

**ESTERIFICATION OF FREE FATTY ACIDS IN
SIMULATED WASTE OIL USING NOVEL SOLID
ACIDIC IONIC LIQUID AS CATALYST**

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**ESTERIFICATION OF FREE FATTY ACIDS IN
SIMULATED WASTE OIL USING NOVEL SOLID
ACIDIC IONIC LIQUID AS CATALYST**

SHABIRAH BINTI EZAN

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

**Faculty of Chemical & Natural Resources Engineering
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JULY 2014

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SUPERVISOR'S DECLARATION

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

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

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Date : JULY 2014

Dedication

To my family, friends, supervisor and myself

ACKNOWLEDGEMENT

Praise to ALLAH SWT for His helps and guidance that I finally are able to finish my Undergraduate Research Project (URP).

I would like to express my deepest gratitude towards my supervisor, Dr. Sumaiya bt Zainal Abidin for her supervision and guidance for all these years. I am deeply thankful for her encouragement and guidance in helping me to understand about my research project title. Thanks a lot for her patience in revising my work which helped me to improve my research contributions. I really appreciate her help in guiding me to overcome my research and other problems.

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Thank You.

ABSTRACT

Issues on petroleum-based fuel shortage can be overcome by producing biodiesel fuel-type or also known as fatty acid methyl ester (FAME). The uses of biodiesel can improve the environmental health and also decrease the worries on the sustainability concerns on world sources of energy (i. e. natural gases). In this study waste cooking oil (WCO); a non-edible type of feedstock was used due to its availability and low cost. Nevertheless, WCO basically has high free fatty acids (FFAs) content which is in the range of 6-15%. Therefore, the study on the esterification of FFAs in a feedstock (WCO) using novel solid acidic ionic liquid as catalyst is carried out to lower the free fatty acid in the WCO. In this case, the use of heterogenous type of acid catalyst is more preferable in the esterification process due to its efficiency. The Bronsted acid ionic liquids (ILs) triethylammonium hydrogen sulphate (Et_3NHSO_4) is chosen to immobilize with solid support, divinylbenzene (DVB) polymer so that it will make separation process smoother and can increase its reusability as a catalyst. The novel solid acidic ionic liquid polymer has been synthesized based on Nuclear Magnetic Resonance ($^1\text{H-NMR}$), Elemental Analysis CHNSO and Scanning Electron Microscopy (SEM). The NMR spectroscopic data for the IL sample was: $^1\text{H-NMR}$ (500 MHz, DMSO) (ppm): δ 1.08-1.11 (triplet, 0.28H), 1.20-1.23 (triplet, 9.04H), 2.06 (singlet, 0.11H), 2.10 (singlet, 0.03H), 3.09-3.14 (sextet, 6.15H), 3.38-3.4 (doublet, 0.1H), 8.95 (singlet, 1H), 11.00 (singlet, 3.19H). The esterification of the FFA of the WCO was carried out using Et_3NHSO_4 as the catalyst in the first stage at the optimum reaction condition of 60°C reaction temperature, 5 wt % catalysts loading and 6:1 methanol to WCO molar ratio for three hours of reaction time. The novel solid acidic ionic liquid, Et_3NHSO_4 supported with DVB display good performance by showing 75.94 % FFA conversion. It was expected that the recycled catalyst will display the same properties with the fresh catalyst due to its properties that can ease the separation process from the reaction mixture. However, the FTIR result shows the difference of IR spectrum data obtained for the fresh catalyst and spent catalyst which indicates that the catalyst was fully separate from the mixture.

ABSTRAK

Isu-isu kekurangan bahan api berasaskan petroleum boleh diatasi dengan menghasilkan jenis bahan api biodiesel atau juga dikenali sebagai asid lemak metil ester (FAME). Kegunaan biodiesel dapat meningkatkan tahap kesihatan alam sekitar dan juga mengurangkan kebimbangan terhadap masalah pengekalan sumber-sumber. Dalam kajian ini, sisa minyak masak (WCO); bahan mentah jenis yang tidak boleh dimakan telah digunakan kerana ketersediaan dan juga kos rendah. Walau bagaimanapun, WCO pada dasarnya mempunyai asid lemak bebas (FFAs) kandungan tinggi dalam lingkungan 6-15%. Oleh itu, kajian mengenai pengesteran FFAs dalam bahan mentah (WCO) menggunakan novel pepejal cecair berasid ionik sebagai pemangkin dijalankan untuk mengurangkan asid lemak bebas dalam WCO. Dalam kes ini, penggunaan pemangkin jenis asid heterogen adalah lebih baik dalam proses pengesteran kerana ia lebih cekap. Asid Bronsted cecair ionik (ILS) triethylammonium hidrogen sulfat (Et_3NHSO_4) dipilih untuk dilumpuhkan dengan sokongan solid, divinylbenzene (DVB) polimer supaya ia akan menjadikan proses pemisahan lancar dan boleh meningkatkan sistem boleh gunapakai sebagai pemangkin. Novel pepejal cecair berasid ionik telah disintesis berdasarkan Magnetic Resonance Nuklear ($^1\text{H-NMR}$), Analisis Elemental CHNSO dan Imbasan Elektron Mikroskop (SEM). Data NMR spektroskopi untuk sampel IL adalah: $^1\text{H-NMR}$ (500 MHz, DMSO) (ppm): δ 1,08-1,11 (triplet, 0.28H), 1,20-1,23 (triplet, 9.04H), 2.06 (singlet, 0.11H), 2.10 (singlet, 0.03H), 3,09-3,14 (musik untuk enam orang, 6.15H), 3,38-3,4 (Doublet, 0.1H), 8.95 (singlet, 1H), 11.00 (singlet, 3.19H). Pengesteran FFA daripada WCO telah dijalankan dengan menggunakan Et_3NHSO_4 sebagai pemangkin di peringkat pertama pada keadaan tindak balas optimum 60°C suhu tindakbalas, 5% berat pemangkin punggah 6:1 nisbah molar metanol kepada WCO selama tiga jam masa tindak balas. Novel pepejal cecair berasid ionik, Et_3NHSO_4 disokong dengan prestasi paparan DVB yang baik dengan menunjukkan 75,94% penukaran FFA. Ia dijangka bahawa pemangkin dikitar semula akan memaparkan sifat yang sama dengan pemangkin segar kerana sifat-sifat yang boleh memudahkan proses pemisahan dari campuran tindakbalas itu. Walau bagaimanapun, hasil FTIR menunjukkan perbezaan data spektrum IR diperolehi untuk pemangkin segar dan pemangkin yang telah digunakan yang menunjukkan bahawa pemangkin tidak terpisah sepenuhnya daripada campuran esterifikasi.

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LIST OF ABBREVIATIONS

Subscripts

C	concentration
f_0	weight fraction of FFAs in the beginning of the reaction
M	sample weight
M_w	molecular weight
V	volume
X	conversion
AV_0	the initial acid value
AV	acid value

LIST OF ABBREVIATIONS

^1H NMR	Proton nuclear magnetic resonance
DVB	Divinyl benzene
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FT-IR	Fourier transforms infrared
IL	Ionic liquid
NMR	Nuclear magnetic resonance
SEM	Scanning electron microscopy
WCO	Waste cooking oil

1 INTRODUCTION

1.1 Motivation and statement of problem

The use of biodiesel can be one of the alternatives in replacing the petroleum-based diesel that is in demand due to the increase in industrialization development and population. Biodiesel or fatty acid methyl ester (FAME) can be classified as nontoxic and biodegradable substitute fuel that can be obtained from renewable sources (Kulkarni and Dalai, 2006). It is mainly produced with transesterification process by using either vegetable oils or animal fats by means of the presence of an acid or base as catalyst that the glycerides react with lower types of alcohol (methanol or ethanol) which then produced a mixture of glycerol, alkyl esters and fatty acids (Araujo et al., 2012). The use of biodiesel has advantages from environmental concerns as it can reduce emission of pollutant gaseous. In producing an economical biodiesel, the major distress is basically the choices of feedstock that has high availability and cheaper.

There are various types of feedstock or raw materials from vegetable and animal sources that can be used in the production of biodiesel. It can be classified into edible and non-edible type of feedstock. The problem that may encountered when choosing the edible type of feedstock such as soybean oil, peanut oil and palm oil was that the production cost might be costly, due to the high cost of raw vegetable oil especially. Therefore, the non-edible feedstock that can be seen in Table 1 is more preferable as it is cheaper.

Table 1-1: Free Fatty Acids (FFAs) content in Various Feedstocks (Jena et al., 2010; Worapun et. al, 2012; Berchmans and Hirata, 2008; Zhang and Jiang, 2008; Zheng et. al, 2006; Russbueldt et. al, 2009; Salimon et. al, 2010; Cowan et. al, 2012; Canoira et. al, 2008).

Feedstocks	Free fatty acid content (%)
Crude mahua oil	13-20
Crude jatropha oil	12-15
Crude jatropha curcas seed oil	15
Crude tobacco seed oil	17
Crude zanthoxylum bungeanum seed oil	25
Waste cooking oil	6-15
Crude palm oil	4.8-7.2
Yellow grease	<15
Brown grease	>15
Animal fat	15
Palm kernel oil	3-7.5

In this present years, it can be seen that there are huge amount of waste cooking oil (WCO) that were not properly managed which mainly came from restaurants, food processing company and food industries that had regrettably contributed to the environmental concerns. Therefore, using WCO as a feedstock is a wise choice based on the economic factor and environment issues. However, the problem when using WCO as the feedstock was that it basically has high free fatty acids (FFAs), due to hydrolysis of triglycerides through frying (Gan et al., 2012). Previous study has clarified that in alkaline transesterification reactions (biodiesel production process), the oil or fat used must contain not more than 1-2% FFAs, which is similar to about 2 mg KOH/g triglyceride. In this matter, saponification has lowered the yield and formation rate of FAME if the FFA level exceeds the 2% FFAs content that may cause difficulties in separation process and catalyst reutilization. (Berrios et al., 2007; Abidin et al., 2012). Thus, WCO need to go through the acid catalysed esterification in lowering the FFAs content.

The type of acid that frequently used in the esterification process was basically the sulphuric acid or hydrochloric acid (homogenous acid catalyst) as it has high conversion properties and also low cost. The major concern when using this type of acid or homogenous catalyst is due to the effluent disposal inconvenience and catalyst-loss reason. Plus, the chemical properties of acid that can cause corrosion also have lead to the high equipment cost. Thus, this problem has brought into the research of using heterogenous-based catalyst in the esterification reaction (Gan et al., 2012). Examples

of heterogenous type of catalysts are ion-exchange resins, activated carbon, zeolites and acidic ionic liquids (ILs).

ILs have garnered much attention during these years due to its outstanding properties. The advantages of ILs are that it has high conductivity, broad electrochemical window, sturdy dissolution activity and insignificant volatile pressure (Liang et al., 2012). Moreover, acidic ILs including the Lewis and Bronsted ones also has high activities in acid-catalytic reactions. Although the efficiency of the esterification process can be obtained due to the uses of ILs, but it have some disadvantages as it can cause purification difficulty due to its certain solubility. Therefore, the solid supported types of ionic liquids or novel solid acidic ionic liquids are more preferable in the esterification process.

Based on the previous research, Qiao et al. (2006) had explained that the ionic liquids are basically supported by immobilizing the chloroaluminate based ionic liquid on solid support through the process of chemical covalent bond (substantial coating on Al_2O_3 , SiO_2 , and TiO_2 or covalent attachment of ionic liquids on the surface of the support such as polystyrene, silica gel, zeolite, and divinylbenzene). The advantages of supported ionic liquid compared to the unsupported one are it plus side on the separation, reusability as well as its capability in providing practical amenities in a continuous system (Xu et al., 2010).

Therefore, this research will concentrate on the esterification of free fatty acids from waste cooking oil using novel solid acidic ionic liquid as catalyst.

1.2 Objectives

The following are the objectives of this research:

1. To synthesize and characterize the solid acidic ionic liquids (ILs) supported with divinylbenzene (DVB).
2. To study about the esterification of free fatty acids (FFAs) from waste cooking oil (WCO) using novel solid acidic ionic liquid as catalyst.

1.3 Scope of this research

In this research, it focused more on synthesizing the catalyst, Bronsted acid ionic liquid (Et_3NHSO_4) supported with DVB. Catalyst characterization is done by Nuclear

Magnetic Resonance ($^1\text{H-NMR}$), Fourier Transform-Infra Red (FT-IR), elemental analysis and Scanning Electron Microscopy (SEM) methods in finding the confirming the immobilization of the active component on the support, characterize the supported ionic liquid polymer and to determine unknown sample based on molecular weight and the effect of cleaning regimes on the surface of the DVB supported Et_3NHSO_4 ionic liquid catalysts for the single formulation of supported ionic liquid polymer.

The esterification of FFAs from simulated waste cooking oil (WCO) using novel acidic polymer as catalyst was studied at optimum reaction condition of 60°C reaction temperature, 5 wt % catalysts loading and 6:1 methanol to WCO molar ratio for three hours of reaction time.

2 LITERATURE REVIEW

2.1 General Overview

These days the diesel fuel is in high demand in various industries and also in automobiles. Nevertheless, the price for the petroleum-based diesel kept growing and people are concerned about the negative effect of this type of fuel towards the environment (Worapun et al., 2012). There are a lot of research that has been made in order to find the suitable renewable sources to replace petroleum-based diesel and the researchers has agreed that biodiesel one of the most advantages type of diesel to be choose from (Nogueira et al., 2010). The discovery of biodiesel begin in the 1890s in Germany by Rudolph Diesel, when he was in search for the fuel to power early diesel engines for agriculture where at that present time the petroleum still has not yet been discovered. A lot of improvement has been made since then in order to produce the most beneficial type of diesel. In producing an economic type of biodiesel, the major concern is basically the type of feedstock to choose from and the suitable methods and materials (type of catalyst especially) for the process as depending on the different processes, they may present with variations of technical challenges.

2.2 Introduction

This paper presents the experimental studies of esterification of free fatty acid in waste cooking oil using novel solid acidic ionic liquid. This study is conducted in order to produce a more economic and efficient biodiesel as an alternative to replace fossil-based fuels. More thorough explanations will be clarified regarding the significance of this study in this chapter.

2.3 Biodiesel

The production of biodiesel that has rise from just 500 gallons in 1999 to 450 million gallons till the year of 2007 in the United States shows that it plays a big part in order to diversify the existing fuel that are slowly depleting and it is assumed that the production will gradually increase within the years (Chand et al., 2009). Biodiesel or Fatty Acid

Methyl Esters (FAME) is basically consisting of alkyl esters of fatty acids. Generally, biodiesel is yield from the transesterification process which is the reaction of triglycerides and alcohol such as methanol with the presence of base or acid catalyst (Wahlen et al, 2012).

This type of diesel that basically derived from renewable biological sources (vegetable oils and animal fats) has many advantages compared to the fuel in the present markets. From the previous studies, it has been found that biodiesel is environmentally friendly as it was able to lessen the pollutant gaseous (Gan et al., 2012). In comparison with the conventional fuels, biodiesel provides cleaner engine emission and this can be proved by the recent researched which states that there are reduction of unburned hydrocarbon particulate and carbon monoxide emissions (Yin et al., 2012; Wahlen et al., 2012). Plus, biodiesel is also biodegradable as it has shorter half-life in comparison with petroleum diesel. Because of its high solubility and biodegradation, biodiesel may also be one of the alternatives to be used in bioremediation in removing oils or polycyclic aromatic hydrocarbons (PAHs) in contaminated soils (Chien et al., 2009). Other than that, biodiesel is advantageous in engine lubricity as it provides better performance rather than the common diesel. The lubricity of diesel fuel was important in providing the protection for better performance. This is vital, as there have been plentiful examples from the field where lack of lubricity in the fuel has caused premature equipment breakdowns and in some cases, catastrophic failures (“Lubricity Benefits”, 2013). Moreover, the availability of the feedstock also gives a huge benefit in the production of biodiesel. There are varieties of feedstock (vegetable oils, animal fats, and waste cooking oils) in synthesizing the biodiesel. Typically, the main feedstock for biodiesel production is refined vegetable oils. However, the prices of these refined vegetable oils have been gradually increased over the past few years, which have caused the biodiesel production from this feedstock is unbeneficial.

2.4 Renewable Energy Sources: Feedstock

The availability and sustainability of sufficient supplies of less costly feedstock will be a fundamental factor in commercializing biodiesel to compete with other type of diesel. As has been mention before, there are several types of feedstock that can be used in producing biodiesel and it can be categorized into two parts which are edible feedstock and non-edible feedstock that includes of vegetable oil and animal fat.

2.4.1 Vegetable Oil

Biodiesel produced from vegetable oils can be used as an alternative diesel fuels because of its characteristics that are approximately similar to the petroleum-based fuels. For instance, they have the same viscosity value as the petroleum-based diesel fuel, their volumetric heating values are a bit lower, however their cetane number and flash points are quite high. The basic constituent of vegetable oils is triglyceride. As can be seen in Scheme 1, it shows the example of typical triglyceride molecule. Vegetable oils basically consist of 90 - 98% triglycerides and small amounts of mono- and diglycerides.

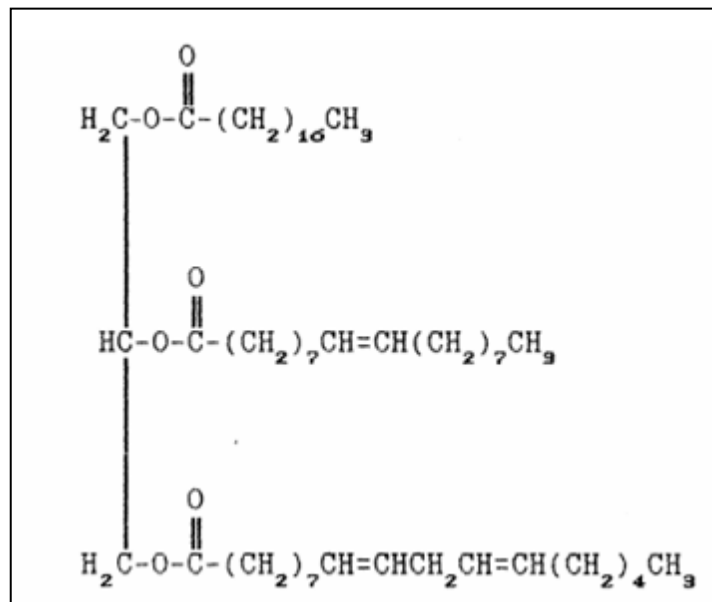


Figure 2-1: Structure of typical triglyceride molecules

These vegetable oils such as palm oil, soybean oil, peanut oil, sunflower seed oil, and cottonseed oil are widely used for the production of biodiesel, but most of this edible type of feedstock requires higher processing cost and the feedstock price itself are costly for most countries. As a future prospective fuel, the right choice of its raw materials must be always based on technical and economical aspects.

2.4.2 Animal Fats and Grease

Waste greases and animal fats can also be used as feedstock because of their availability and low cost. The use of animal fats without modification can improve fuel oil's

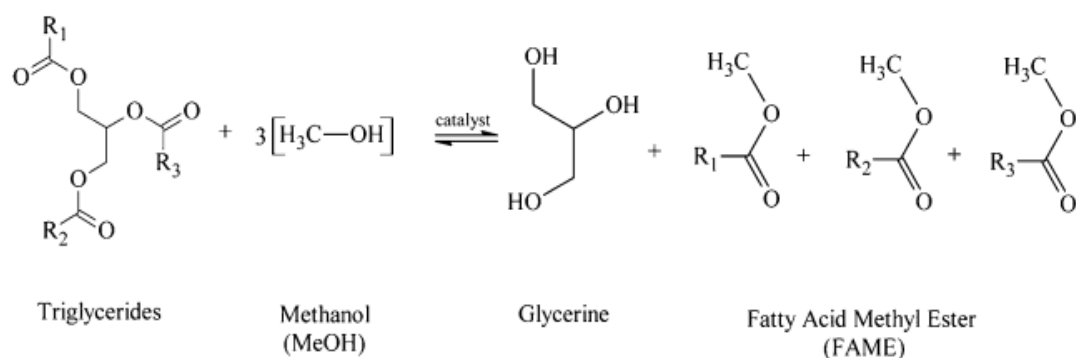
rheological properties. The problems that has arise where these waste greases ended up being disposed and can only be used in the soap industry can be solved by making it as the raw material in biodiesel production. Besides, animal fats are classified as low quality feedstock contrast to the refined vegetable oils due to their free fatty acids (FFA) content that may increase up to 15 wt % by contrast with refined soybean oil, which typically contains less than 0.5 wt % FFA (Canoira et al., 2008). The price of this yellow animal fat is around 419 euros/ton in contrast to the 2007 price of soybean oil of 780 euros/ton (“Agra Informa Ltd”) and probably increasing throughout the year. The use of waste animal fat feedstock for biodiesel production is a smart way in lowering the overall biodiesel production costs due to this price difference. Plus by using this type of feedstock has the advantages in various aspects such as quality, engine performance, and environmental problems.

2.4.3 Waste Cooking Oil (WCO)

The use of sustainable feedstock such as waste cooking oil (WCO) has become a main research distress due to the need to replace the used of edible vegetable oils as the biodiesel raw material despite the fact that the production of these vegetable oils has increase over the years. It has found out that the increase in industrial waste oil has caused the disposal problems to arise (Zhang et al., 2003) which has led to the environmental concern. Thus, this problem may be overcome by using these disposals as the feedstock for the biodiesel production. These low cost raw materials such as non-edible oil and WCO that representing 70% of the present biodiesel production cost (Demirbas, 2009) is likely popular among the researchers as a benefiting source to be used as the feedstock. The price of these WCO can be 2.5 to 3.5 times lower than the refined vegetable oil. Several studies have been carried out on biodiesel production from various oils that concentrate on type of oil, temperature of reaction, types of; ratio of alcohol to WCO, free fatty acid and moisture content. All of these factors are the critical aspect in the biodiesel production.

2.5 Production of Biodiesel

In the production of biodiesel, transesterification is one of the most commonly used methods. The reaction for the biodiesel process can be seen in Scheme 1 below.



^aR₁, R₂, and R₃ represent the fatty acids groups attached to the backbone of triglycerides.

Figure 2-2: General Reaction Scheme for Biodiesel Production^a (Abidin et al., 2012)

2.5.1 Transesterification

Transesterification process is a process where catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. Triacylglycerols, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol, the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters, the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters. Glycerol is the by-product of the process. Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes. Generally in a typical biodiesel reaction process, low temperatures will result in lower conversion, while higher temperatures lead to excessive methanol loss due to evaporation (boiling point of methanol is 64.7 °C). In base-catalyzed transesterification reaction, feedstock (oils and fats) of high FFAs content cannot be directly used. From the previous study, the FFAs content cannot be at least greater than 2% as the conversion of ester may be decrease if it is higher than that (Berrios et al., 2007). This is due to the stable emulsions are formed during saponification process which has lead to problems in separation process and also catalyst reutilization.

2.5.2 Esterification

Esterification is a chemical reaction where two reactants, an alcohol and an acid form an ester as the final product of reaction. It is a reversible reaction, thus many esterification reactions can be considered as equilibrium reactions. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel, and crude glycerol. Usually, methanol or ethanol is the alcohol used in the production where methanol produces methyl esters and ethanol produces ethyl esters where as potassium or sodium hydroxide is the base catalysed. Scheme 2.3 shows the reaction for esterification process where FFA is converted to FAME.

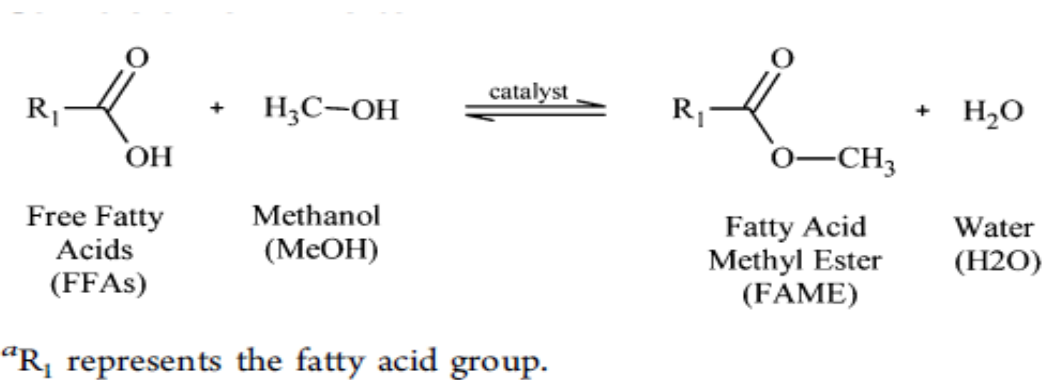


Figure 2-3: Reaction Scheme for Esterification Process: Conversion of FFA to FAME (Abidin et al., 2012)

2.6 Processes Variables Effecting Esterification

2.6.1 Catalyst

In obtaining vegetable oils with high quality, the alkaline catalysts show high performance, but the major concern is that the oils have quite number of FFA which cannot be converted into biodiesel but produce soap instead (Cardoso et al., 2008). Other option to process these vegetable oils is by using a Brønsted and Lewis acid catalyst. Nevertheless their high cost and high viscosities limited their applications in the industries.

2.6.1.1 Homogenous Catalyst

In the present years, homogenous acid types of catalyst are widely used in the biodiesel processes. The most common catalyst are sulphuric (H₂SO₄) acid and hydrochloric (HCl) acid. These types of catalyst have it disadvantages as it is soluble in the methanol. Some of the drawbacks that has arise by using this type of catalyst are it can cause the equipment to be corrosive, side reactions may exists, a substantial amount of wastewater may be generated, a high cost production due to supplementary equipment or reagents for separation or neutralization processes, and problems in catalyst reusability (Abidin et al., 2012).

2.6.1.2 Heterogenous Catalyst

Heterogenous type of catalyst such as zeolites, activated carbon, ion-exchange resins, single and mixed metal oxides and organic acid catalysts is the most suitable in the biodiesel processes (production and purification) due to its superficial properties that can ease the separation process from the reaction mixture. Therefore, the catalyst will able to be recycled for several times. Plus, this will lead to the waste reduction from the biodiesel production and lessen the environmental problems. Nevertheless, despite all of these advantages, the heterogenous type of catalyst also has it drawbacks in the terms of causing purification difficulty due to its certain solubility. In order to solve this problems further researched has been made on the investigation of supporting acid catalyst (ionic liquids) supported onto the surface of solid support (DVB). The supported acid catalysts has many advantages in comparison with the unsupported one as the separation process will be less difficulties, it has higher reusability and it will be very practically for the continuous process (Xu et al., 2010).

a) Zeolites Catalyst

Zeolites are popular catalysts for organic synthesis. General advantages for zeolites are that they can be synthesized with different crystal structures, framework Si/Al ratios, and proton exchange levels. This level of control when synthesizing zeolites makes it possible to maintain different properties such as size and structure of pores, strength of acid sites and their distribution, and surface hydrophobicity which offers

the additional advantages in achieving effective segregation of water which otherwise is reported to poison the catalyst acid sites. Although zeolites are active catalysts for esterification, they catalyze the reaction rather slowly due to the steric hindrance associated with bulky fatty acids, or due to poor adsorption inside zeolite pores. Plus, even though zeolite catalysts show high activity, the reaction always gives a variety of undesired by-products due to the use of higher reaction temperatures. Scheme 4 shows the basic structure of zeolite.

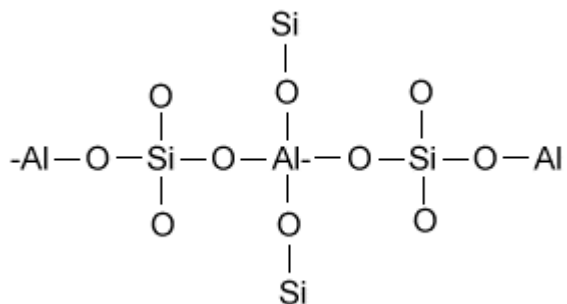


Figure 2-4: Basic structure of zeolite

b) Activated Carbon Catalyst

Multiplicity of reactions can be catalysed by using carbon. Due its low cost and variations of distinct physicochemical properties and morphologies, carbons are anticipated catalytic materials. Plus, as a catalyst support in liquid and vapour phase reactions, activated carbon is proven to be extremely effective (Buasri et al., 2012). The advantages of this catalyst are that it has a large surface area that lets the catalyst to diffuse over efficiently besides can be produced from a variety of raw materials.

Figure 5.2 shows the close up figure of activated carbon.

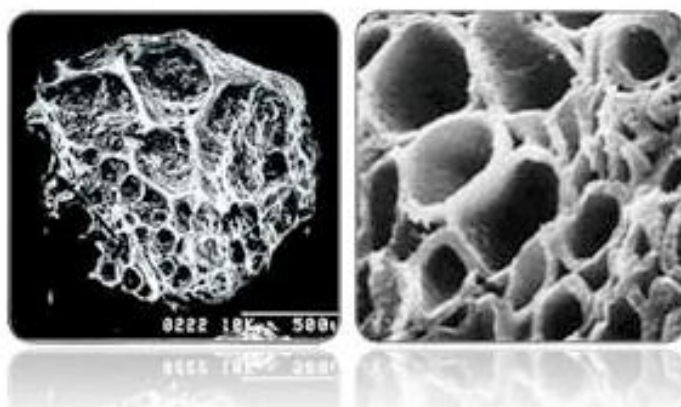
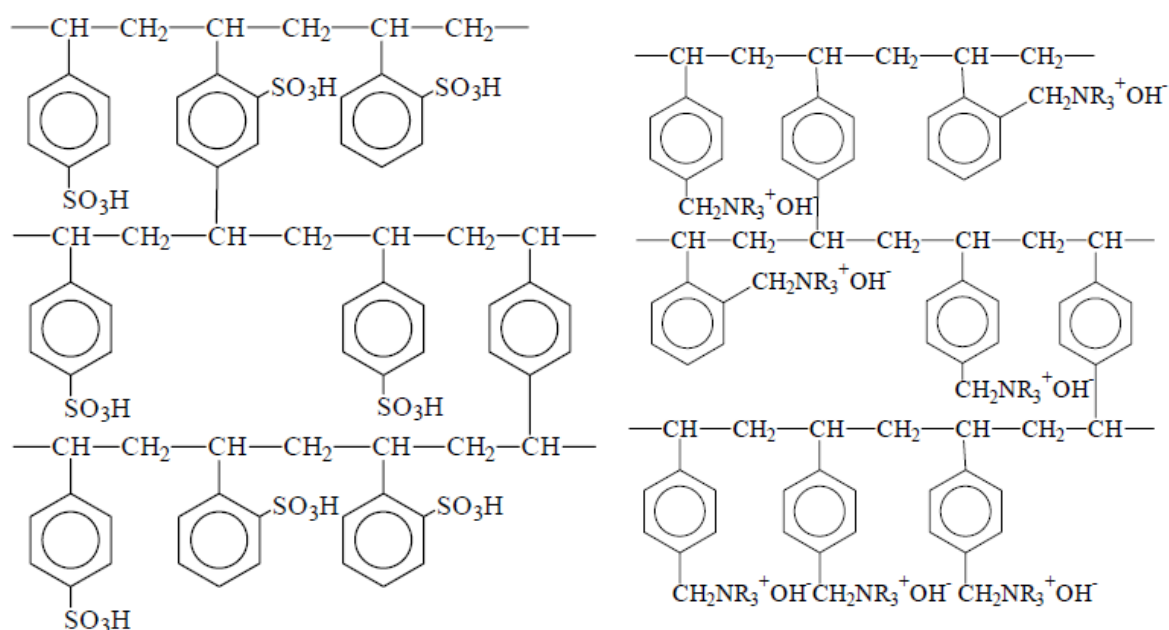


Figure 2-5: Close up figure of activated carbon

c) Ion-exchange Resins Catalyst

Ion-exchange resins are a type of polymers. They act by exchanging particular ions within the polymer with ions in a solution that is passed through them. The synthetic resins are used primarily for purifying water, but also for various other applications including separating out some elements.

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical adjustment to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers). Scheme 2.5 below shows some structures of ion-exchange resins.



A strongly acidic sulphonated polystyrene cation ammonium Exchange resin

A strongly basic quaternary anion exchange resin

Figure 2-6: Some examples of ion-exchange resins

Ion-exchange resins such as Amberlyst-15 and Nafion® are assured to be active catalysts for esterification due to its properties that have medium acid strength. Nevertheless, they have some drawbacks which the sulfonic acid cation exchange resins are not stable at temperatures higher than 140°C that inhibits the implication of these catalysts in a reaction that run at higher reaction temperature and they show

less activity due to diffusion limitations although they contain highly acidic sites in the reaction of carboxylic acids with long chains of hydrocarbon moieties (Suwannakarn, 2008).

d) Silica Mesoporous Catalyst

Silica mesoporous materials modified with sulfonic groups are utilized in pretreatment esterification reactions of high free fatty acid oils. This type of organic hybrid mesoporous silicas functionalized with sulfonic acid groups have shown successful results for acid catalyzed esterification by incorporating functionalized organic groups (Hermida et al., 2008). The hydrophobic character of SO_3H -mesoporous materials is beneficial for the overall conversion and selectivity. Fine tuning of catalyst hydrophobicity has been achieved by introducing methyl groups on the catalyst surface by a variety of well-known procedures. Figure 2.2 shows the structures of mesoporous M41S family of silica and aluminosilicates.



Figure 2-7: Structures of Mesoporous M41S Family: a. MCM-41 (2D hexagonal, space group $p6mm$); b. MCM-48 (cubic, space group $Ia\bar{3}d$); c. MCM-50 (lamellar, space group $p2$) (Hoffman et al., 2006)

e) Solid Supported Ionic Liquid Catalyst

Ionic liquid (IL) is a constituent that composed utterly of ions which appear in a liquid phase at room temperature. The IL comprises of organic cations and inorganic anions, even though it is not restricted to these combinations. IL is believed to have melting point of less than $100\text{ }^\circ\text{C}$, or accurately less than $50\text{ }^\circ\text{C}$, beside the fact that the IL can have a high melting temperature such as in the case of the molten salt form of NaCl . Due to the outstanding properties of ILs such as high conductivity, slight volatile pressure, wide electrochemical window and strong dissolution ability it has received high interest over the years. ILs of huge quantity have been applied in

the chemical synthesis where the ILs are used as solvents or as the catalysts (Liang et al., 2012).

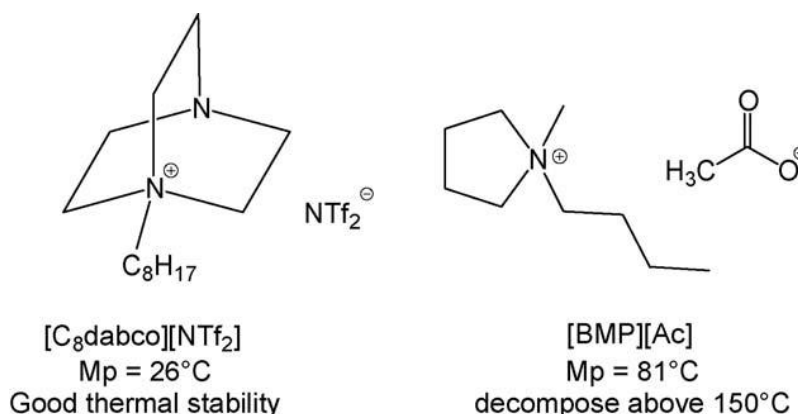


Figure 2-8: Examples of Basic ILs structure

The sulfonic acid groups functionalized ionic liquids owned high activities for acid-catalytic reactions (Sugimura et al., 2007). There are still some drawbacks even though the efficient procedures for various reactions (esterification, acetalization, and alkylation) are developed using the ILs. For an example, as certain solubility with some organic compounds, especially the polar molecules, this not only made the catalyst loss, but also had caused difficulty in the purification. Hence, the immobilization of ILs is a wise option. Some of the solid supported ionic liquid examples are where the acidic ionic liquids were immobilized on silica-gel and it high activities for acetalization were obtained (Miao et al., 2011). The sulfonic acid functionalized acidic ionic liquid modified silica catalyst was prepared and shown to be effective in the hydrolysis of cellulose. The polystyrene supported acidic ionic liquid showed high activities for esterifications (Xu et al., 2010). Besides the expensive reagents were used for the synthetic procedure, the recycled catalytic activities of the immobilized ionic liquid dropped a lot. The acidic molecules were dispersed on the surface, which decreased the synergistic effect. On the other hand, the acidic sites attached to the surface easily fell off, which made the recycled activities drop quickly. Polymeric ionic liquids which is a new class of materials, has develop an outstanding properties as electrolytes for electrochemical devices (Yamada et al., 2009). For this research, novel acidic polymeric ionic liquid from Brønsted acidic ionic liquid triethylammonium hydrogen sulphate (Et₃NHSO₄) and divinylbenzene (DVB) was studied. In order to confirm the cooperative effect of the ions, the monomer was polymerized and afterwards the oligomers were copolymerized with DVB. For the high polarity Ionic liquid was difficult to form the solid polymer. The use of DVB as the high hydrophobic BET

surface supplier has improved the mass transfer efficiency as well as prevents the acid sites releasing (Xu et al., 2010).

The selection of an appropriate catalyst is very crucial in designing the suitable transesterification process (Sivasamy et al., 2009). Thus after considering many aspects, ionic novel solid acidic ionic liquid seems the best choice for this experiment due to its advantages other than other type of catalyst.

2.7 Free Fatty Acid (FFA)

Fatty acid is a carboxylic acid with a long aliphatic tail or chain, which is either saturated or unsaturated. Fatty acids are usually derived from triglycerides or phospholipids. When these fatty acids are not attached to other molecules, they are called as free fatty acids. There are basically two types of free fatty acids. Fatty acids that have carbon-carbon double bonds are known as unsaturated and fatty acids without double bonds are known as saturated. Fatty acid chains can be differentiating via its length which classify as from short to very long.

- Short-chain fatty acids (SCFA) are fatty acids with aliphatic tails of fewer than six carbons (i.e. butyric acid).
- Medium-chain fatty acids (MCFA) are fatty acids with aliphatic tails of 6–12 carbons, which can form medium-chain triglycerides.
- Long-chain fatty acids (LCFA) are fatty acids with aliphatic tails 13 to 21 carbons.
- Very long chain fatty acids (VLCFA) are fatty acids with aliphatic tails longer than 22 carbons

2.7.1 Unsaturated FFAs

Unsaturated fatty acids have one or more double bonds between carbon atoms. The two carbon atoms in the chain that are bound next to either side of the double bond can occur in a *cis* or *trans* configuration. Table 2-1 below shows the examples of unsaturated fatty acids.

Table 2-1: Examples of unsaturated fatty acids

Common name	Chemical structure	Δx	C:D	n-x
Myristoleic acid	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	cis- $\Delta 9$	14:1	n-5
Palmitoleic	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	cis- $\Delta 9$	16:1	n-7

acid					
Sapienic acid	$\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$	cis- $\Delta 6$	16:1	n-10	
Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	cis- $\Delta 9$	18:1	n-9	
Elaidic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	trans- $\Delta 9$	18:1	n-9	
Vaccenic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_9\text{COOH}$	trans- $\Delta 11$	18:1	n-7	
Linoleic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	cis,cis- $\Delta 9,\Delta 12$	18:2	n-6	
α -Linolenic acid	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	trans,trans- $\Delta 9,\Delta 12$	18:2	n-6	

2.7.2 Saturated FFAs

Saturated fatty acids are long-chain carboxylic acids that usually have between 12 and 24 carbon atoms and have no double bonds. Thus, saturated fatty acids are saturated with hydrogen. Table 2.2 shows the example of saturated fatty acids.

Table 2-2: Example of saturated fatty acids

Common name	Chemical structure	C:D
Caprylic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	8:0
Capric acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	10:0
Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	12:0
Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	14:0
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	16:0
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	18:0
Arachidic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	20:0

2.7.3 Effect of FFAs

The amount of free fatty acid in vegetable oils can have a significant effect on the transesterification reaction. This feedstock frequently has noteworthy quantities of free fatty acids which make them unfitting for existing homogeneous alkaline-catalyzed processes (Suppalakpanya et al., 2011). It is said that free fatty acid levels above 5% can lower the ester conversion rate below 90%. When the FFA content is lower than 2.0%

wt, it was suitable for the raw material in transesterification process to produce biodiesel.

2.8 Water Content

In the transesterification of oil with alkaline catalysts, the vegetable oil and alcohol should be water free. When more water was added to the vegetable oil, the amount of methyl esters formed will be significantly reduced. The amount of water in the reaction mixture will determine the direction reaction. When there is little or no water, only esterification and transesterification are favored and when there is excess water in the reaction mixture, hydrolysis is the favored reaction when there is. The ester conversion is strongly inhibited by the presence of water in the oil. If the water concentration is greater than 0.5%, the ester conversion rate may drop below 90%. The presence of water also may cause ester saponification under alkaline conditions (Zhang et al., 2003).

2.9 Molar Ratio of Alcohol to oil and Type of Alcohol

Molar ratio of alcohol to oil is one of the important factors that affect the process conversion efficiency and the production cost of biodiesel. According to Garlapati et al. (2013), further increase in the alcohol (methanol) to oil ratio resulted in a decrease in the formation of esters. This may be due to the inhibitory effect of methanol on catalyst activity. Meanwhile, regarding the research by Canakci and Gerpen, (1999), they have found out that the higher conversion rates found for the longer chain alcohols compared with methyl ester are probably due to the higher reaction temperatures allowed by their higher boiling points. This effect apparently dominates any decrease in reaction rate associated with the longer chain alcohols. Table 2.3 shows some of the effect of alcohol type on ester conversion and specific gravity of ester.

Table 2-3: Effect of alcohol type on ester conversion and specific gravity of ester (Canakci and Gerpen, 1999)

Alcohol Type	Boiling Temperature (°C)	Reaction Temperature (°C)	Ester Conversion (%)	Ester S.G.
Methanol	65	60	87.8	0.8876
2-Propanol	82.4	75	92.9	0.8786

1-Butanol	117	110	92.1	0.8782
Ethanol	78.5	75	95.8	0.8814

Test conditions:

Molar ratio: 6:1; Sulfuric acid amount: 3%; Reaction time: 48 h.

It can be concluded that the ester conversion efficiency is strongly affected by the molar ratio of alcohol to oil. In acid-catalyzed esterification, a higher molar ratio is required than that of alkali-catalyzed (Zhang et al., 2003)

2.10 Reaction Time and Temperature

Reaction time and temperature are some of the important factor that affects the conversion of WCO to its ester. Heating is required for faster reaction and the reaction time may vary from a few minutes to several hours for acid catalysts.

The reaction time is not necessary to be long to increase the conversion of waste oil when the yield of FAME has been increased enough to avoid saponification and hydrolysis reaction in the transesterification reaction (Buasri et al., 2012).

From the research by Canakci and Gerpen (1999), the highest reaction temperature, 60°C, was selected because it is near the boiling point of methanol (65°C). By using sulphuric acid catalyst and a fix molar ratio of methanol to oil it shows that the ester conversion increased almost linearly with increasing reaction. It can be concluded that alcohols with high boiling temperature increase ester conversion. The higher reaction temperatures allowed by longer chain alcohols apparently dominate any tendency toward reduced reaction rates for these alcohols. Meanwhile, research by Buasri et al., (2012) also showed that the temperature led to higher reaction conversion with increasing temperature in studying the effect of reaction temperature on the conversion of WCO to FAME by using KOH supported on coconut shell activated carbon as a catalyst.

2.11 Mixing Intensity and Mode of Stirring

The rate of the transesterification reaction of vegetable oil with alkaline methanol solution strongly depends on the rate of mass transfer at the interface between glycerol–methanol and oil–ester phases. Generally, low reaction rates are observed in transesterification as a result of a poor dispersion of the methanol and oil phases, and an induction period can be often seen on the kinetic curves (slow initial reaction before

steady-state concentrations are reached). Therefore, intense mixing is very important for the transesterification process. Nouredini et al., investigated the effect of variations in mixing intensity during the transesterification of triglycerides to methyl esters in a pilot plant. The optimum stirring rates were in the range of 1000 rpm using both motionless and high-shear mixers.

2.12 Summary of Literature Review

Due to the high demand of diesel fuels especially in various industries such as automobiles industry, the production of biodiesel by using WCO seems the right decision because of the increasing price for the petroleum-based diesel worldwide. Moreover the effect which has caused by this type of non-environmental friendly diesel towards our worrisome environment condition also can be another factor in producing this type of biodiesel. In this chapter, detail review has been given regarding the process of biodiesel production. This thesis will mainly focus on the esterification process by using novel solid acidic ionic liquid as a catalyst. Next chapter will discuss about the materials and methodology for this thesis which will focus more on the catalyst characterization.

3. MATERIALS AND METHODS

3.1 Overview

This study will focus more on the characterization of the solid supported catalyst which are triethylammonium hydrogen sulphate ($\text{Et}_3\text{NH}\text{SO}_4$) supported with divinylbenzene (DVB). The FFA analysis by esterification reaction using a single formulation of supported ionic liquid polymer as a catalyst was studied.

3.2 Materials

Alpha-naphtholbenzein (indicator grade), divinylbenzene (DVB) (78.0-80.0%), diethyl ether ($\geq 98.0\%$), 0.1 M volumetric standard sodium hydroxide (NaOH), triethylamine ($\geq 99.5\%$), trimethyl-1-pentene (99.9%), acetonitrile (anhydrous, $\geq 98.0\%$), sulphuric acid ($\leq 98.0\%$ purity), azobisisobutyronitrile (99.0% purity), acetone ($\geq 99.5\%$), ethanol ($\geq 99.5\%$), 0.1 M potassium hydroxide solution in isopropanol, methanol (anhydrous, $> 99.8\%$), toluene (99.8%), 0.1 M volumetric standard hydrochloric acid ($\geq 37.0\%$), methyl red (99%) and isopropanol ($\geq 99.5\%$) were obtained from Sigma Aldrich Malaysia. The highly acidified oil will be prepared by mixing the cooking oil with oleic acid at certain proportion where the acid value is set at 15 mg KOH/g oil.

3.3 Experimental Methods

3.3.1 Catalyst Preparation

56 ml of triethylamine (0.4 mol) and 10 mL of anhydrous acetonitrile was mixed and stirred in a 250 mL round-bottom flask equipped with a reflux condenser, magnetic stirrer and N_2 gas inlet under cold condition. The mixture was continuously stirred for 4 hours under vigorous stirring. During the 4 hours of vigorous stirring, 21.32 ml (0.4 mol) of sulfuric acid were added in drop wise manner at room temperature. After the reaction completed, the mixture was washed with diethyl ether and trimethyl-1-pentene and dried under vacuum at 70 °C for 12 hours. The colourless Bronsted acid ionic liquid was obtained after repeated washing with diethylether and trimethyl-1-pentene. This viscous and colourless liquid was dried under vacuum at 60 °C for 12 hours, giving

Et₃NHSO₄ with 98% purity. The data of NMR spectroscopic, Fourier Transform Infra-Red (FTIR) and elemental analysis for the Et₃NHSO₄ sample was recorded.

Et₃NHSO₄ monomer (3.14 g, 10 mmol) 20 mL ethanol and 0.01 g Azobisisobutyronitrile (AIBN) were mixed together to form solution. After stirring at 70 °C for 4 hours, (DVB, 1.3g, 10 mmol) and AIBN (0.01g) were added to the mixture and stirred for another 4 hours. Then, the mixture was left for 12 hours at 80 °C to form a white organic gel. The gel was dried at room temperature overnight and ground to powders. The solid were washed with hot acetone and water until there were no traces of acidity detected from the filtrate. The novel solid acidic ionic liquid polymer were ready after drying at 120 °C overnight in a vacuum oven. The catalyst was characterized using surface area measurement, Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscopy (SEM). Figure 3-1 shows the synthesis route of the novel acidic ionic liquid polymer for this study.

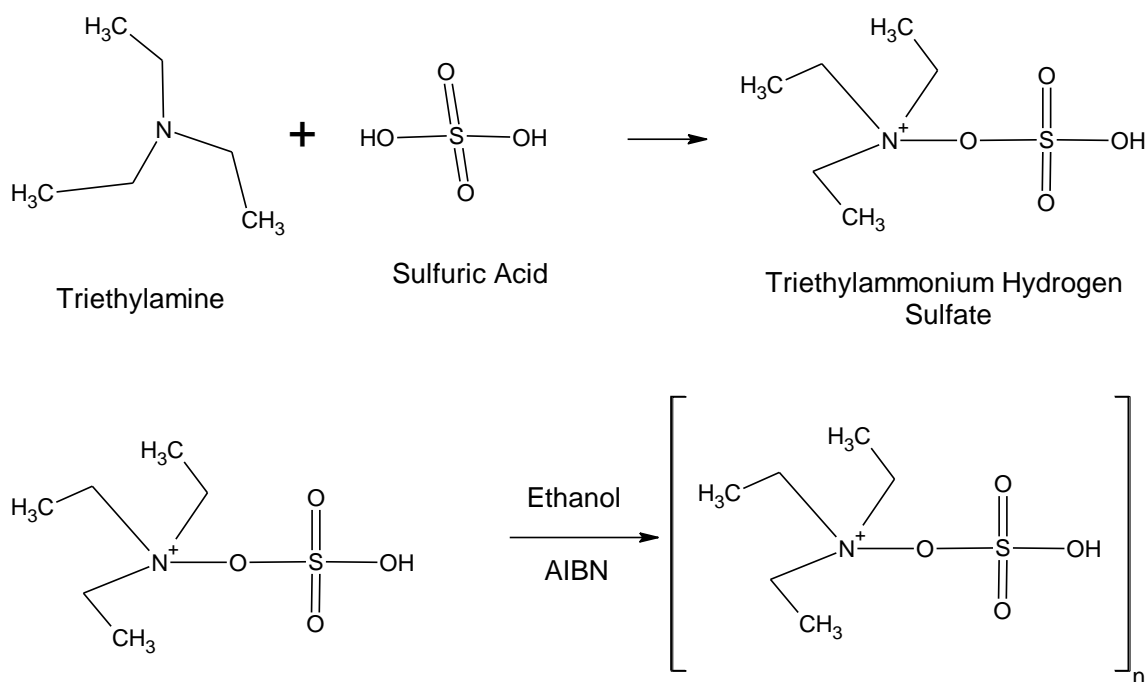


Figure 3-1: The synthesis route of the novel acidic ionic liquid polymer

3.3.2 Catalyst Characterization

a) Analysis of Nuclear Magnetic Resonance (NMR)

The analysis of NMR was conducted using Bruker AVANCE III, 500MHz Fourier Transform NMR (FT-NMR). This analysis provide support to magnetic resonance

research related activities such as identification of unknown substances, structure verification and elucidation, verification of compound purity for raw materials, quality control for chemical products, chemical reaction research, development of chemical products and structural properties of a materials, including amorphous and crystalline solids. In analyzing this analysis, the ^1H NMR spectrum of the ionic liquids supported with DVB were recorded after dissolution of the complex in CDCl_3 with TMS as reference (200 MHz). Figure below shows the 500 MHz Liquid/Solid NMR instrument.



Figure 3-1: 500 MHz Liquid/Solid NMR

b) Analysis of CHNS

The analysis of CHNS was conducted using Macro Elemental Analyzer CHNSO. It was used to determine Carbon, Nitrogen, Hydrogen and Sulfur content in the ionic liquid sample. For the CHNS analysis, freeze-dried and crushed samples are weighed (5-10 mg) and mixed with an oxidizer (vanadium pentoxide [V_2O_5]) in a tin capsule, which is then combusted in a reactor at 1000°C . The sample and container melt, and the tin promote a violent reaction (flash combustion) in a temporarily enriched oxygen atmosphere. The combustion products CO_2 , SO_2 , and NO_2 are carried by a constant flow of carrier gas (helium) that passes through a glass column packed with an oxidation catalyst of tungsten trioxide (WO_3) and a copper reducer, both kept at 1000°C . At this temperature, the nitrogen oxide is reduced to N_2 . The N_2 , CO_2 , and SO_2 are then transported by the helium to, and

separated by, a 2-m-long packed column (Poropak Q/S 50/80 mesh) and quantified with a TCD (set at 290°C). The chromatographic responses are calibrated against preanalyzed standards, and the CHNS elemental contents are reported in weight percent. Eager 200 software is used for running the equipment, storing the data, and for post-run analysis.



Figure 3-2: CHNOS Analyzer

c) Analysis of Scanning Electron Microscopy (SEM)

In analysing the morphology of the supported ionic liquid, scanning electron microscope method was used (Carl Zeiss EVO50). In order to eliminate the moisture, the catalyst was dried at 100 °C for 6 h time and stored in desiccators. Then by using a carbon conductive pad, the samples were mounted on a metal stub. The silver metals which acts as conductor were placed at both sides the sample. Lastly, under vacuum state and in an argon atmosphere, the samples were coated with gold and were observed. Figure below shows the Scanning Electron Microscope (Carl Zeiss EVO50) instrument.



Figure 3-3: Scanning Electron Microscope (Carl Zeiss EVO50)

3.4.3. Preparation of Simulated Waste Cooking oil

The simulated waste cooking oil was prepared by mixing the oleic acid of 5 wt% and the palm cooking oil. The solution was then stirred in the conical flask by using magnetic stirrer for about 10 minutes. The simulated waste cooking oil was then tested for its acid value by using titration method. The detail calculation can be seen in Appendix D.

3.4.4. Esterification of Free Fatty Acids (FFAs) in Waste Cooking Oil (WCO)

A 3-neck 250 mL round-bottom flask type of reactor was used for the esterification process. The reactor was aided by a mechanical stirrer, heating mantle, sampling outlet and reflux condenser to avoid from loss of reactant that may affect by the vaporisation. The temperature need to be monitored by using thermometer.

The reaction was started by adding WCO and methanol of specified quantity into the reactor. The mixtures was then stirred and heated. The time was set to zero when the required temperature was achieved and the catalyst was added into the reactor. Then the FFAs from the mixtures was analysed from time to time for about 3 hours hours in optimum catalytic condition (reaction temperature - 60°C, quantity of catalyst used – 5 wt%, methanol to WCO ratio – 6:1). In order for the samples to form two layers, the mixtures were moved into the separation funnel by allowing it to rest for overnight. The upper layer forms were consisted of excess methanol as well as the impurities. The bottom layer which were the mixtures of unreacted WCO, methanol traces, glycerine, esters and the retained catalysts were drained out from the separating funnel accompanied with the catalyst. The reusability study of the catalyst at optimum was also analyzed.

3.4.5. Free Fatty Acid (FFA) Analysis

ASTM standard method was used to analyse the FFA content in the esterification. In determining the acid value, ASTM D974 standard method was used with a mixture of toluene, isopropanol and small amount of water in forming a single solution phase. ASTM D974 acts as an equipment to identify the acidic and alkali constituents of

highly coloured oils and fats by mixing the sample in the mixture of isopropanol, toluene and small quantity of water which then form a solution of single phase. The consequential solution was then titrated at room temperature in the company of an alcoholic base solution. The end point is detected by the indicator, alpha-naphtholbenzein as the solution colour turned from orange to green. The acid value (AV) of the sample was defined as follows:

$$AV = \frac{M_w \times C \times V}{m \times f_0}$$

where M_w is the molecular weight of KOH, C is the molar concentration of KOH, V is the volume of KOH used in the titration procedure, m is the sample weight, and f_0 is weight fraction of FFAs in the beginning of the reaction. After the acid value was determined, the conversion of FFAs to fatty acid methyl esters (biodiesel) can be calculated by equation:

$$X = \left(\frac{FFA_0 - FFA}{FFA_0} \right) \times 100$$

where X is given as the conversion and FFA_0 is the initial free fatty acid value before the esterification reaction.

3.4 Summary

In this chapter, the materials and methodology has successfully elaborated for the research. Next, the result that had been obtained from this experiment will be discussed in detail.

4 RESULTS AND DISCUSSION

4.1 Overview

This chapter presents on the characterization of Et_3NHSO_4 IL and Et_3NHSO_4 supported with DVB as a catalyst. Plus, the results of esterification of FFA by using Et_3NHSO_4 supported with DVB as a catalyst will be further analysed.

4.2 Introduction

In this section, the results from the test that were made will be reviewed. The characterization by $^1\text{H-NMR}$, CHNS elemental analysis and FTIR for the Et_3NHSO_4 IL will be discussed. Then, the novel solid supported IL (Et_3NHSO_4 polymerized with DVB) will be further analyzed by the characterization of SEM, Surface Area Analyzer and FTIR. The FFA conversion of simulated cooking oil by using the first step esterification was discussed. The FTIR result of fresh catalyst and recycled catalyst were compared.

4.3 Characterization of Et_3NHSO_4 IL as a Catalyst

In this subtopic, characterization of Et_3NHSO_4 IL will be further discussed.

4.3.1 Analysis of Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$)

Figure 4-1 shows the NMR data for Et_3NHSO_4 IL sample.

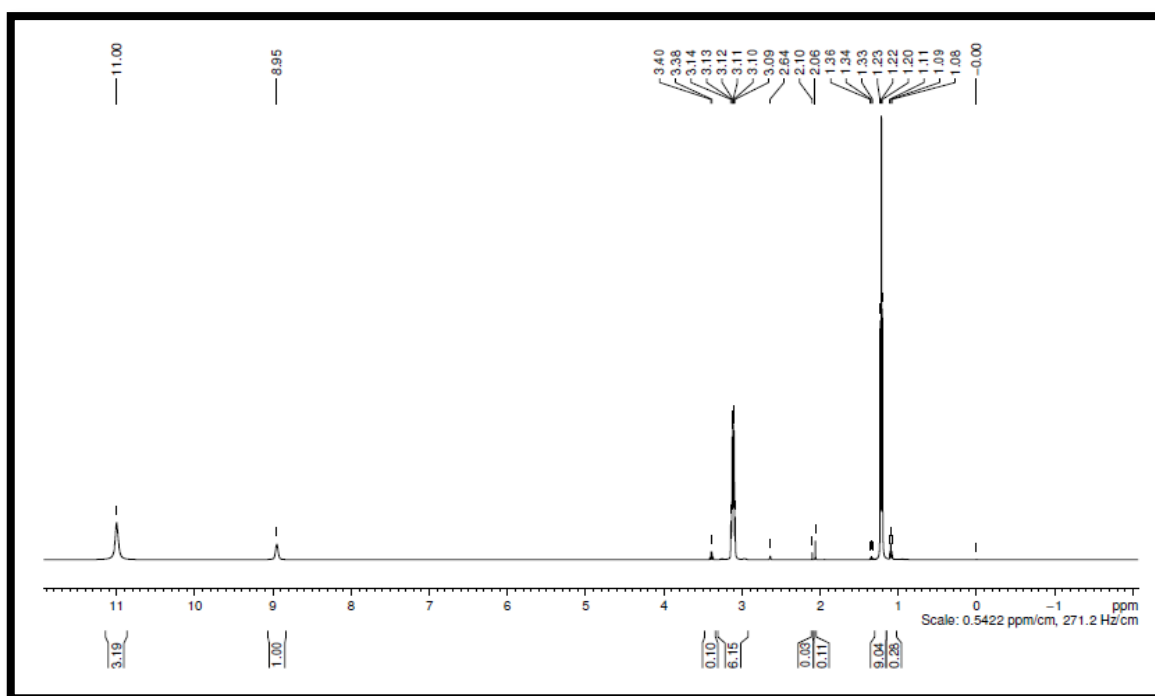


Figure 4-1: NMR data for Et₃NHSO₄ IL

From these data, the hydrogen integral obtained can be used to identify the number of hydrogen proton. The neighbour can be identify by using the equation of number of peak for each absorption (i.e.: triplet = 3 peak) minus with one. By identifying all of these data we can obtain the non-equivalent proton recognized and the structure for Et₃NHSO₄ IL sample can be obtained. Table 4-1 shows the summary of NMR spectroscopic data for the IL sample. Detail calculation on the integration can be found from Appendix C.

Table 4-1: NMR spectroscopic data for the IL sample

Absorption	ppm	Hydrogen Integral	No of H Proton	Neighbour	Non-equivalent proton recognized
[Ha] triplet	1.08-1.11	0.28	0	2	-
[Hb] triplet	1.20-1.23	9.04	7	2	H ₅ , H ₆ , H ₇
[Hc] singlet	2.06	0.11	0	0	-
[Hd] singlet	2.10	0.03	0	0	-
[He] sextet	3.09-3.14	6.15	5	5	H ₃ , H ₄
[Hf] doublet	3.38-3.40	0.10	0	1	-
[Hg] singlet	8.95	1.00	1	0	H ₁
[Hh] singlet	11.00	3.19	3	0	H ₂

The NMR spectroscopic data recorded for the IL samples can be summarised as: ^1H -NMR (500 MHz, DMSO) (ppm): δ 1.08-1.11 (triplet, 0.28H), 1.20-1.23 (triplet, 9.04H), 2.06 (singlet, 0.11H), 2.10 (singlet, 0.03H), 3.09-3.14 (sextet, 6.15H), 3.38-3.4 (doublet, 0.1H), 8.95 (singlet, 1H), 11.00 (singlet, 3.19H). Figure 4-2 shows the comparison between Structure of Et_3NHSO_4 IL obtained from NMR analysis and the expected structure of Et_3NHSO_4 IL. The structure obtained were not exactly the same but the numbers of hydrogen proton were still the same (16 hydrogen proton).

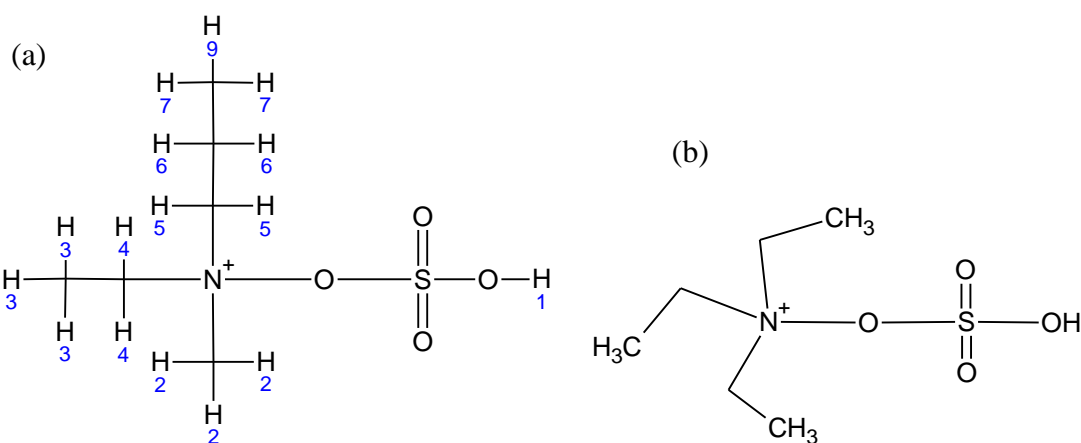


Figure 4-2: (a) Structure of Et_3NHSO_4 IL obtained from NMR analysis (b) Expected structure of Et_3NHSO_4 IL

4.3.2 Elemental Analysis

Elemental analysis is done by using CHNS analyzer. The result of elemental analysis is presented in Table 4-2

Table 4-2: Elemental Analysis for Et_3NHSO_4 IL ^a

Compounds	Molecular Weight	% Analysis found (Calculation)				
		C	H	N	S	O ^b
Et_3NHSO_4	199.27	26.01 (36.16)	6.21 (8.60)	8.12 (7.03)	19.9 (16.09)	39.76 (32.12)

^a Percentage are in w/w %. ^b Oxygen by difference.

As oxygen could not be obtained in this analysis, the oxygen content can be getting by the difference of C, H, N, S elements' weight percentage. From the calculation, the expected weight percentage of C, H, N, S, and O can be seen in Table 4-2. Results of

the expected value must be within $\pm 10\%$ of true values from the CHNS analysis for the catalyst to be considered accurate.

Table 4-3 Et_3NHSO_4 true values and control limits ($\pm 10\%$ true Values)

Element	Expected Values	True Values	$\pm 10\%$ true Values
C	36.16	26.01	23.4–28.61
H	8.60	6.21	5.59–6.83
N	7.03	8.12	7.31–8.93
S	16.09	8.12	17.99–21.99
O	32.12	39.76	35.78–43.74

When comparing with the expected values for CHNS wt % of Et_3NHSO_4 with the true values, the values exceed the control. Nevertheless, the error of the standard values and control limits were not that much of difference.

From the elemental analysis, the empirical formula can be found for the Et_3NHSO_4 catalyst and can be compared with the actual value.

Table 4-4: Empirical data for Et_3NHSO_4

Element	Weight %	No of mole	Mole ratio
C	26.01	2.17	4
H	6.21	6.16	11
N	8.12	0.58	1
S	19.9	0.62	1
O	39.76	2.49	4

From the Table 4-3 above, the no. of mole for each element can be get by the formula:

$$= \text{Weight percentage of element} \times \frac{1 \text{ mol of element}}{\text{Molecular weight of element}}$$

Detail calculation on the CHNS result can be found in Appendix C.

From the no of mole of each element, the ratio for CHNSO is 2.17: 6.16: 0.58: 0.62: 2.49. Thus, by dividing the lowest no of mole ratio, the empirical formula for this sample is $\text{C}_4\text{H}_{11}\text{NSO}_4$. The empirical formula from this analysis is differed with the expected empirical formula which is $\text{C}_6\text{H}_{16}\text{NSO}_4$. The values might be slightly exceeding the limits due to the IL that was produced was not that purified. During the

catalyst preparation, the vacuum line was not available during the process. The vacuum line was supposedly used after the process of removing the reaction by product (water) for further purification of the IL as the catalyst. Because of the unavailability of this type of equipment, the IL that was produced was not that purified.

4.3.3 Analysis of FTIR

An FTIR spectroscopic study has been done in determining the functional group of Et_3NHSO_4 IL. Table 4.4 below shows the peak that has been found in the analysis (detail peaks value can be seen in Appendix C).

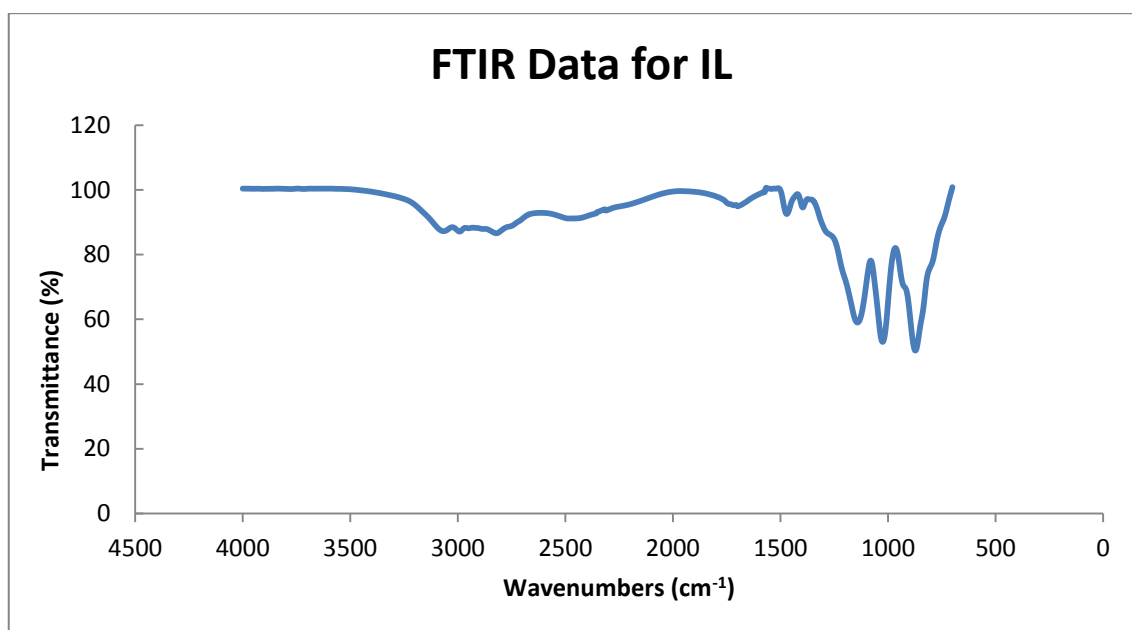


Figure 4.3: The IR spectrum for Et_3NHSO_4

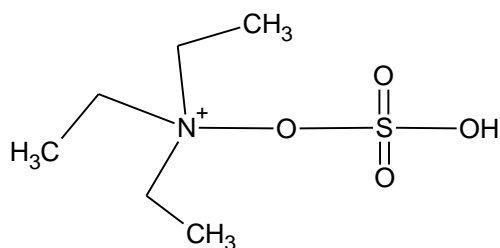


Figure 4-3: Structure of Et_3NHSO_4 IL

Table 4-5: FTIR Analysis Data for Et_3NHSO_4

Wavenumber (cm^{-1})	Bond Type	Functional Group
1141.61 & 1395.97	S = O	Sulfones

1024.74	C – N	Amines
3065.84 - 2821.10	C – H	Alkanes
3779.14 - 3716.51	O – H	Alcohols
1540.87 -1470.44	N – O	Nitro compounds

From figure 4.4, the characteristics peak at 1395.97 cm^{-1} , and 1141.61 cm^{-1} were due to the stretching vibration of sulfonic acid group S=O. The peaks at 1024.74 cm^{-1} was due to presence of C-N alkyl stretching vibration. Meanwhile, the bands from 3065.84 cm^{-1} to 2821.10 cm^{-1} indicate the C-H stretching vibration of alkanes. The peak at 3716.51 cm^{-1} exhibits the weak O-H absorption as O-H absorption was normally at $3600 - 3200\text{ cm}^{-1}$.

4.4 Characterization of Novel Solid Acidic IL (Et_3NHSO_4 Immobilized with DVB)

4.5 Analysis of SEM

SEM was performed to characterize the morphology of polymerized IL Et_3NHSO_4 supported with DVB. Figure 4.1 shows the images of SEM for supported IL. From the images, it can be seen that the supported IL presence in irregular sphere like and within a size range of 1-2 μm structure. As the particles portrayed uniform structure, it was assumed that throughout the synthetic process the copolymerization were successfully done (Liang et al., 2013). Moreover, the cross-linked products and the structure were generally ties with each other.

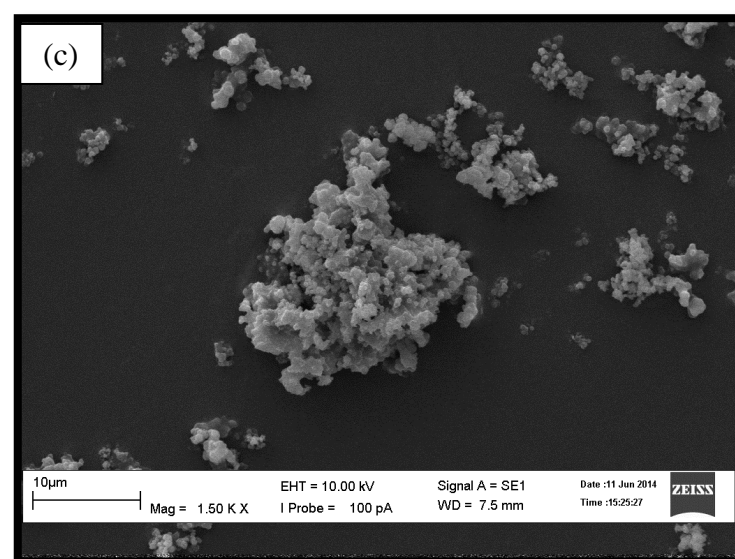
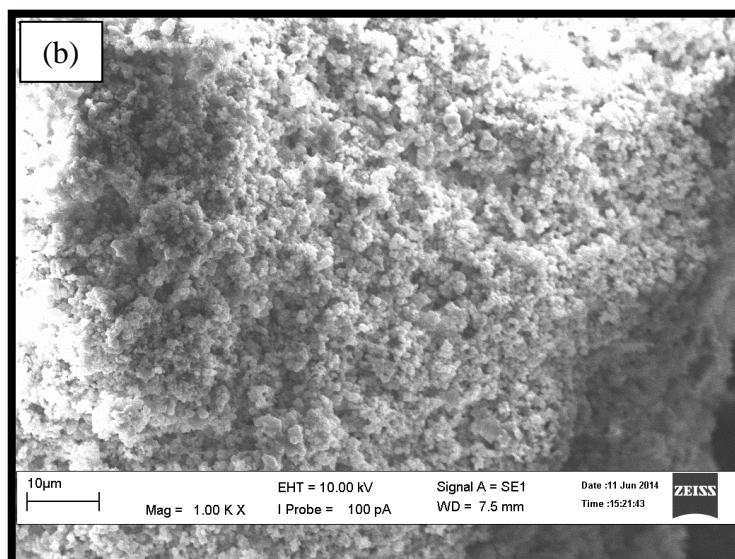
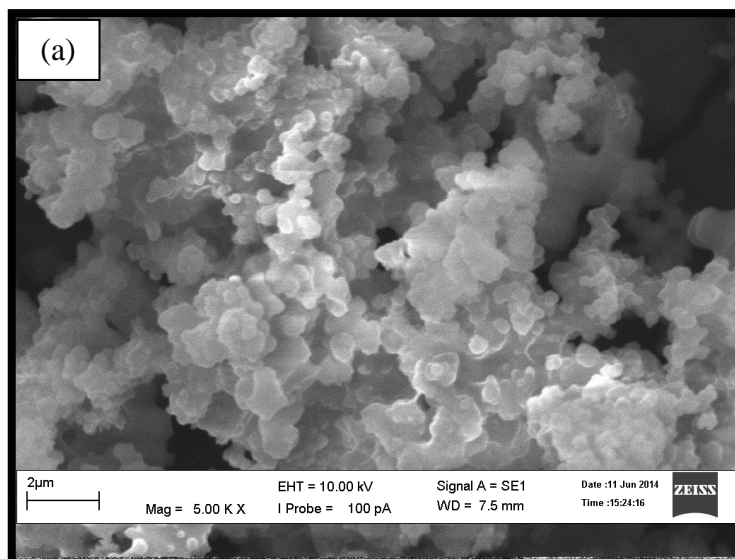


Figure 4-4: The SEM images of Et_3NHSO_4 polymerized with DVB

4.6 Characterization Study of Supported IL Polymer: Comparison between Fresh Catalyst and Recycled Catalyst

FTIR studies was carried out in order to check on the presence of structure bonding during the immobilization of Et₃NHSO₄ component on the support DVB and to ensure the stability of the catalyst.

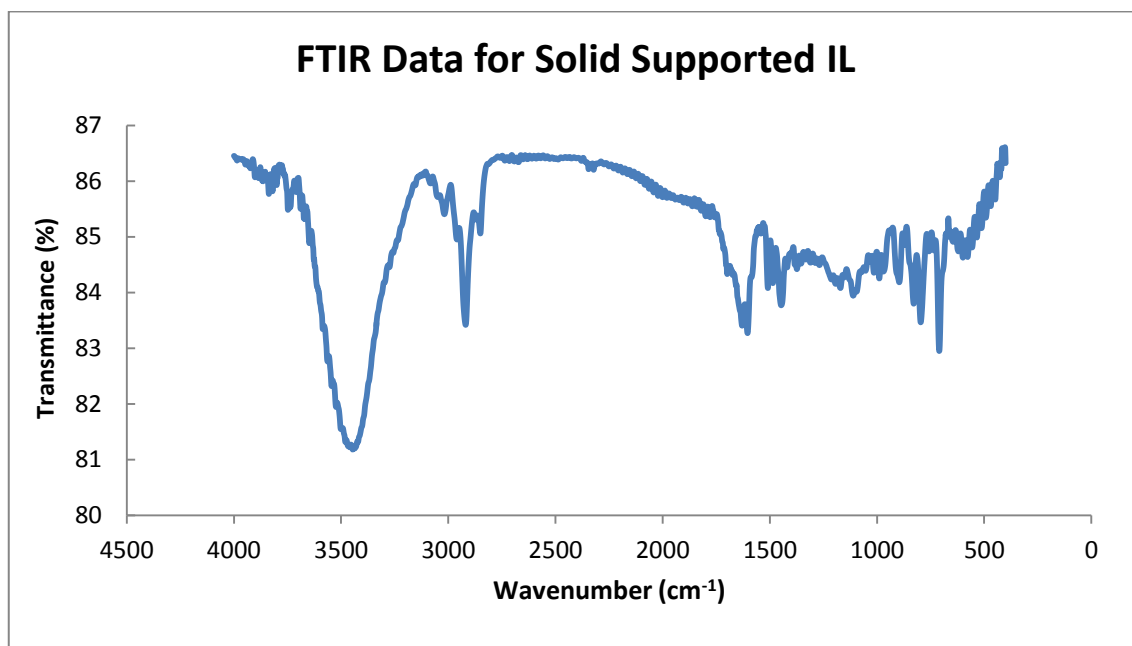


Figure 4-5: The IR Spectrum of Et₃NHSO₄ polymerized with DVB

From Figure 4-5, it shows signal 1014.37 cm⁻¹ and 806.46 cm⁻¹ showed the presence of the sulfonic acid group. The result also shows the presence of C-C at peak 1171 cm⁻¹, Ar-H bond at peak 2959.94 cm⁻¹ and O-H at peak 3446.13 cm⁻¹. Nevertheless, there are also some peak that was identified to be C = C (1698.95 – 1604.04 cm⁻¹) and C-H (709.63 – 896.46 cm⁻¹) bond aromatic type of functional group in this analysis which were recognized to be from DVB structure. The other peaks that were not mentioned were identified as contaminants in the sample. Detail peaks value can be seen in Appendix C. Table 4-5 below shows the summary for FTIR analysis for Et₃NHSO₄ supported with DVB.

Table 4-6: Table of Summary for FTIR analysis for Et₃NHSO₄ supported with DVB

Wavenumber (cm ⁻¹)	Bond Type	Functional Group
1171.00 & 1354.07	S = O	Sulfones
1193.59 – 1031.74	C – N	Amines
2959.94 – 2919.06	C – H	Alkanes

3446.13	O – H	Alcohols
1540.87 -1470.44	N – O	Nitro compounds
1698.95 – 1604.04	C = C	Aromatic
709.63 – 896.46	C - H	Aromatic
1171	C - C	Ketones

Figure 4-6 shows the IR spectrum of recycled Et_3NHSO_4 polymerized with DVB. From the graph, it can be seen that the IR spectrum data for the recycled solid supported catalyst has changed as compared to the fresh solid catalyst. All of the functional group was available in the structure. It shows that at peak $1166.94.00\text{ cm}^{-1}$ and 1377.12 cm^{-1} the sulfonic acid group absorbability occurs. The result also shows that the catalyst have residence functionalities including of C-C at peak 1166.94 cm^{-1} , Ar-H at peak $2959.94 - 2919.06\text{ cm}^{-1}$ and O-H at peak 3414.55 cm^{-1} . There were also some peak that was identified to be C = C ($1744.22 - 1638.38\text{ cm}^{-1}$) and C-H ($709.10 - 903.75\text{ cm}^{-1}$) bond aromatic type of functional group in this analysis which were recognized to be from DVB structure. However, same with the analysis of the fresh catalyst, there were some peak that was identified to be contaminants in the sample. Detail IR spectrum data value can be seen in Appendix C.

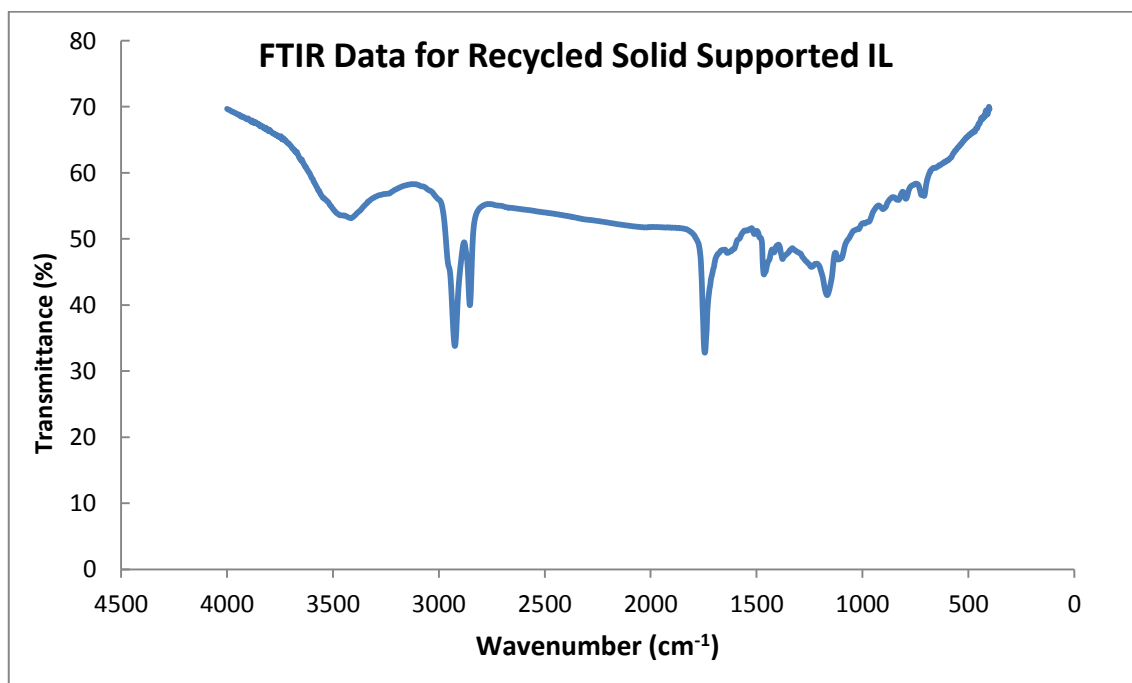


Figure 4-6: The IR Spectrum of Recycled Et_3NHSO_4 polymerized with DVB

Table 4-6 below shows the summary for FTIR analysis for Et_3NHSO_4 supported with DVB.

Table 4-7: Table of Summary for FTIR analysis for Recycled Et₃NHSO₄ Supported with DVB

Wavenumber (cm ⁻¹)	Bond Type	Functional Group
1166.94.00 & 1377.12	S = O	Sulfones
1114.16 – 1240.76	C – N	Amines
2959.94 – 2919.06	C – H	Alkanes
3414.55	O – H	Alcohols
1510.67 -1417.30	N – O	Nitro compounds
1744.22 – 1638.38	C = C	Aromatic
709.10 – 903.75	C - H	Aromatic
1166.94	C - C	Ketones

Figure 4-7 shows the comparison of IR spectrum for Et₃NHSO₄ polymerized with DVB and recycled Et₃NHSO₄ polymerized with DVB. It can be seen that the IR spectrum data for both analysis was slightly different. This can be due to the yield that has obtained for both catalysts were not the same. For the fresh catalyst, the weight obtained is 3.9 g but after the process of recycled to recover the catalyst, the weight obtained was 4.7 g which was slightly increased. This must be due to the process of separating the catalyst with the oil after esterification process, the oil was not completely removed from the catalyst. In order for the catalyst to have high stability and the properties of the catalyst to not changed, the yield must be constant (Liang et al., 2013).

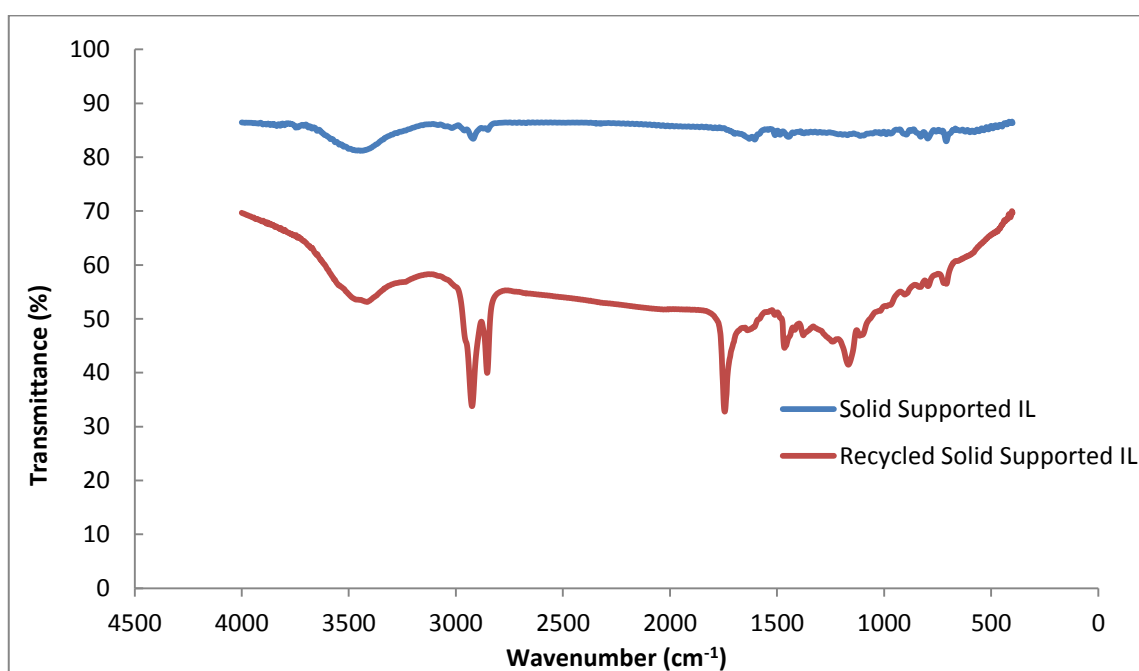


Figure 4-7: The comparison of IR Spectrum of Et₃NHSO₄ polymerized with DVB and Recycled Et₃NHSO₄ polymerized with DVB

4.7 Esterification of FFA Using Novel Solid Acidic IL (Et₃NHSO₄ polymerized with DVB) as a Catalyst

The esterification of the FFA of the simulated waste cooking oil with the acid value of 12 mg KOH/g sample was carried out using Et₃NHSO₄ polymerized with DVB as the catalyst in the first stage at the optimum reaction condition. Reaction temperature of 60°C was chosen for the optimum temperature as according to Leung and Guo, (2006), the outcomes of their study indicates that any temperature above 50 °C shows good catalytic activity for used oil but negative outcome for virgin oil. According to Srilatha et al. (2009), with the increase of catalyst quantity, the rise in activity is expected, as the number of available catalytic active sites is growing. Thus, based on their study the quantities of catalyst used was 5 wt%. 6:1 methanol to WCO molar ratio was used for this reaction as excess methanol could lead the solubility of glycerine to increase which cause the reduction of FAME yield as glycerol stays in the pre-treated WCO phase (Abidin et al., 2012). Table 4-5 shows the data of FFA value mg KOH/g sample.

Table 4-8: Data for FFA Analysis

Time (hour)	Time (minutes)	Burette Reading	Weight	Acid Value (mg KOH/g sample)	FFA Value (mg KOH/g sample)	FFA conversion (%)
	0	3.3	2.038	8.81	4.37	0.00
1st hour	30	3.0	2.001	8.13	4.03	7.70
	60	2.6	2.161	6.49	3.22	26.32
	90	2.1	2.019	5.56	2.75	36.91
2nd hour	120	1.5	2.018	3.89	1.93	55.82
	150	1.0	2.123	2.38	1.18	73.00
3rd hour	180	0.9	2.086	2.12	1.05	75.94

Figure 4-4 shows the graph of FFA Conversion (%) varies with time by using Et₃NHSO₄ Polymerized with DVB as the Catalyst. From this graph, it can be seen that after 180 minutes (3 h) of reaction time, the FFA conversion that has been achieved is 75.94 %. The conversion of FFA increased as time escalates. However, in between 1–2.5 h the conversions reached their maximum values and after that there was no much variation. This esterification reaction of the FFA in WCO by using the novel solid

acidic ionic liquid, Et_3NHSO_4 supported with DVB can be said to display good performance according to the conversion obtains. Nevertheless, it is still not as good as previous study which some of them can obtain up to 98.2 % FFA conversion based on the same type of catalyst - novel solid acidic ionic liquid polymer (Liang et al., 2013). As this reactions was conducted for only three hours time, the validity of the optimum conversion could not be affirmed as based on other researches that study about esterification of FFA, most of them conduct the experiment for about 8 to 14 hours (Zhang et al., 2009; Liang et al., 2013)

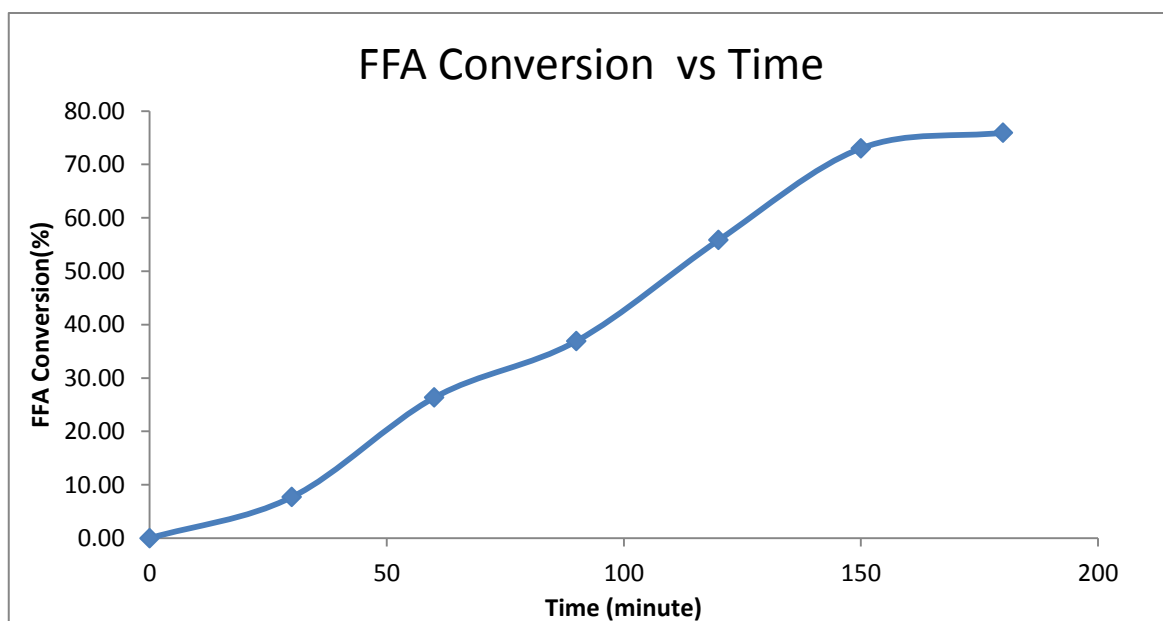


Figure 4-8: FFA Conversion (%) using Et_3NHSO_4 Polymerized with DVB as the Catalyst

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, this research was conducted in order to synthesize the esterification of free fatty acids in a feedstock namely waste cooking oil (WCO) by using the DVB supported Et_3NHSO_4 Bronsted acidic ionic liquid catalysts. The novel solid acidic catalyst has been studied by synthesizing and characterizing using $^1\text{H-NMR}$ Nuclear Magnetic Resonance analysis, elemental analysis (CHNS), Fourier Transform-Infra Red (FT-IR) and Scanning Electron Microscopy (SEM) analysis which is the focus of this study based on previous researched. Some preliminary works has been done and the expected result was obtained. For the esterification reaction of the FFA in WCO, the novel solid acidic ionic liquid, Et_3NHSO_4 supported with DVB display good performance by showing 75.94 % FFA conversion in three hours reaction time in the optimum catalytic reaction conditions. Nevertheless, it is still not as good as previous study which some of them can obtain up to 98.2 % FFA conversion based on the same type of catalyst - novel solid acidic ionic liquid polymer (Liang et al., 2013). For the reusability study, it can be seen from FTIR analysis that the peak of the fresh catalyst and recycled catalyst was slightly different due to the yield of both of the catalyst are differed.

5.2 Recommendations

For this study there are some recommendations that can be done in order to improve the catalyst performance and to obtain better FFA conversion. The esterification reaction should be tested with varies of molar ratio of methanol to WCO, effect of reaction temperature, mass transfer resistance and catalyst loading. Plus, the experiment should be repeated three times to ensure the validity of conversion FFAs obtain. Other than that, the catalyst should be prepare meticulously with the aid of fully equipped equipment.

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APPENDICES

APPENDIX A CATALYST PRODUCTION

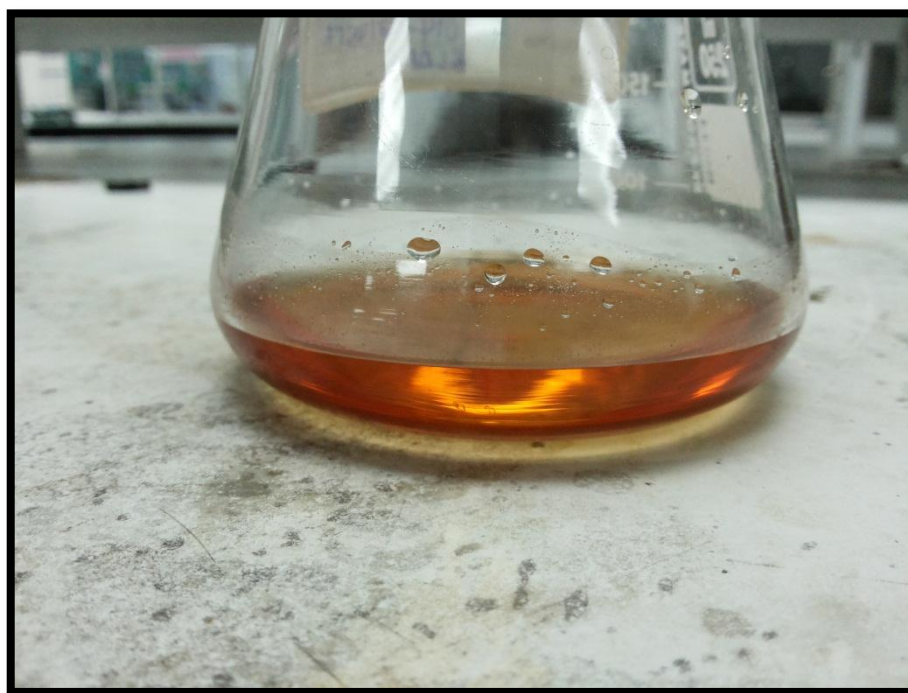


Figure Appendix 1: Triethylammonium hydrogen sulphate IL obtained

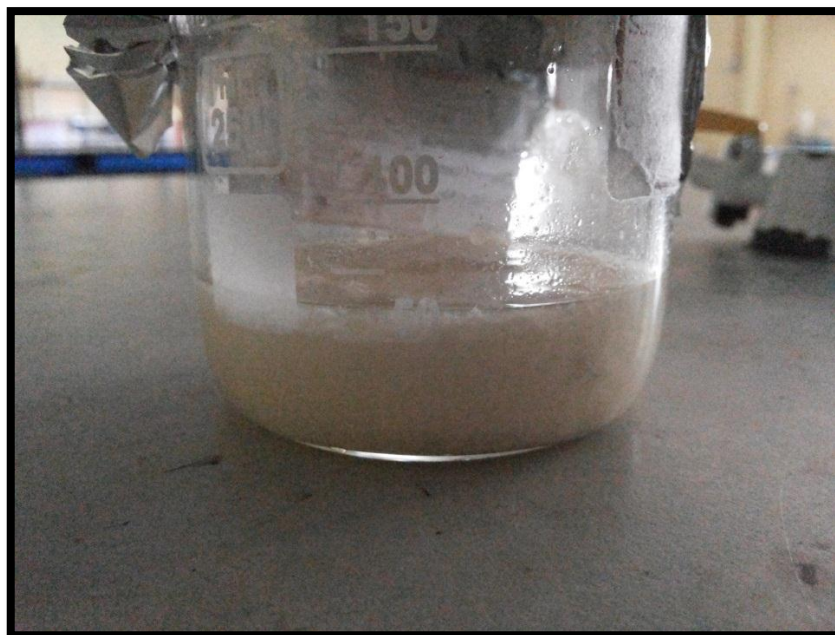


Figure Appendix 2: Solid Supported IL obtained after drying in 80°C oven for 12 hours



Figure Appendix 3: Solid Supported IL obtained

APPENDIX C

CHARACTERIZATION OF CATALYST

H-NMR Data

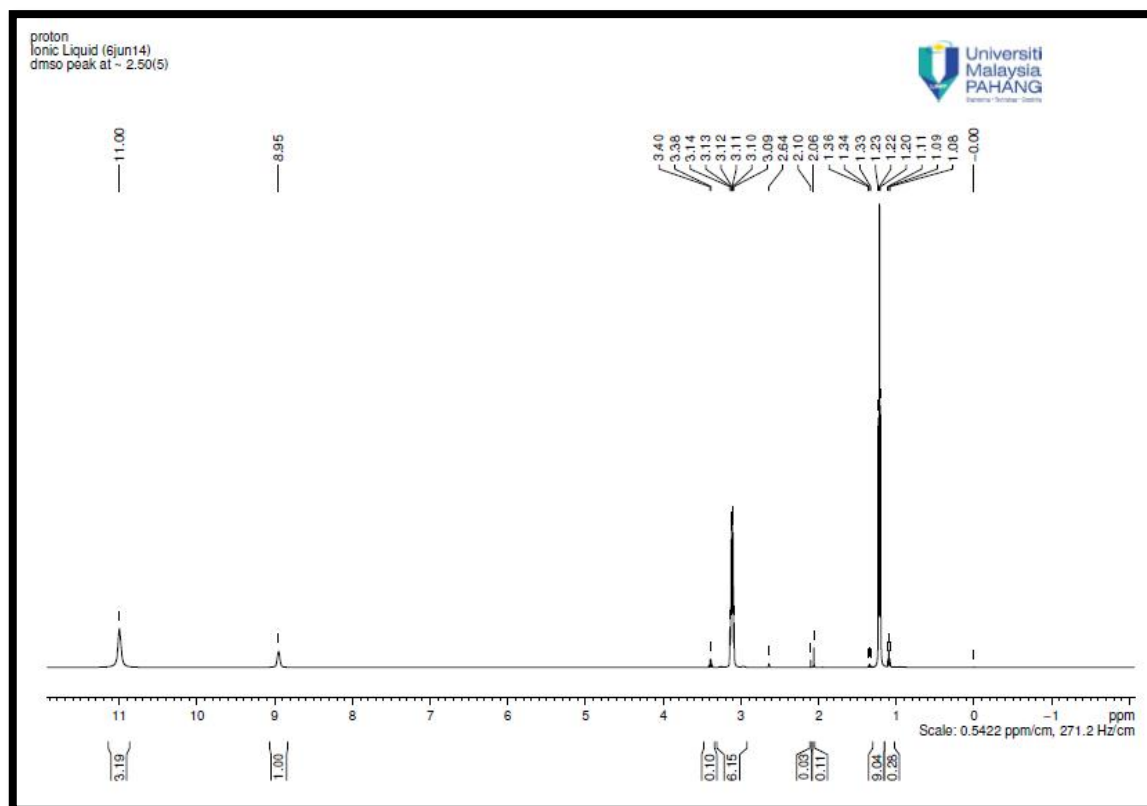


Figure Appendix 4: H-NMR Data for Et₃HSO₄ IL

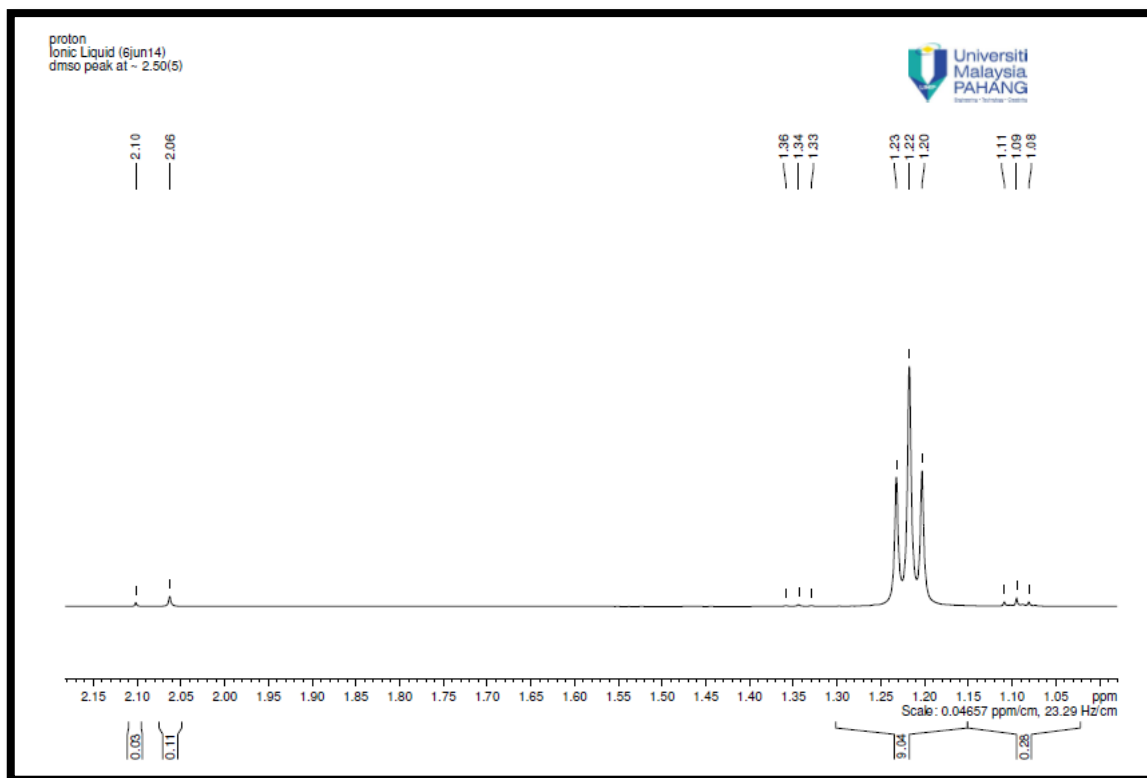


Figure Appendix 5: H-NMR Data for Et₃HSO₄ IL zoom 1

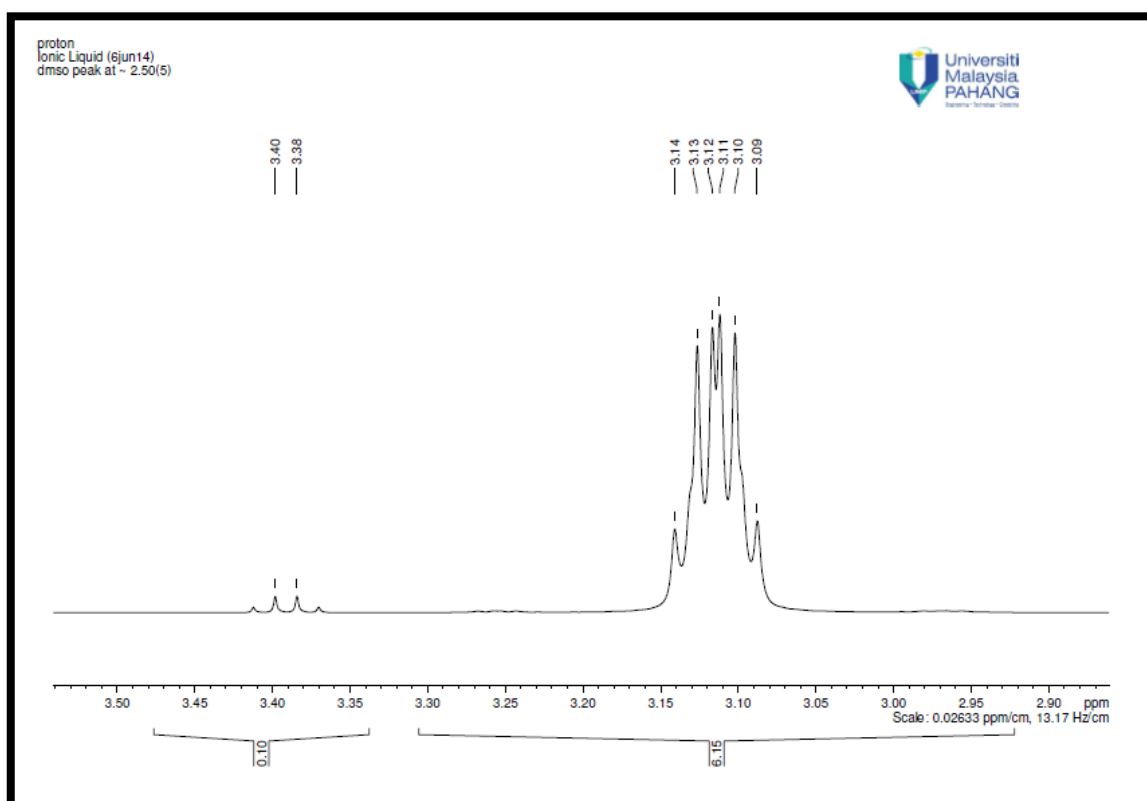


Figure Appendix 6: H-NMR Data for Et₃HSO₄ IL zoom 2

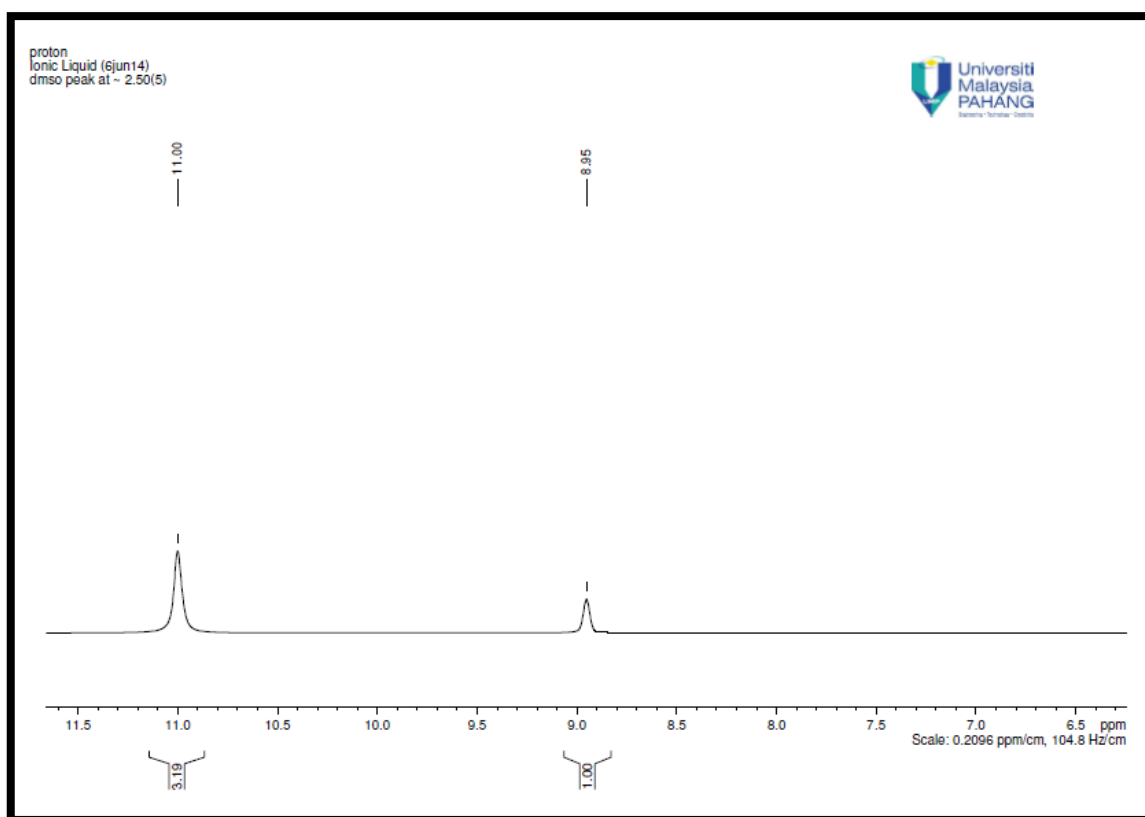


Figure Appendix 7: $^1\text{H-NMR}$ Data for Et_3NHSO_4 IL

Calculation for $^1\text{H-NMR}$ Data

In determining the number of hydrogen proton in the sample, we must sum all the hydrogen integral from the NMR data.

$$\text{Sum of integral} = 0.28 + 9.04 + 0.11 + 0.03 + 6.15 + 0.10 + 1.00 + 3.19 = 19.9$$

As we know that in Et_3NHSO_4 there are 16 hydrogen atoms ($\text{C}_6\text{H}_{16}\text{NSO}_4$).

Then, a/b can be get by dividing summation of integral with the number of Hydrogen proton for the expected IL structure as can be seen in table below.

Sum of integral, a	No of Hydrogen Proton, b	a/b
19.9	16	1.24375

Thus, the number of hydrogen proton can be get by the equation:

$$\text{No of H proton} = \text{Hydrogen integral} / (a/b)$$


Absorption	ppm	Hydrogen Integral	No of H Proton	Neighbour
[Ha] triplet	1.08-1.11	0.28	0	2
[Hb] triplet	1.20-1.23	9.04	7	2
[Hc] singlet	2.06	0.11	0	0
[Hd] singlet	2.10	0.03	0	0
[He] sextet	3.09-3.14	6.15	5	5

[Hf] doublet	3.38-3.40	0.10	0	1
[Hg] singlet	8.95	1.00	1	0
[Hh] singlet	11.00	3.19	3	0

The neighbour number can be get from the number of peak of each integral minus with 1. For example, if the number of peak is three (triplet), the number of neighbour is 2. Thus, the

CHNS data

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CERTIFICATE OF ANALYSIS (COA)

To :	SHABIRAH BINTI EZAN	Attn :	
Address :	FAKULTI KEJURUTERAAN KIMIA & SUMBER ASLI, UMP		
C.C. :		Page :	1 pages
Fax No :		Tel No :	014-5288849
		Sample Lab No :	2014/207

Sample description : 1 liquid sample
 Sample marking : Ionic Liquid
 Date of sample received : 08/04/2014
 Date reported : 09/04/2014

RESULTS:

No	Sample	N [%]	C [%]	H [%]	S [%]	Method
1.	Ionic Liquid	3.202	16.770	6.616	21.528	In House-Method
	Ionic Liquid	3.225	16.885	6.645	21.634	In House-Method

The certificate shall not be reproduced except in full without the written approval of the laboratory.
 The above analysis is based on the sample submitted by the customer.



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Figure Appendix 8: Elemental analysis CHNS data

Calculation for CHNS data

Empirical Formula Calculation

The no. of mole for each element can be get by the formula:

$$= \text{Weight percentage of element} \times \frac{1 \text{ mol of element}}{\text{Molecular weight of element}}$$

For Carbon, C:

$$26.01 \text{ g of C} \times \frac{1 \text{ mol C}}{12.01 \text{ g of C}} = 2.17 \text{ mol of C}$$

For Hydrogen, H:

$$6.21 \text{ g of H} \times \frac{1 \text{ mol H}}{1.008 \text{ g of H}} = 6.16 \text{ mol of H}$$

For Nitrogen, N:

$$8.12 \text{ g of N} \times \frac{1 \text{ mol N}}{14 \text{ g of N}} = 0.58 \text{ mol of N}$$

For Sulphur, S:

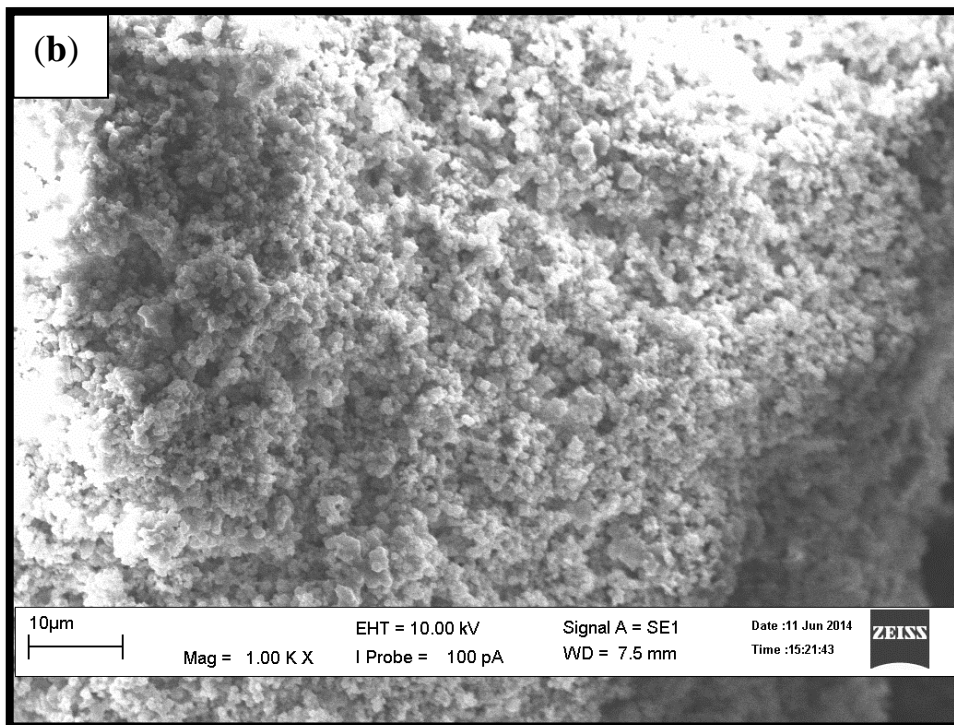
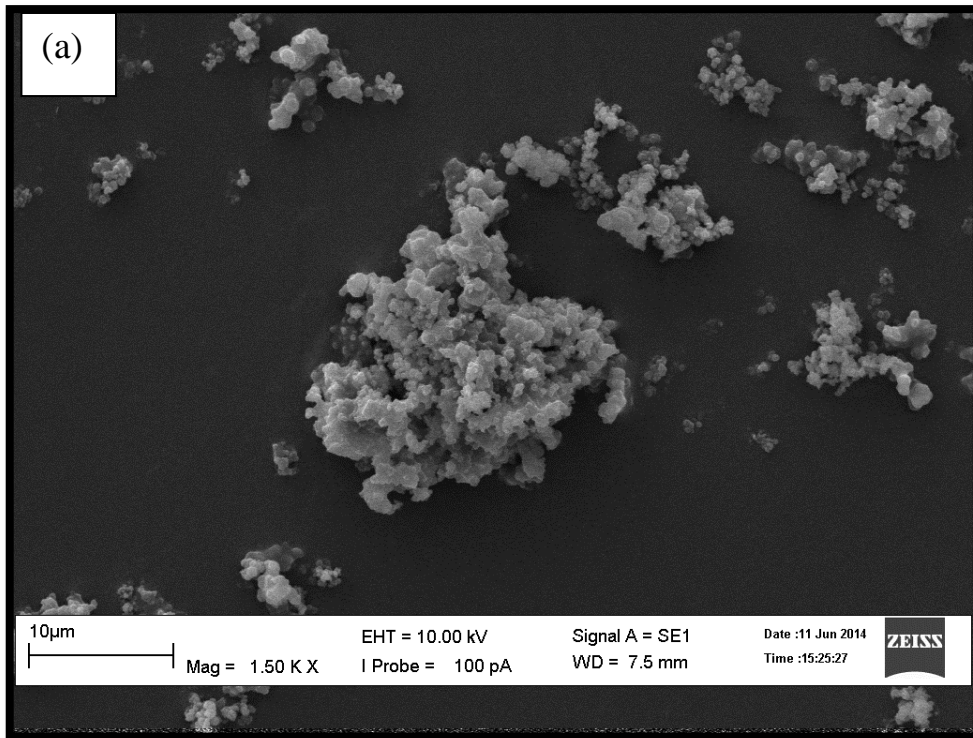
$$19.9 \text{ g of S} \times \frac{1 \text{ mol S}}{32 \text{ g of S}} = 0.62 \text{ mol of S}$$

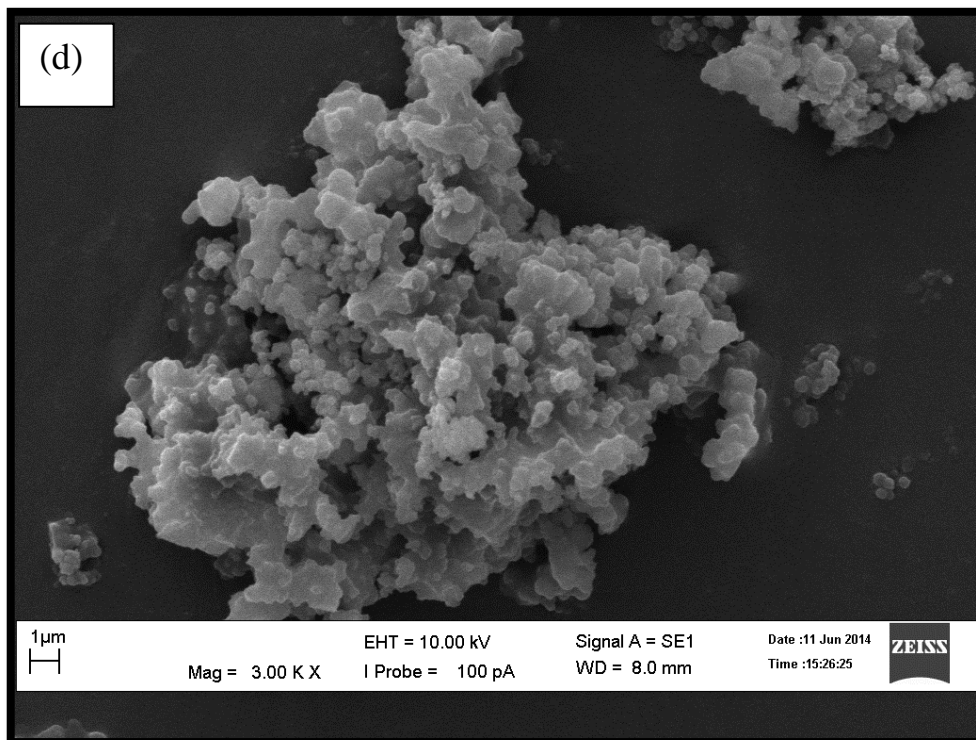
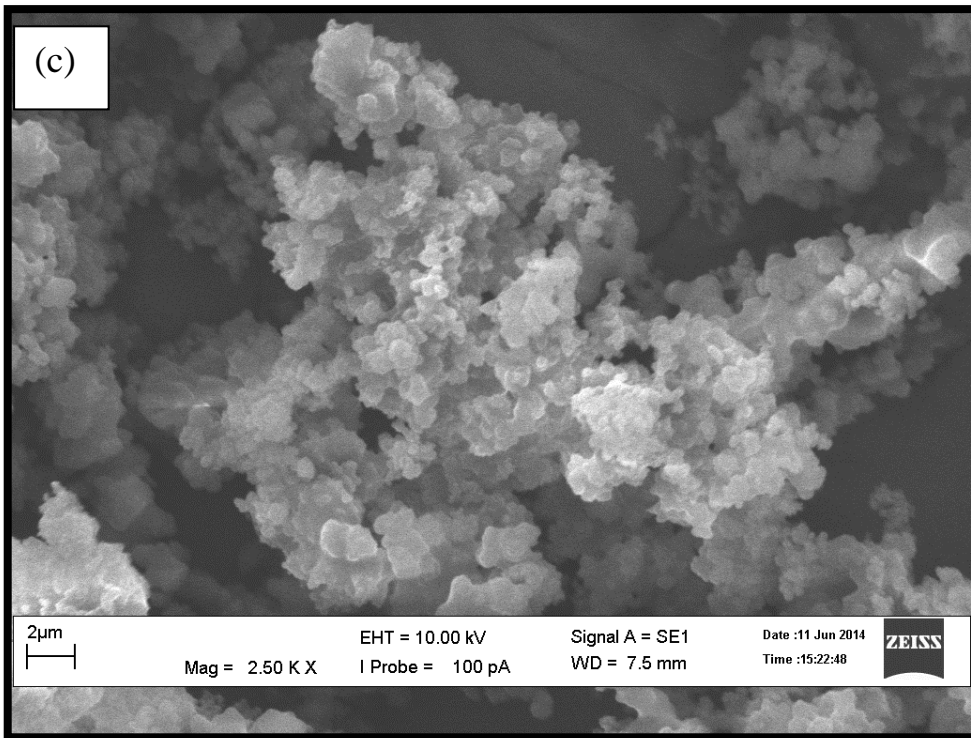
For Oxygen, O:

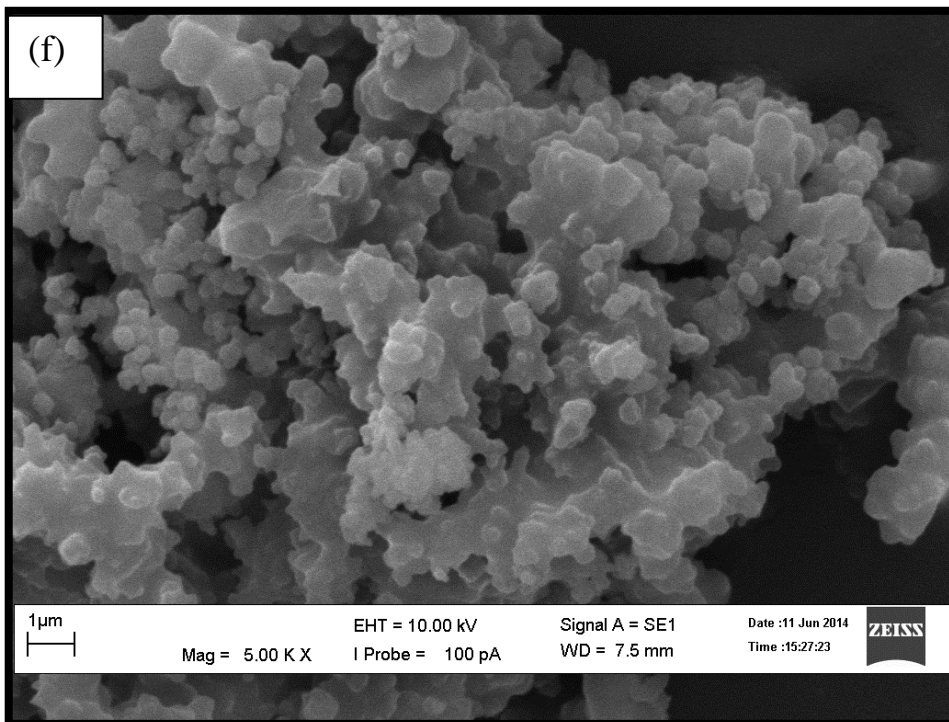
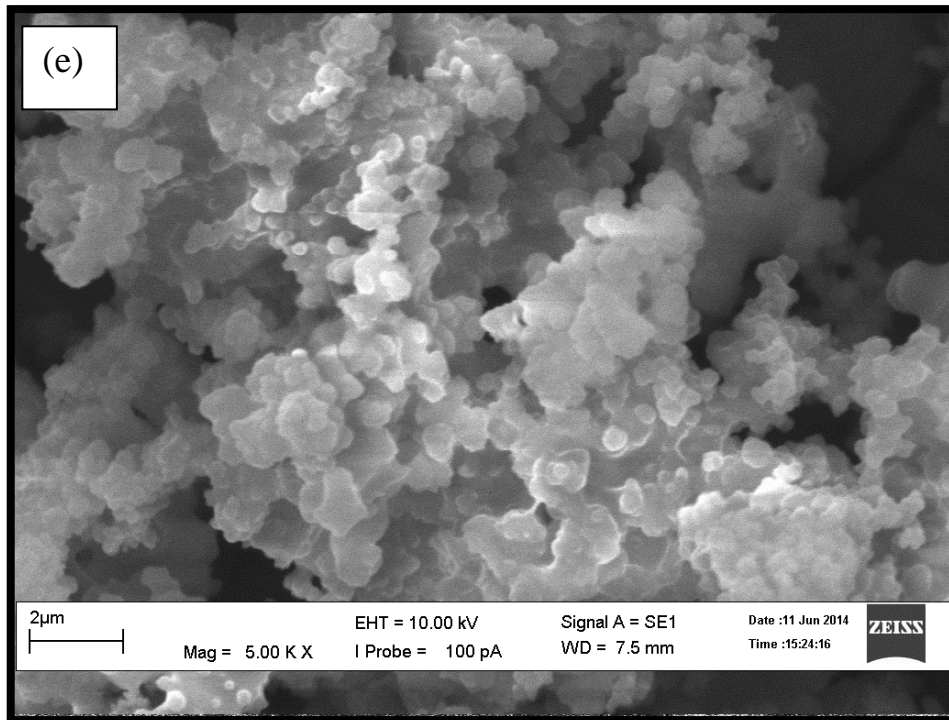
$$39.76 \text{ g of O} \times \frac{1 \text{ mol O}}{16 \text{ g of O}} = 2.49 \text{ mol of O}$$

Thus, the ratio for the CHNSO element was 2.17:6.16:0.58:0.62:2.49. By dividing the lowest no of mole ratio, the empirical formula for this sample is $\text{C}_4\text{H}_{11}\text{NSO}_4$.

SEM Data







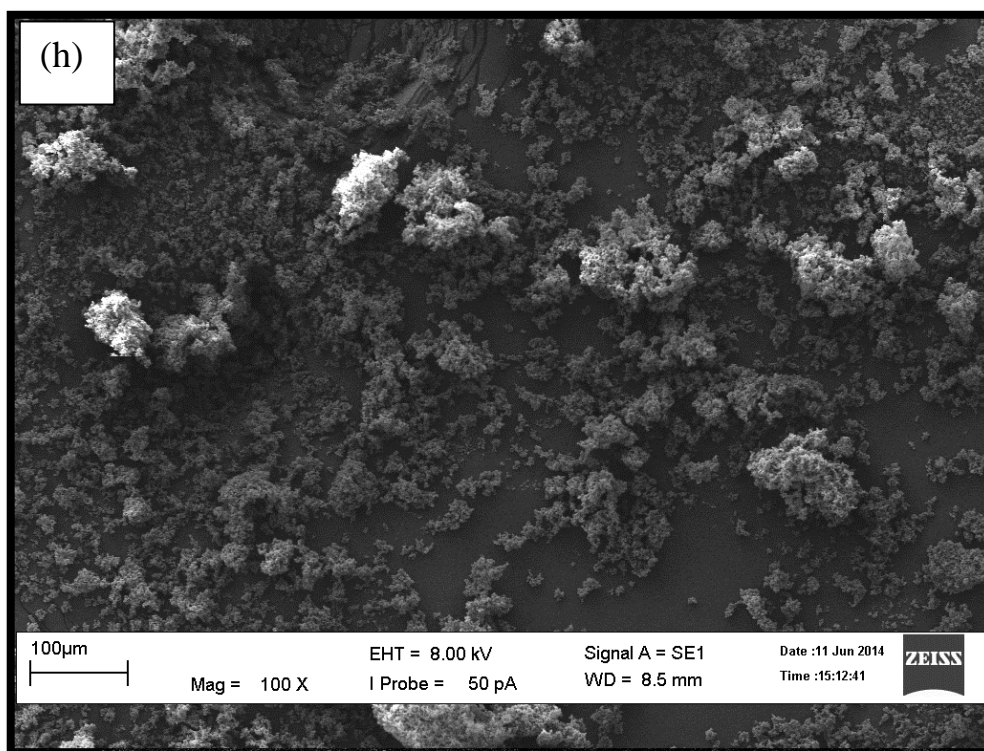
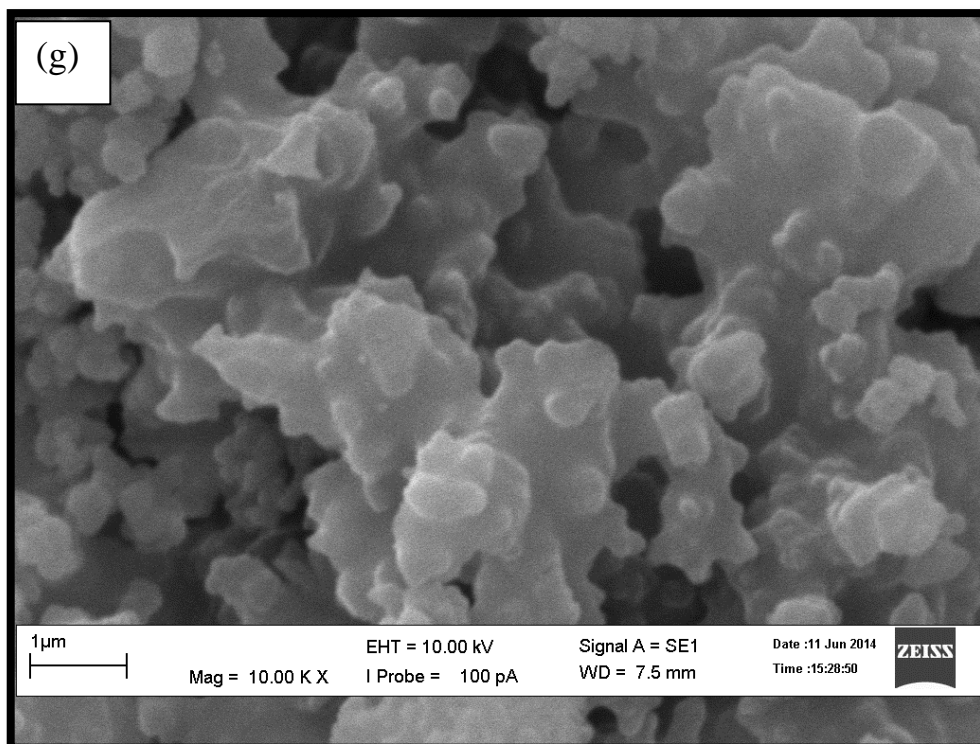


Figure Appendix 9 (a) – (h): SEM images of Solid Supported IL at various zoom

FTIR data

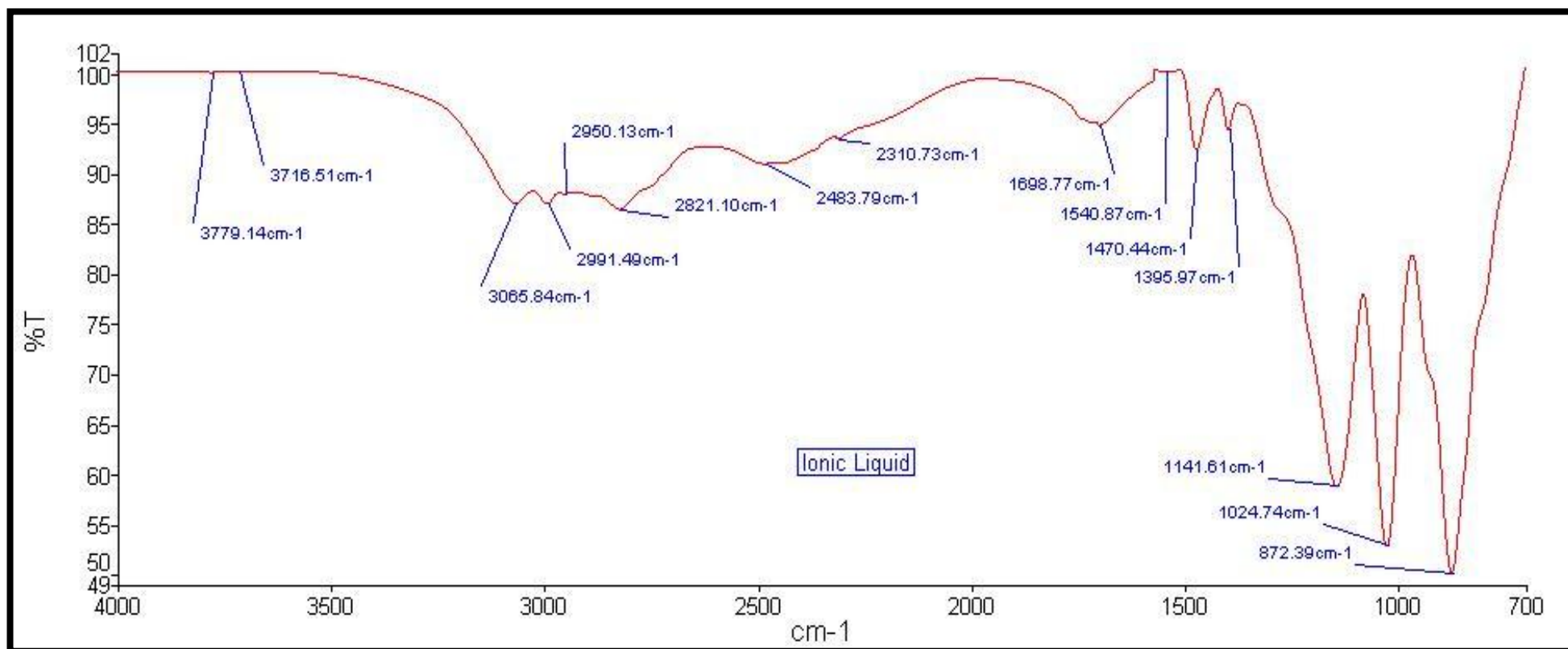


Figure Appendix 10: The IR spectrum for Et₃NHSO₄

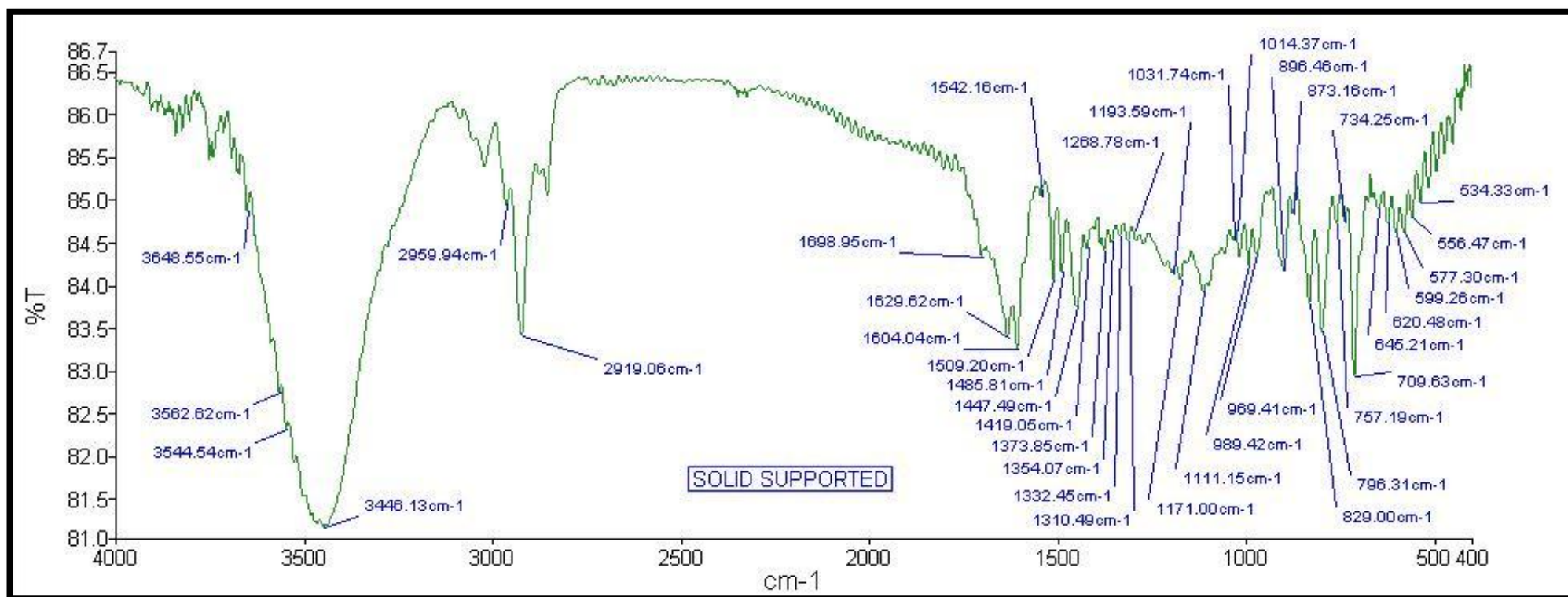


Figure Appendix 11: The IR Spectrum of Et₃NHSO₄ polymerized with DVB

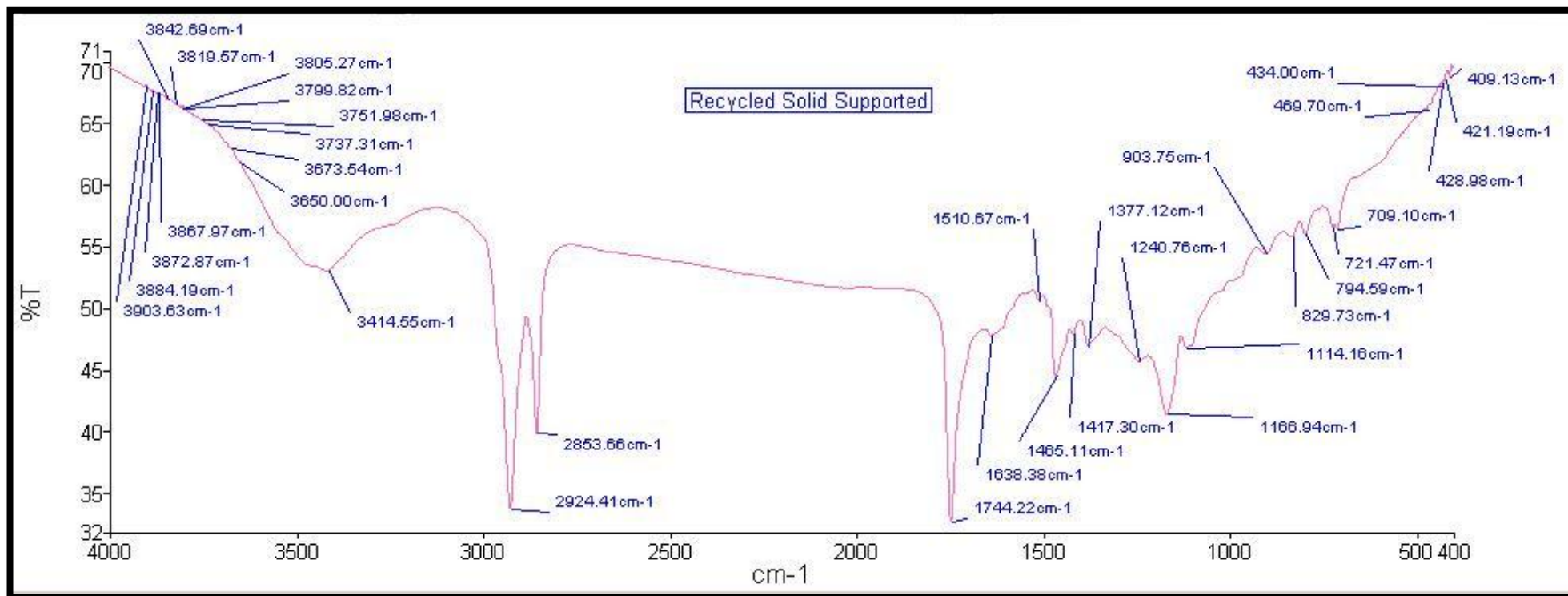


Figure Appendix 12: The IR Spectrum of Recycled Et₃NHSO₄ polymerized with DVB

APPENDIX D

ESTERIFICATION OF FFA

Simulated Waste Cooking Oil Calculation

Palm oil (g)	Oleic acid (g)	% Oleic acid	Intial burette	Final burette	Burette reading	Weight	Acid Value (mgKOH/g sample)
30	1.57894	0.05	34.7	30.1	4.6	2.064	12.2311

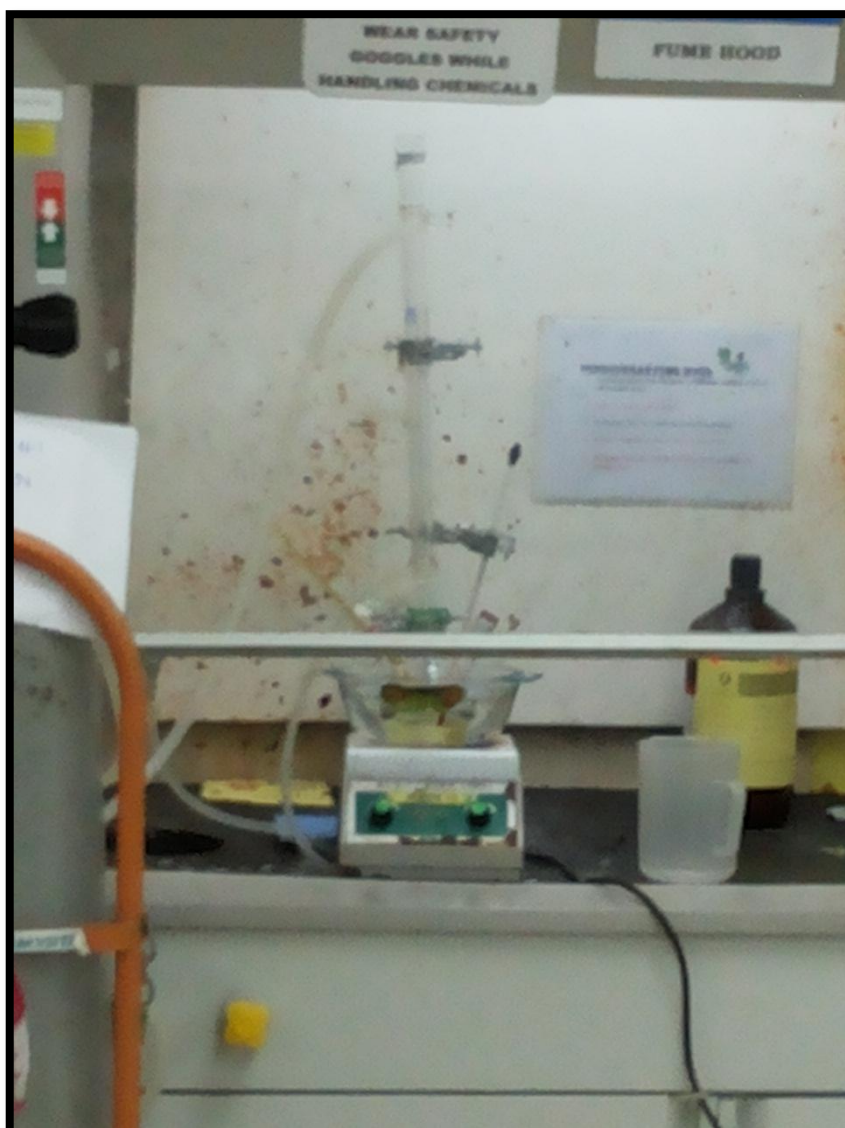


Figure Appendix 13: The set up for the esterification reaction