and also an organic compound used in the manufacture of a variety of products. 2-Ethylhexanol is produced industrially by aldol condensation of *n*-butyraldehyde, followed by hydrogenation. 2-Ethylhexanol can easily be converted into esters that have diverse usage. The main use of 2-ethylhexanol is in the production of the diester (2-ethylhexyl) phthalate (DEHP), a plasticizer. Being a fatty alcohol, esters of 2-ethylhexanol tend to have emollient properties.The structure of 2-Ethylhexanol is shown in Figure 3.4 below:

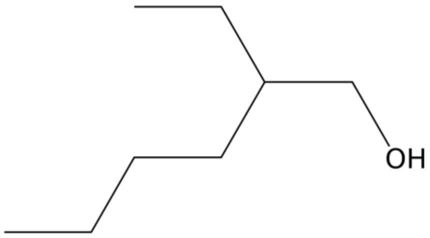


Figure 3.42- Ethylhexanol Structure, $C_8H_{18}O$

2-Ethylhexanol chemical properties are shown in Table 3.3 below:

Table 3.3 2- EthylhexanolChemical Properties

PRODUCT IDENTIFICATION	
Synonyms	Isocotyl alcohol, Isooctanol,Oxooctyl alcohol
CAS Number	104-76-7
Molecular Weight	130.22 g/mol
Chemical Formula	$CH_3CH_2CH_2CH(C_2H_5)CH_2OH$
PHYSICAL AND CHEMICAL PROPERTIES	
Appearance	clear, colorless liquid
Flash Point	75 °C
Solubility	1.1 g/l (20 °C)
Boiling Point	184 °C (1013 hPa)
Melting Point	-76 °C
Vapor Pressure	0.13 hPa (20 °C)
Density	0.832 g/cm³ (20 °C)

3.3.3 2- Ethyl Hexyl Acrylate

2-Ethyl Hexyl Acrylate is produced from this research. This is an ester that is used to produce acrylate polymer that belongs to a group of polymers. It is a potential monomer that is used in homopolymer and copolymer production.

The structure of 2-Ethyl Hexyl Acrylate is shown in Figure 3.5 below:

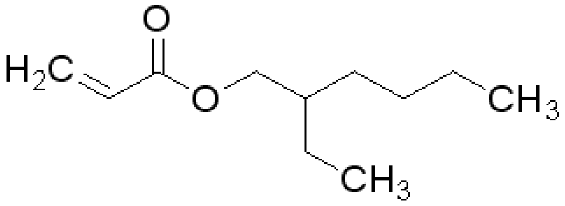


Figure 3.5 2- Ethyl Hexyl Acrylate Structure, $C_{11}H_{20}O_2$

2-Ethyl Hexyl Acrylate chemical properties are shown in Table 3.4 below:

Table 3.42- Ethyl Hexyl AcrylateChemical Properties

PRODUCT IDENTIFICATION	
Synonyms	Acrylic acid 2-ethylhexyl ester
CAS Number	103-11-7
Molecular Weight	184.27 g/mol
Chemical Formula	$C_{11}H_{20}O_2$
PHYSICAL AND CHEMICAL PROPERTIES	
Appearance	clear, colorless liquid
Flash Point	86 °C
Solubility	0.1 g/l (25 °C)
Boiling Point	229 °C (1013 hPa)
Melting Point	-90 °C
Vapor Pressure	0.12 hPa (20 °C)
Density	0.887 g/cm³ (20 °C)

3.3 Sulfated Ferum Promoted Zirconia (ZFS)

The heterogeneous catalyst used in the esterification of acrylic acids and 2-Ethyl Hexanol is sulfated zirconia. Solid acids are use due to its less toxic properties and facilitate the recovery and recycling of the catalysts.Sulfated zirconia is choosen as the catalyst due to its importance of its catalytic activity, reusability and thermal resistant. This modified-zirconia catalyst is thermally stable than resin-type catalyst when used at higher temperature.Sulfated Zirconia (SZ) is an important and suitable catalyst for heterogeneous esterification that experiences broad industrial application. Ferum become the promoter for sulphated zirconia to improve deactivation of catalyst.

3.3.1 Catalyst Preparation

The catalyst is prepared according to N. Essayem*et al.* (2007), where 20 g of Zirconia (IV) Hydroxide will have contact with 40 cm³ of aqueous solution containing 3.96 x 10^{-3} mol $Fe(NO_3)_3.9H_2O$ for 1 hour stirring. The solution needs to evaporate the excess water and the solid produced needs to dry at 353K for a day in oven. The solid produced is known as FZ.

Then, the sulfation of FZ is performed by subsequently contacting 5g FZ solid with 75 cm³ sulphuric acid H_2SO_4, 0.2N solution for 15 minutes under stirring. The solid then filtered and dried for a day at 353 K in oven before it further calcine under flowing air through the catalyst bed for 2 hour at 823K reach after a ramping of 10 °C min $^{-1}$. After sulfation, this sample is design as ZFS, which is sulphatedferum promoted zirconia. Table 3.5 shows list of chemical use in catalyst preparation and table 3.6 shows List of Apparatus use in Catalyst Preparation.

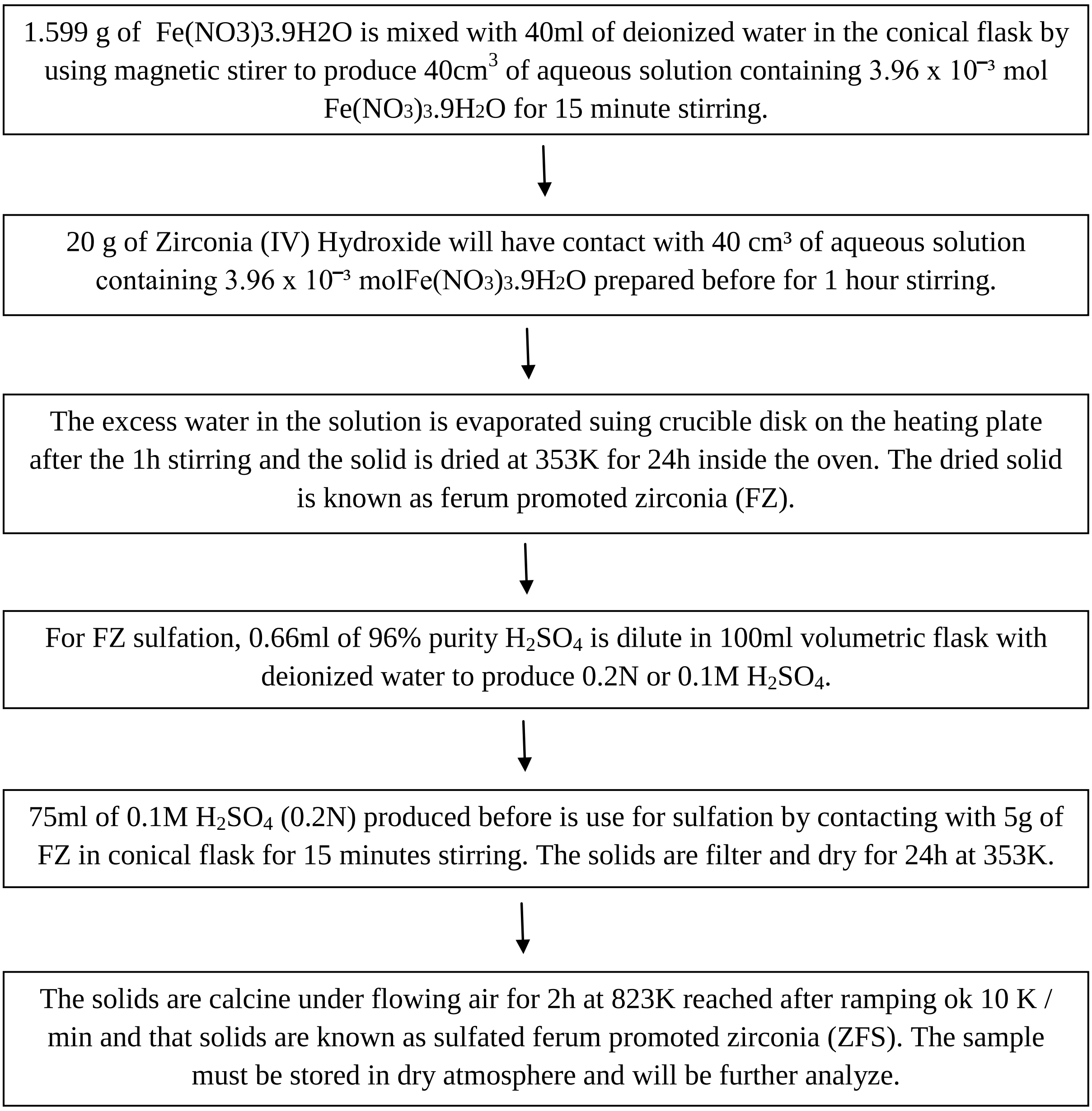
Table 3.5 List of Chemical use in Catalyst Preparation

LIST OF CHEMICAL	FUNCTION
Zirconium (IV) Hydroxide 97%	Catalyst Production Component
$Fe(NO_3)_3.9H_2O$	Catalyst Promoter
H_2SO_4	Catalyst Sulfation

Table 3.6 List of Apparatus use in Catalyst Preparation

LIST OF APPARATUS	FUNCTION
Furnace	Catalyst Calcination
Magnetic Stirrer	Mixer
Hot Plate& Magnetic Stirrer	Heater, Evaporator& Catalyst Mixer
Crucible Disk	Evaporator Disk & Calcination
Conical Flask	Reactor
Spatula	Adding & Removing
Weighing Boat	Weighing Container
Weight Scale	Weighing
Oven	Dryer

Figure 3.6 shows the steps for catalyst preparation



1.599 g of Fe(NO3)3.9H2O is mixed with 40ml of deionized water in the conical flask by using magnetic stirer to produce 40cm^3 of aqueous solution containing 3.96 x 10^{-3} mol Fe(NO$_3$)$_3$.9H$_2$O for 15 minute stirring.

20 g of Zirconia (IV) Hydroxide will have contact with 40 cm^3 of aqueous solution containing 3.96 x 10^{-3} molFe(NO$_3$)$_3$.9H$_2$O prepared before for 1 hour stirring.

The excess water in the solution is evaporated suing crucible disk on the heating plate after the 1h stirring and the solid is dried at 353K for 24h inside the oven. The dried solid is known as ferum promoted zirconia (FZ).

For FZ sulfation, 0.66ml of 96% purity H_2SO_4 is dilute in 100ml volumetric flask with deionized water to produce 0.2N or 0.1M H_2SO_4.

75ml of 0.1M H_2SO_4 (0.2N) produced before is use for sulfation by contacting with 5g of FZ in conical flask for 15 minutes stirring. The solids are filter and dry for 24h at 353K.

The solids are calcine under flowing air for 2h at 823K reached after ramping ok 10 K / min and that solids are known as sulfated ferum promoted zirconia (ZFS). The sample must be stored in dry atmosphere and will be further analyze.

Figure 3.6 Catalyst Preparation

3.4 Esterification of Acrylic Acid with 2- Ethyl Hexanol

Esterification of acrylic acid with 2-Ethyl Hexanol produces 2-Ethyl Hexyl Acrylate, abbreviate as 2EHA. Different operating parameter will be the main focus of the study in this esterification process that uses the catalyst that prepared before in this research. High Performance Liquid Chromatography (HPLC) will be use in analytical analysis.Previous study by Muthu et al., (2006) show that increasing temperature will increase the conversion efficiency, but the conversion efficiency of the esterification reaction has less effect when the temperature is raised beyond the boiling point of alcohol that is used in the study. Based from Dupont et al., (1996) research on esterification of propanoic acid with 2-ethyl hexanol catalyzed by heteropolyacids pure shows that, the experimental temperature condition is 333K (60ºC).

3.4.1 Equipment Apparatus

List of equipments and apparatus are shown in Table 3.7 below:

Table 3.7 List of equipments and apparatus.

LIST OF APPARATUS	FUNCTION
Rotamantle	Mixer& Heater
3 Neck Round Bottle	Reactor
Reflux Condenser	Condenser
Thermometer	Reaction Temperature Reading
Magnetic Stirer	Stirer
Micro filter 4.5	Catalyst Separator
Syringe	
Chillers	Sample Storage

The synthesis will be carried out in a batch reactor from a beaker in this research. High Performance Liquid Chromatography will be used to analyze the amount of acrylic acid left in the product.

3.4.2 Experimental Procedure

This esterification research will involve several steps as in figure 3.7:

Certain amount of acrylic acid and 2-ethylhexanol based on molar ratio parameter will react by putting together into the 3 neck bottle in thermal oil bath for certain hour based on parameter studies including the catalyst weight %.

⇩

The stirrer is on at constant speed, 500 rpm to mix the raw material with catalyst throughout the reaction

⇩

The sample from the reaction mixture will be collected for further analysis using HPLC

⇩

The sample taken must be filter using micro filter to remove the catalyst, before keep in the chiller under 4°C temperature to reduce further reaction.

Figure 3.7 Summary of Esterfication Process

3.4.3 Experimental Studies on the Effect of Difference Operating Parameters

There are four parameters that will be studied in order to obtain the optimum condition for the 2-Ethyl Hexyl Acrylate production. The parameters are:

(i) The effect of reaction temperature (test 1 until 12)

(ii) The effect of reaction time (test 1 until 12)

(iii) The effect of molar ratio of acid to alcohol (test 13 and 14)

(iv) The effect of catalyst loading (test 15 and 16)

Table 3.8 shows operating condition for the study of second parameter, molar ratio of acid to alcohol. A,B,C and D shows the best temperature, reaction time, molar ratio and catalyst weight percent respectively.

Table 3.8 Reaction Parameter Summary

TEST NUMBER	RATIO H:OH	WEIGHT % CAT	TEMPERATURE	TIME	STIRER
1	1:1	0.5	50	2	500
2	1:1	0.5	50	4	500
3	1:1	0.5	50	6	500
4	1:1	0.5	50	8	500
5	1:1	0.5	70	2	500
6	1:1	0.5	70	4	500
7	1:1	0.5	70	6	500
8	1:1	0.5	70	8	500
9	1:1	0.5	90	2	500
10	1:1	0.5	90	4	500
11	1:1	0.5	90	6	500
12	1:1	0.5	90	8	500
13	1:2	0.5	A	B	500
14	1:3	0.5	A	B	500
15	C	1.0	A	B	500
16	C	1.5	A	B	500
OPTIMUM OPERATING CONDITION	C	D	A	B	500

Detail amount of raw material for each test as shown in the table 3.8 is shown in table 3.9. For test 15 and 16, amount of 2 ethyl hexanol shown in the table 3.9 is based on HPLC result gain from test 13 and 14 that determine the optimum molar ratio for esterification. X symbols shows in the table 3.9 was refered to the best amount of acrylic acid, 2- ethyl hexanol and ZFS based on test 13 and 14 results. Test 15 used 1.0 wt % catalyst loading and test 16 used 1.5 wt % catalysts loading.

Table 3.9 Raw Material Amount for Each Test

TEST NO	ACRYLIC ACID (ml)	2 ETHYL HEXANOL (ml)	SULFATED FERUM PROMOTED ZIRCONIA, (g)
1	30.4458	69.5542	0.4493
2	30.4458	69.5542	0.4493
3	30.4458	69.5542	0.4493
4	30.4458	69.5542	0.4493
5	30.4458	69.5542	0.4493
6	30.4458	69.5542	0.4493
7	30.4458	69.5542	0.4493
8	30.4458	69.5542	0.4493
9	30.4458	69.5542	0.4493
10	30.4458	69.5542	0.4493
11	30.4458	69.5542	0.4493
12	30.4458	69.5542	0.4493
13	17.9564	82.0436	0.4356
14	12.7331	87.2670	0.4299
15	X	X	X
16	X	X	X

3.4.4 Analytical Method

The final product of this experiment will be analyzed by High Performance Liquid Chromatography (HPLC). The sample of each parameter will be injected into this equipment and at the end of the process; the amount of unreacted acrylic acid in the product will be showed in term of graph.List of chemical use for analytical analysis of 2- Ethylhexyl Acrylate esterification and list of equipments and apparatus are shown in table 3.10 and table 3.11 respectively.

Table 3.10 List of Chemical use in HPLC Analysis

LIST OF CHEMICAL	FUNCTION
Trifluoroacetic Acid	HPLC Mobile Phase
Methanol HPLC Grade	
Ultrapure Water	HPLC Dilution Water
2 Ethylhexyl Acrylate	HPLC Sample
Acrylic Acid	HPLC Standard

Table 3.11 List of equipments and apparatus.

LIST OF APPARATUS	FUNCTION
HPLC Agilent 1200 Infinity Series	Determine Acrylic Acid Amount
10 ml volumetric flask	Dilution
1L volumetric flask	
100nl volumetric flask	
Micropipet 10µl	Pipet
Vial	HPLC Sample Bottle
Ultrasonic Water Bath	Remove Bubble
Micro filter 4.5	Filter Sample
Syringe	
Scott Bottle	HPLC Mobile Phase Storage

HPLC analysis need several things to be considered which are types of column and condition of columns, types of mobile phase used, preparation of standard solution in order to have calibration curve as well as the preparation of sample solution. The condition of the High Performance Liquid Chromatography (HPLC) is as shown in Table 3.12 according to Arvind et al., (2009) research, esterification of acrylic acid with 1- butanol.

Table 3.12 High Performance Liquid Chromatography (HPLC) Condition

HPLC AGILENT 1200 INFINITY SERIES	
Types of Column	C_8
Column Diameter	4.6 x 150 mm , ID = 5µm
Column Pressure	67.5 bar
Column Length	15 cm
Column Flow	1.0 mL/min
Linear velocity	0.161 cm/s
Temperature	35^0C
Injection volume	10µl
Detection	UV at 220nm, 16 (Ref: 360nm, 100)
Mobile Phase	3% methanol; 97% water with 0.1% trifluoroacetic acid (TFA)
Type of Signal	DAD (220 16 360 100)

3.4.4.1 Preparation of Standard Solution

The standard solution is prepared in order to do calibration curve as a reference for acrylic acid analysis. The standard solution is prepared for 1000ppm first and then, it was diluted to 0ppm, 5ppm, 10ppm, 20ppm, 30ppm and 40ppm.

The preparation of standard solution is prepared by using equation of $M_1V_1 = M_2V_2$ where

M_1: Initial acrylic acid concentration (520 237 ppm)

M_2: Final concentration needed (100ppm)

V_2: Final volume of solution (1000 mL)

V_1: Initial volume acrylic acid needed from 520 237 ppm solutions

Therefore, initial volume of acrylic acid needed to dilute the solution to 100 ppm is

$$V_1 = \frac{M_2V_2}{M_1}$$

$$= \frac{(100\text{ppm})(1000\text{mL})}{(520\ 237\text{ppm})}$$

$$= 0.1922\ \text{mL}$$

$$= 192.22\ \mu\text{L}$$

After that, this standard solution is diluted to 5 difference concentrations which are 5ppm, 10ppm, 20ppm, 30ppm and 40ppm. The diluted standard solution is prepared by using same equation of $M_1V_1 = M_2V_2$ where

M_1: Initial stock solution concentration (100ppm)

M_2: Final concentration needed (5ppm, 10ppm,20ppm, 30ppm and 40ppm)

V_2: Final volume of solution (10mL)

Therefore, initial volume of stock solution needed to dilute the solution to 5 ppm is

$$V_1 = \frac{M_2 V_2}{M_1}$$

$$= \frac{(5\text{ppm})(10\text{mL})}{(100\text{ppm})}$$

$$= 0.5 \text{ mL}$$

$$= 500 \ \mu\text{L}$$

The same procedure of calculation is done as above but with different value of M_2 which are 50ppm, 100ppm and 150ppm. Therefore, the initial volume of stock solution, V_1 needed are as shown in table below:

Table 3.13 Value of V_1 for Different Concentration of Stock Solution

Concentration (ppm)	**Initial Volume of Stock Solution, V_1 (µL)**
5	500
10	1000
20	2000
30	3000
40	4000

3.4.4.2 Preparation of Sample Solution

In order to dilute the samples, there are several methods that need to be considered as indicates in chart below:

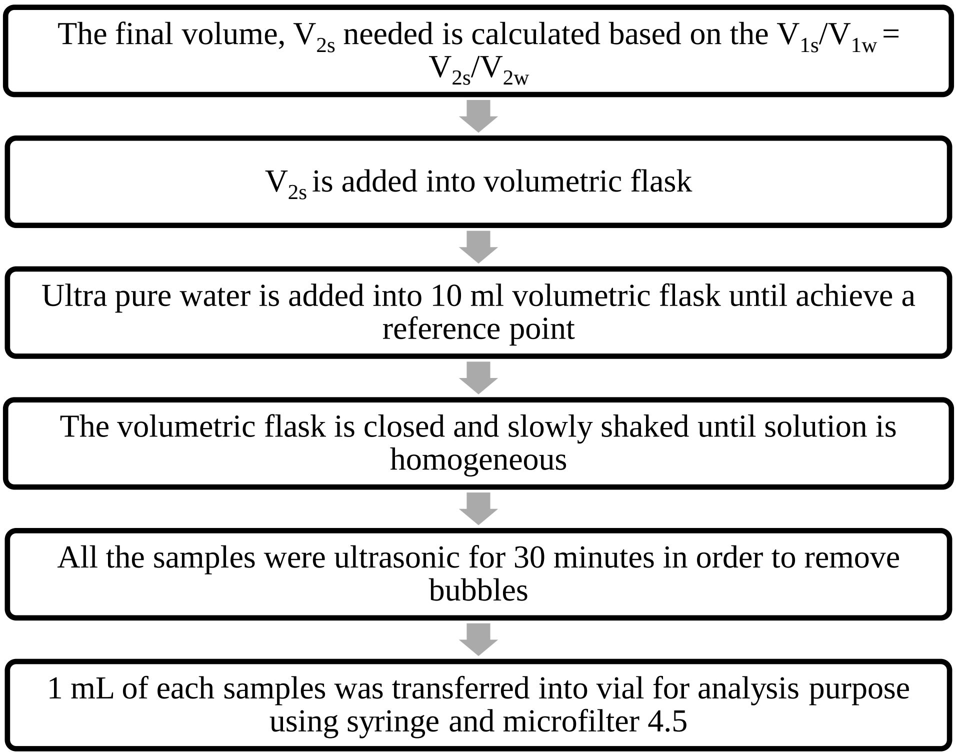


Figure 3.8 Methods for HPLC Analysis

Concentration of remaining acrylic acid in the product can be get from HPLC analysis. 2 – Ethylhexyl Acrylate solubility in water is 0.1 ml in 1000 ml water. In order to get the HPLC peak under the range, 0.05 ml sample in 1000 ml water is the initial volume. Ratio calculation is use to get the final volume of sample that need to dilute in 10 ml volumetric flask

The preparation of solution of each samples is by using equation $V_{1s}/V_{1w}= V_{2s}/V_{2w}$ where

V_{1s}: Initial 2 ethylhexyl acrylate (sample) volume (0.001ml)

V_{1w}: Initial ultrapure water volume (1000 ml)

V_{2s}: Final 2 ethylhexyl acrylate (sample) volume (calculation)

V_{1w}: Final ultrapure water volume (10 ml)

Therefore, final volume of acrylic acid needed to dilute the solution to 0.05 ml sample /1000ml ultrapure water in 10 ml volumetric flask

$$\mathrm{V_{2s}} = \frac{\mathrm{V_{1s}V_{2w}}}{\mathrm{V_{1w}}}$$

$$= \frac{(0.1\mathrm{ml})(10\mathrm{mL})}{(1000\ \mathrm{ml})}$$

$$= 0.001\ \mathrm{mL}$$

$$= 1.00\ \mu\mathrm{L}$$

3.4.4.3 HPLC Mobile Phase Preparation

Mobile Phase uses for detection Acrylic Acid amount using HPLC are 97% Trifluoroacetic Acid (TFA) solution and 3% Methanol HPLC grade. For TFA solution, 0.1 % of TFA is dilute in ultrapure water (1ml of TFA dilute with ultrapure water in 1L volumetric flask). TFA solution and methanol HPLC grade is transfer into different scott bottle and ultrasonic for 15 minutes before use as HPLC mobile phase.

3.5 Catalyst Characterization

The catalyst, sulfated ferum promoted zirconia characteristic will be study in this research. The surface and bulk properties of acid catalysts will be examined by spectroscopic and non-spectroscopic techniques, namely X-ray powder diffraction, Fourier Transform Infrared Spectroscopy and Thermogravimetric Analysis. Table 3.12 shows list of equipment use to characterize the catalyst and its function.

Table 3.14 Catalyst Characterization List of Equipment and Function

Equipment	Function
Thermogravimetric Analysis (TGA)	Thermal Stability
Fourier Transform Infrared Spectroscopy (FTIR)	Adsorbed Sulfated Species & Acid Site
X Ray Diffraction (XRD)	Crystal Phase

The X-ray diffraction (XRD) patterns of the sulfated zirconia will be recorded on an X-ray diffractometer. X-ray diffractometer will operate under 40 KV and 40 mA with the scan rate of 2°/min. Cu Kα X-ray is nickel filtered according Essayem et al., (2007) In TGA analysis, according to Sikabwe et al the sample is heat up to 873K with 10ºC min^{-1}temperature increment. The sample weight is 5mg.

CHAPTER 4

RESULTS& DISCUSSION

4.1 Research Analysis

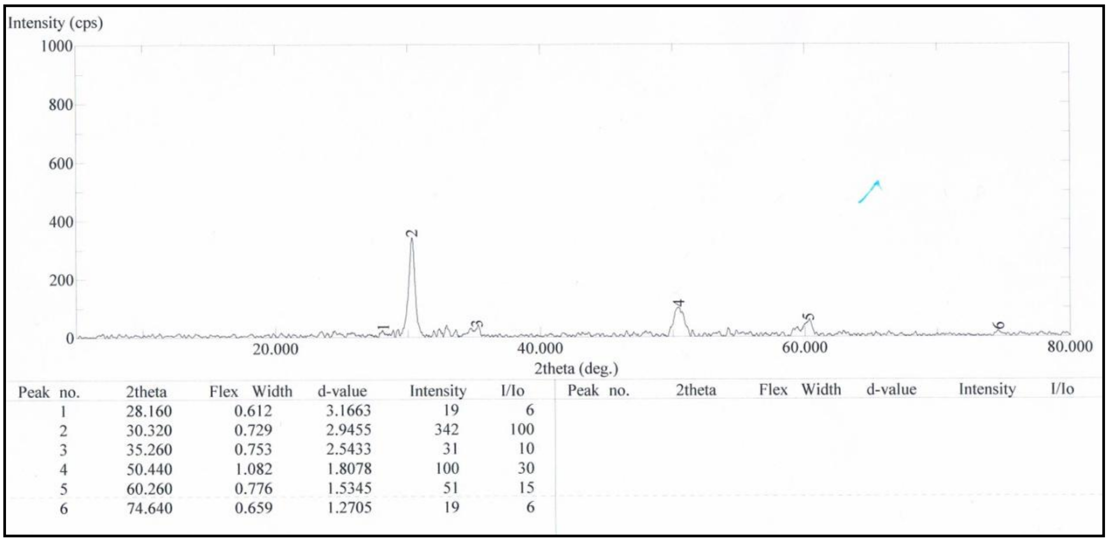
Esterification of 2- Ehtylhexyl Acrylate (2EHA) research analysis is based on the characterization of Sulfated Ferum Promoted Zirconia (ZFS) catalyst and research on reaction parameter to determine the optimum reaction condition to produce 2EHA using ZFS.

4.2 Characterization of Sulfated Ferum Promoted Zirconia

Characterization of Sulfated Ferum Promoted Zirconia is done by using X-Ray Diffraction (XRD) to determine the phase of the catalyst particle, Thermogravimetry Analysis (TGA) to find out thermal stability of the catalyst and Fourier Transform Infrared Analysis (FTIR) to determine catalyst acid site and adsorbed sulfated species.

4.2.1 X- Ray Diffraction

X ray Diffraction (XRD) is used to determine the phase of sulphated ferum promoted zirconia used in the esterification reaction to shows that the catalyst produce is in crystallize shape and it is Sulfated Ferum Promoted Zirconia according to the literature review. XRD result is shown in figure 4.1.



Peak no.	2theta	Flex Width	d-value	Intensity	I/Io	Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	28.160	0.612	3.1663	19	6						
2	30.320	0.729	2.9455	342	100						
3	35.260	0.753	2.5433	31	10						
4	50.440	1.082	1.8078	100	30						
5	60.260	0.776	1.5345	51	15						
6	74.640	0.659	1.2705	19	6						

Figure 4.1 X-ray Diffraction (XRD) Analyses for Sulfated Ferum Promoted Zirconia

Based on Figure 4.1, XRD analyses indicated the presence of tetragonal phase after calcinations of the catalyst based on the intensity of the catalyst at the degree of XRD flex rotation. Crystallization of the catalyst occurs after the calcinations and sharp peak of X-ray diffractogram shows the present of crystal in the sample and absence of the sharp peak will shows amorphous nature of the material (Petal et al., 2008).Sulfated Ferum Promoted Zirconia is a catalyst that is in crystal nature of material. The phase and crystalline nature of the catalyst form XRD analysis is important to make sure that the catalyst produce in this research is sulfated ferum promoted zirconia according to literature review. The result can be compared to the XRD analyses of Essayem et al (2007) as shown in figure 4.2.

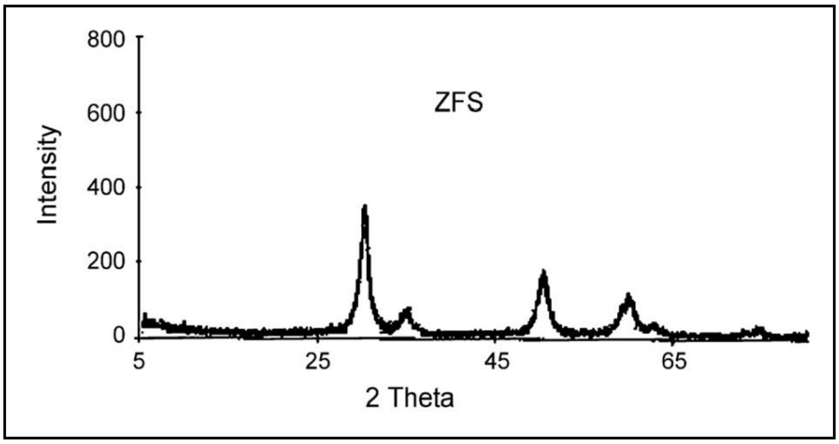


Figure 4.2XRD Pattern of SulphatedFerum Promoted Zirconia Catalyst

XRD analysis result for ZFS range 2θ = 5-80°. Characteristic lines of pure ZFS are at 2θ = 30.3°, 35.1°, 50.2°, 60.0° and 74.5° (Essayem et al., 2007). Figure 4.1 shows that at 2θ = 30.3° (342cps), 35.3° (31cps),50.4° (100cps), 60.3° (51cps), and 74.7° (19cps) to presence of crystalline ZFS. The result proves that the catalyst produced is sulfated ferum promoted zirconia.

4.2.2 Thermogravimetry Analysis

Figure 4.3 shows the result of Thermogravimetry Analysis for Sulfated Ferum Promoted Zirconia. This analysis is used to determine the thermal stability of the catalyst used in the reaction.

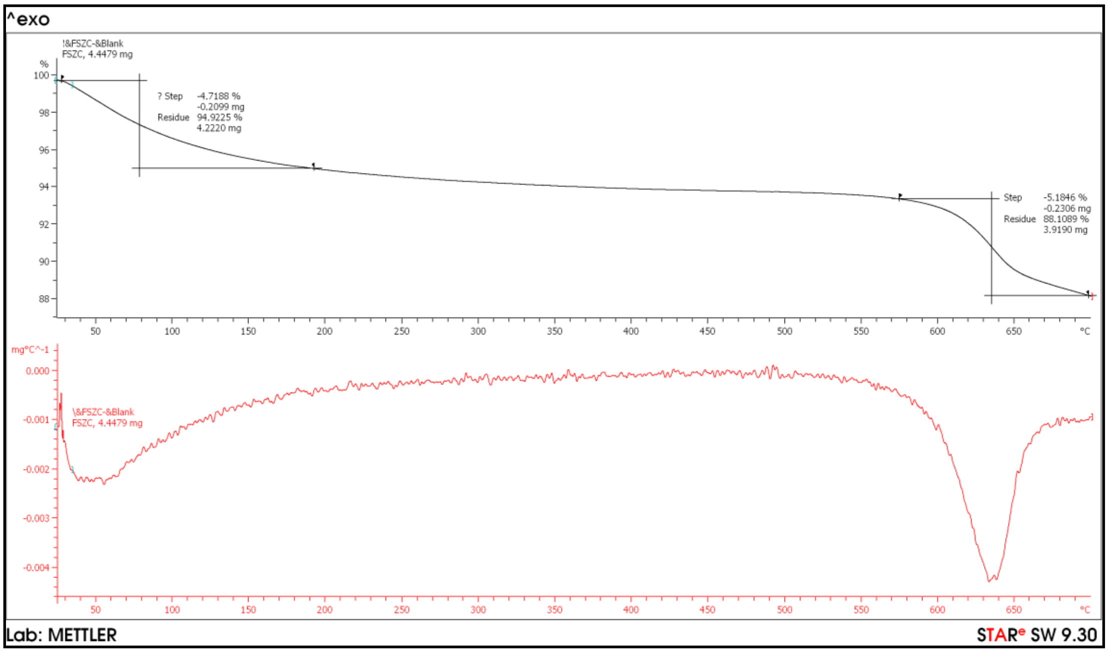


Figure 4.3 Thermogravimetry Analysis (TGA) Analyses for Sulfated Ferum Promoted Zirconia

TGA analyses of the catalyst were completed with 5 mg samples of catalyst heated at a constant heating rate of 10 °C/min in an atmosphere of oxygen at a constant purge rate of 40 mL/min at the pan. Based on the TGA graph shown in Figure 4.3, the mass of the catalyst start to decrease at approximately after 45 °C until 200 °C and it continues its decrease constantly until 570 °C before rapidly decrease until 700 °C. The initial inflection point is at 60 °C with 4.7188 % (0.2099 mg) weight loss and the second inflection point is at 640 °C with 5.1846 % (0.2306 mg). Thus, the residue value for first inflation is94.9255 % (4.222mg) and residue value at second inflation is 88.1089 % (3.9190 mg). This shows that the catalyst is stable to catalyze the reaction up until 570°C with total decomposition of 11.89 %. The loss of % weight of the sample is attributed to the possible presence of hydrated water at first inflation. Water has been used as solvent for catalyst preparation and air moisture may trap together with the catalyst produced. Second inflation is attributed by condensation of structural hydroxyl group. Both % weight losses as shown in TGA inflation point are explained according to Patel et al. (2008).

4.2.3 Fourier Transform Infrared Spectrometry

Figure 4.4 shows the result of Fourier Transform Infrared Spectroscopy (FTIR) Analyses for Sulfated Ferum Promoted Zirconia. This analysis is used to determine the acid site and adsorbed sulphated series.

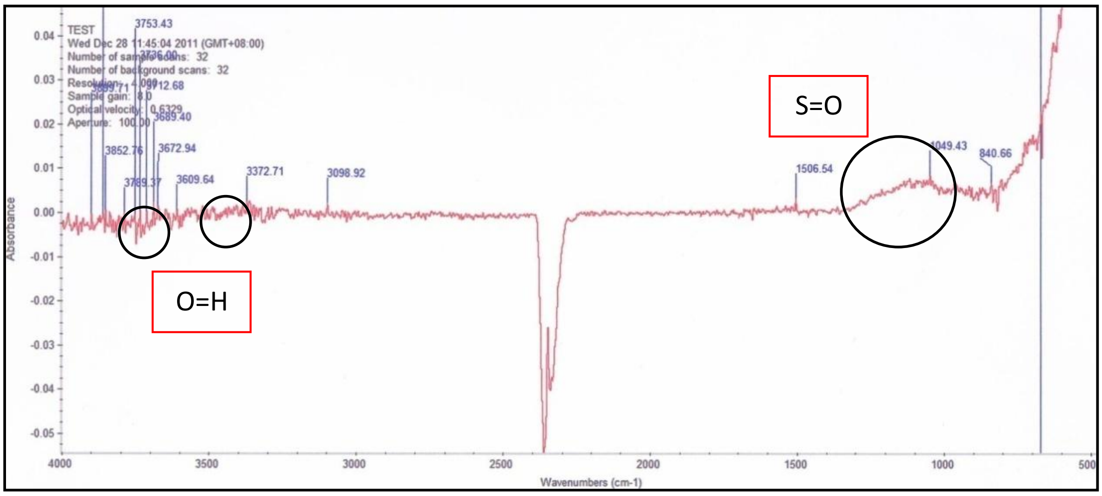


Figure 4.4 Fourier Transform Infrared Spectroscopy (FTIR) Analyses for Sulfated Ferum Promoted Zirconia

Infrared spectroscopy (FTIR) was used to check sulfated metal oxides presence. According to Alekandra et al., (2010), sulfated metal oxides with high surface area are the current interest in catalytic research because of their enhanced surface acidity, which will cause high activity in catalytic processes. High frequency component of S=O region is known as pyrosulfates group where the reaction conversion depends on the amount of these group S=O stretching region is in between 1340 – 1440 cm^{-1} and OH stretching region is 3300 – 3800cm^{-1} and it is shown in Figure 4.5.

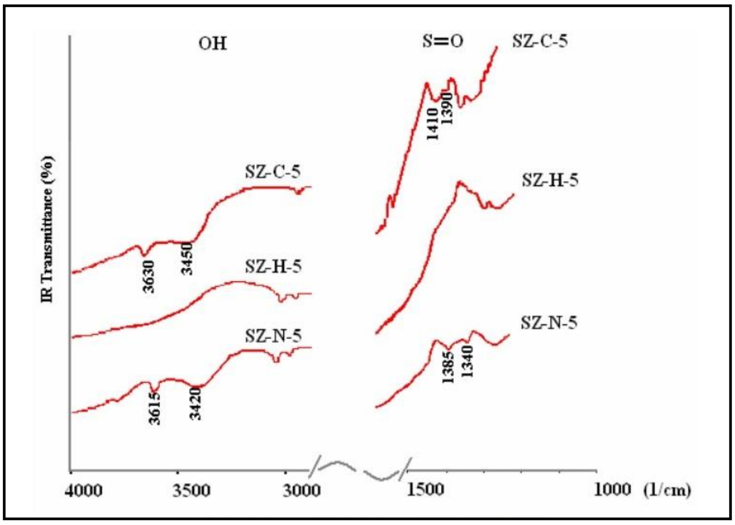


Figure 4.5 FTIR spectra of Sulfated Zirconia

Figure 4.4 is compared to Figure 4.5 that shows the presence of the pyrosulfates group in the catalyst at the same stretching region as in literature review of 1340 – 1440 cm^{-1}. OH stretching region is in between 3300 – 3800cm^{-1} in figure 4.4 that corresponds to OH groups of heist acidity. Polysulfates and OH group involved in donating the Hydrogen ion to the acid and remove the Hydrogen ion from the acrylate in the reaction mechanism.

4.3 Studies on the Effect of Different Operating Parameter

Different operating parameter introduce to the reaction to determine the optimum reaction parameter. The reaction parameters involved are reaction time, reaction temperature, molar ratio and catalyst loading weight percent. Result obtained from High Performance Liquid Chromatography (HPLC) analysis shows the amounts of acrylic acid remain in the product for each reaction test. Percent conversion for each parameter is use to determine the optimum parameter for this research. Reaction conversion can be calculated by having acrylic acid initial amount that use in the reaction. HPLC Standard Calibration Curve is shown in figure 4.6 below.

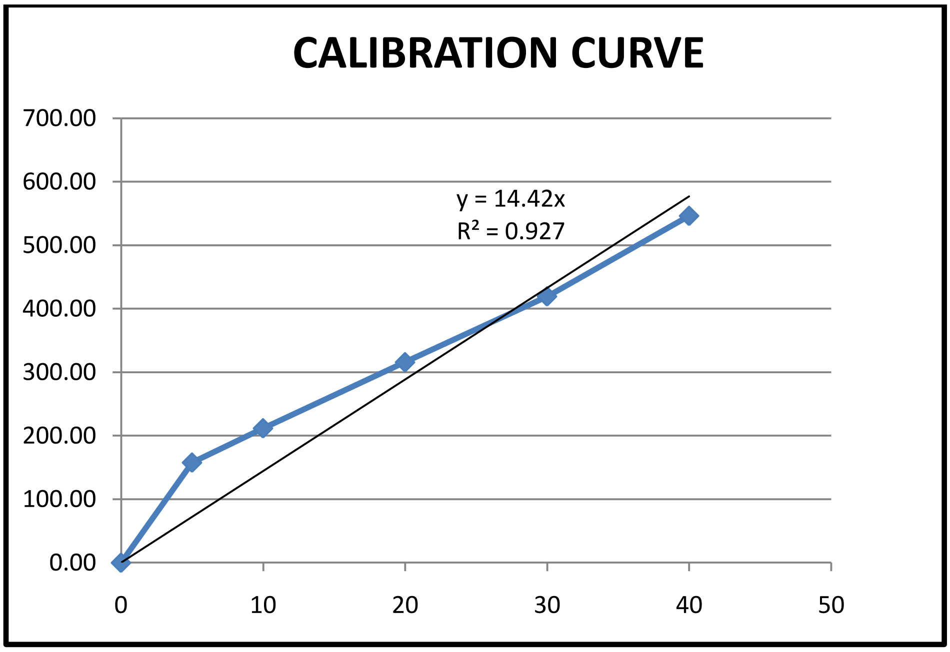


Figure 4.6 Standard Calibration Curve for Acrylic Acid

Figure 4.6 is used to calculate the amount of acrylic acid exists in the sample using the area from the curve of each sample. The retention time for acrylic acid is between 3 to 4 minutes for C8 HPLC column.

The reaction conversion is calculated based on the amount of acrylic acid remain in the product that detected by the chromatography. The initial amount of acrylic acid in the reaction is 0.978 g/ml.

4.3.1 Overall Result

Table 4.1 shows the overall result from the reaction parameter analysis. The parameters are:

(i) The effect of reaction temperature (test 1 until 12)

(ii) The effect of reaction time (test 1 until 12)

(iii) The effect of molar ratio of acid to alcohol (test 13 and 14)

(iv) The effect of catalyst loading (test 15 and 16)

Table 4.1 Overall Reaction Parameter Analysis Result

TEST NUMBER	RATIO ACID:ALCOHOL	WEIGHT % CAT	TEMPERATURE	TIME	STIRRER
1	1:1	0.5	50	2	500
2	1:1	0.5	50	4	500
3	1:1	0.5	50	6	500
4	1:1	0.5	50	8	500
5	1:1	0.5	70	2	500
6	1:1	0.5	70	4	500
7	1:1	0.5	70	6	500
8	1:1	0.5	70	8	500
9	1:1	0.5	90	2	500
10	1:1	0.5	90	4	500
11	1:1	0.5	90	6	500
12	1:1	0.5	90	8	500
13	1:2	0.5	90	8	500
14	1:3	0.5	90	8	500
15	1:3	1.0	90	8	500
16	1:3	1.5	90	8	500
BEST OPERATING CONDITION	1:3	1.5	90	8	500

Table 4.1 explains that, reaction temperature and reaction time is done from test 1 until test 12. Result from Test 1 until test 12 determines the best reaction time and reaction temperature that is used for the study of molar ratio parameter reaction. The best reaction temperature for esterification of 2EHA is 90°C for 8 hour reaction

time and this operation parameter is used for molar ratio analysis in test 13 and 14. 1:3 is the best molar ratio for the reaction from the research. Further analysis for catalyst weight loading analysis in test 15 and 16 using the previous best reaction condition shows 1.5 wt% catalyst weight loading is the best weight percent catalyst loading from this research. Detail discussion about the effect of each parameter is explained below.

4.3.2 Effect of Reaction Temperature and Reaction Time

Table 4.2 shows the result gained from HPLC analysis for the parameter of Reaction Time and Temperature.

Table 4.2 HPLC Result for Reaction Time and Temperature Parameter

TEMP (ºC)	TIME (h)	AREA (mAU*s)	AMOUNT (C_A) (g/ml)	CONVERSION (%)
50	2H	1257.03979	87.1733558	10.84126407
50	4H	703.54657	48.789673	50.09917478
50	6H	641.18304	44.4648433	54.52246635
50	8H	579.79297	40.2075569	58.87671280
70	2H	1038.63171	72.0271644	26.33241119
70	4H	665.20581	46.1307774	52.81859045
70	6H	615.52106	42.6852330	56.34260738
70	8H	573.10028	39.7434313	59.35140881
90	2H	754.08887	52.2946512	46.51433394
90	4H	645.68048	44.7767323	54.20347401
90	6H	598.93939	41.5353252	57.51870439
90	8H	517.57635	35.8929508	63.28958440

Calculation data from Table 4.2 shows the amount of unreacted acrylic acid in the sample product and reaction conversion for different reaction temperature and reaction time parameter. Effect of reaction temperature and reaction time to the reaction conversion is shown in figure 4.7 below.

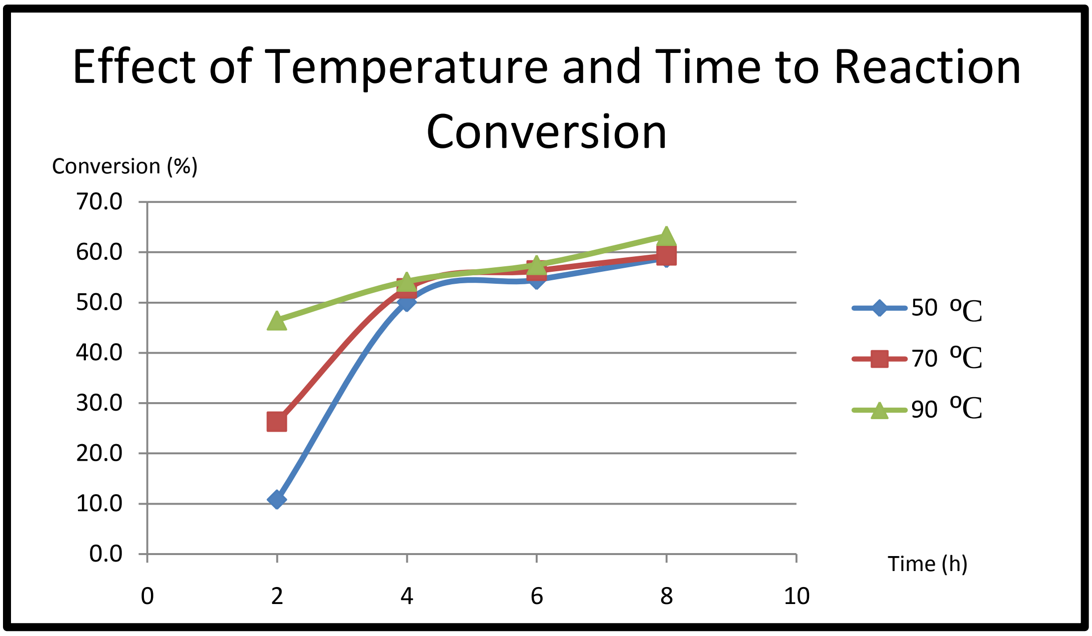


Figure 4.7 Effects of Reaction Temperature and Time to Reaction Conversion

Table 4.2 shows that the reaction conversions of Acrylic Acid for each temperature increase as the reaction time increases from 2 hours to 8 hours. After 8 hours reaction, reaction temperature at 90ºC has the highest reaction conversion and reaction temperature at 50ºC has the lowest reaction conversion in this research. Figure 4.7 shows that reaction conversion increase with time and temperature. The reaction conversion still increases after 8 hours for all 3 reaction temperature and this shows that the reaction has not achieve equilibrium after 8 hour. The optimum reaction time is more than 8 hours and further research can be carried away to find out the optimum reaction time.

Arrhenius equation may explain the relationship of reaction temperature to the reaction rate. Arrhenius equation is shown as below;

$$k(T_{\circ}) = A\mathrm{e}^{-E/RT}$$

According to the Arrhenius equation, increasing the reaction temperature may increase the reaction rate, and this is explained that 90 º C reaction temperatures has the highest reaction conversion compared to other. Besides, for endothermic reaction, increasing the reaction temperature will increase thermodynamic equilibrium value and this is explain that 90 º C reaction temperature gives the highest reaction conversion compared to lower reaction temperature.

Based on previous studies done by Muthu *et al*., (2010) which is using sulphated zirconia on the synthesis of biodiesel from Neem oil via transesterification, the studies show that increasing temperature will increase the conversion efficiency, but the esterification reaction conversion efficiency has less effect when the temperature is raised beyond the boiling point of alcohol that is used in the study. But, in this research, 2-ethyl hexanol is used as the reactant with boiling point of 229ºC and reaction temperature cannot higher than 100ºC to avoid solidified of the acrylic acid. Once the reaction temperature achieved more than 100ºC, the acrylic acid will start to solidified and no reaction occurs. According to Mehmet and Elif (2009), 0.3 wt% Phenothiazine can be use as an inhibitor to avoid polymerization of acrylic acid during the reaction. Figure 4.8 shows solidified acrylic acid from this research with reaction temperature 100ºC.


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Figure 4.8 Acrylic Acid Polymers

4.3.3 Effect of Molar Ratio

Table 4.3 shows the result gain from HPLC analysis for Molar Ratio Parameter.

Table 4.3 HPLC Result for Molar Ratio Parameter

MOLAR RATIO	AREA (mAU*s)	ACTUAL AMOUNT (C_A) (g/ml)	CONVERSION (%)
1:1	517.57635	0.358929508	63.28958440
1:2	460.70712	0.319491761	67.32317880
1:3	390.36801	0.270712906	72.31215861

Table 4.3 shows the reaction conversion for the effect of different molar ratio of acrylic acid to 2- ethyl hexanol toward esterification process. Effect of molar ratio to the reaction conversion for 8 hours reaction is shown in figure 4.9.

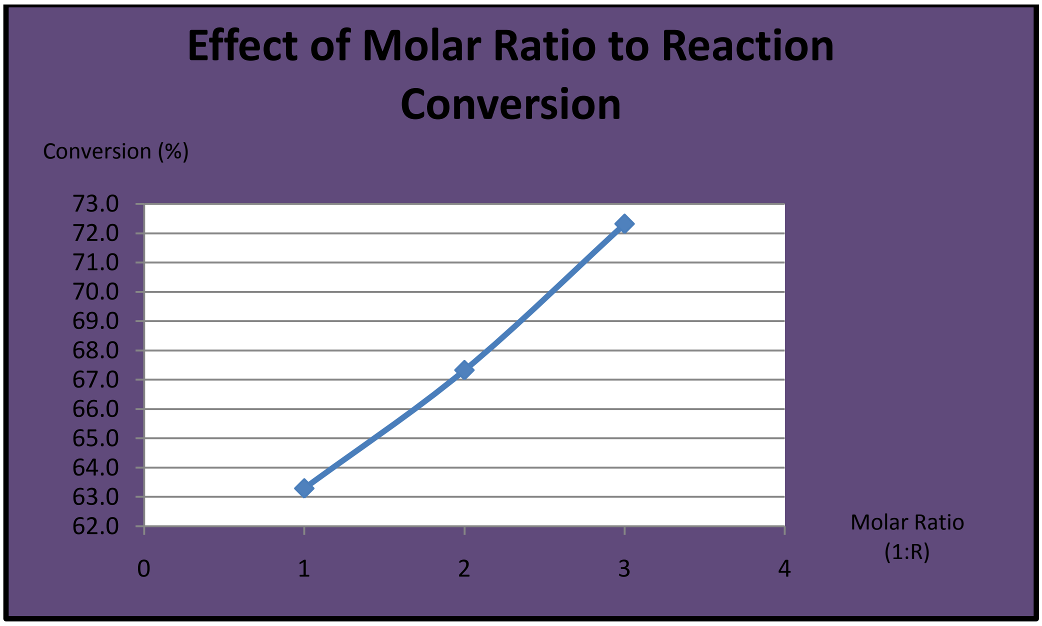

Figure 4.9 Effect of Molar Ratio to Reaction Conversion

Based on the graph shown in Figure 4.9, reaction conversion increases with molar ratio of acrylic acid to 2 ethyl hexanol from 1:1 to 1:3. The reaction is taken place for 8 hours at 90°C. According to Patel et al., (2008), esterification is reversible reaction and based on Le Chatlier's principle, any equilibrium reaction can be driven to product side by controlling the concentration of the reactant. This can be achieved by used of large excess of reactant.

Reaction conversion for 1:3 gives the highest conversion compared to others. Increasing amount of the reactant will shift the equilibrium to product site and hence speeding up the rate of reaction to achieve equilibrium as explained by Le Chatlier's Principle. From Figure 4.9, the reaction do not achieve equilibrium as explained before in the effect of reaction temperature and time research analysis and it is shown that 1:3 molar ratio make the highest reaction conversion due to the amount of the alcohol reactant that make the equilibrium conversion faster than other molar ratio for 8 hours reaction time at 90°C.

Molar ratio 1:3 is decided as the best molar ratio for the reaction according to this research. Further analysis about the effect of molar ratio can be done in the future by increasing the 2-ethyl hexanol ratio in the reaction.

4.3.4 Effect of Catalyst Loading

Table 4.4 shows the result gained from HPLC analysis for the study of the effect of Catalyst Loading.

Table 4.4 HPLC Result for Weight Percent Catalyst Loading Parameter

CAT WEIGHT %	AREA (mAU*s)	ACTUAL AMOUNT (C_A) (g/ml)	CONVERSION (%)
0.5	390.36801	0.270712906	72.31215861
1.0	357.75269	0.248094792	74.21458059
1.5	321.24927	0.222780354	77.21458059

Table 4.4 shows the reaction conversion in the sample product for different catalyst loading. Effect of catalyst loading to the reaction conversion is shown in figure 4.10.

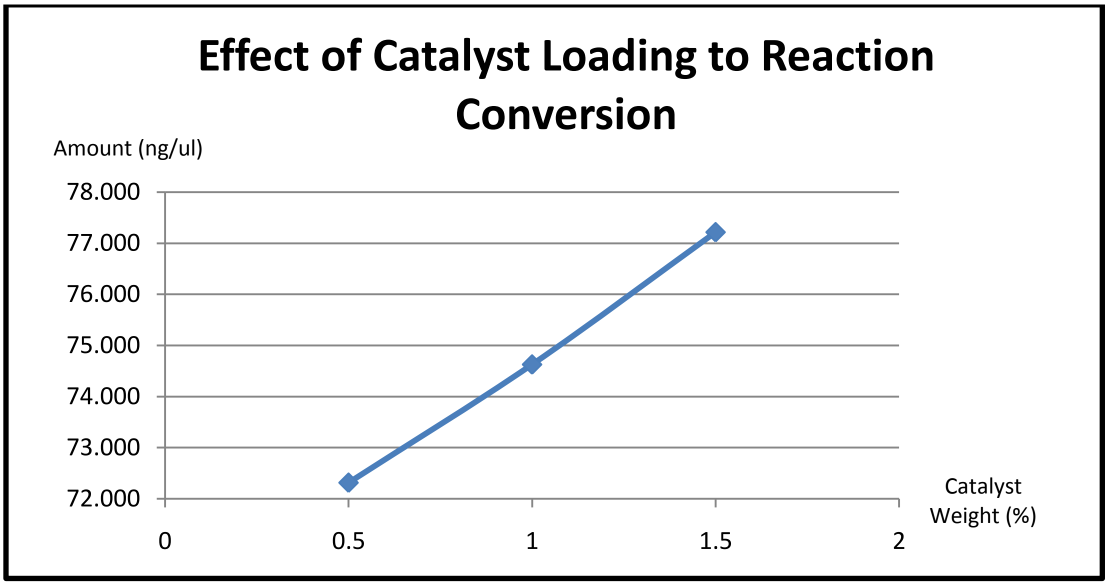

Figure 4.10 Effect of Catalyst Loading to Reaction Conversion

Figure 4.10 show that the increasing the reaction conversion for this reaction with the increasing of weight percent of catalyst loading. Sulfated Ferum Promoted Zirconia is used as catalyst for this reaction where it will enhance the rate of reaction. Increasing the amount of catalyst use for the reaction will provide more catalyst surface for the reaction unless there is catalyst deactivation such as the effect of the water produced from the reaction as reaction by product. In this research, water produced is not removed during the reaction and once it is condensed, it will return back to the reaction solution. Even there is no water removal from the reaction, the catalyst used in this experiment still able to catalyze the reaction and higher reaction conversion can be achieved at 8 hours if the water is removed. As the reaction is in equilibrium, a complete conversion can only achieve by elimination of water by forming an azeotrope (Dupont et al., 1995)

1.5 wt% is the optimum catalyst loading for the reaction from this research and further analysis by increasing the weight percent of catalyst loading and water removal can be done to get the optimum catalyst loading for this reaction.

CHAPTER 5

CONCLUSION& RECOMMENDATION

5.1 Conclusion

As the 2-EthylHexyl Acrylate (2EHA) is widely used especially in polymer production industry for decades, improvement for the reaction process is needed due to the world demand. From the research, Sulfated Ferum Promoted Zirconia shows the presence of tetragonal phase shape from XRD analysis which is a crystal shape and proved that the catalyst produces is ZFS. Thermal stability studies using TGA shows that the catalyst is stable to catalyze the reaction up until 570°C with total decomposition of 11.89 % (1.081mg). FTIR analysis shows the presence of component of S=O region which is known as pyrosulfates group and OH group where the reaction conversion depends on the presence of these group. From the reaction analysis, the best reaction condition for esterification of 2-Ethyl Hexyl Acrylate using Sulfated Ferum Promoted Zirconia catalyst is 90ºC for 8 hours with 1:3 acrylic acids to 2 ethyl hexanol molar ratio using 1.5wt% catalyst loading. The reaction conversion from this reaction condition is 77.22%.

5.2 Recommendation

Further analysis of reaction optimum condition for 2-Ethyl Hexyl Acrylate by using Sulfated Ferum Promoted Zirconia can be done by increasing the reaction time, reaction temperature, molar ratio of acrylic acid to 2 ethyl hexanol and catalyst weight % by using this research method. Water elimination from the reaction analysis can be done by forming azeotrope with an organic solvent and connect the reaction system to a vacumm line via pressure regulation system. Water elimination during the reaction can shift the equilibrium to the product side and improve the optimum reaction analysis result. The reaction temperature further analysis can be done with addition of polymer inhibitor Phenothiazine. Addition of Phenothiazine as inhibitor may make the reaction analysis more precise to avoid acrylic acid polymerization due to the thermal effect.

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