SYNTHESIS OF SEAWEED BASED CARBON ACID CATALYST BY THERMAL DECOMPOSITION OF AMMONIUM SULFATE FOR BIODIESEL PRODUCTION

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **“SYNTHESIS OF SEAWEED BASED CARBON ACID CATALYST BY THERMAL DECOMPOSITION OF AMMONIUM SULFATE FOR BIODIESEL PRODUCTION”** was prepared by **TANG ZO EE** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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Specially dedicated to
my beloved mother, father,
relatives and friends

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ABSTRACT

Experiment was carried out to study the biomass solid acid catalyst synthesis method for the production of biodiesel using high free fatty acid content feedstock (Palm Fatty Acid Distillate). Seaweed was selected as the biomass to be carbonised into carbon material as the catalyst support. The effect of carbonisation temperature at 200, 300, 400, 500 and 600 °C on the catalyst properties was studied. Sulfonation of seaweed based carbon material was carried out by thermal decomposition of ammonium sulfate, $(NH_4)_2SO_4$. The effect of reaction parameters on the biodiesel yield was studied by varying the concentration of ammonium sulfate (5, 10, 20, 30 and 40 w/v%) and reaction time (15, 30, 60 and 90 minutes). Characterisations of catalyst were carried out to study the catalyst surface morphology with Scanning Electron Microscope (SEM), acid density with back titration, functional group attached with FT-IR and thermal stability by Thermogravimetric Analysis (TGA). Production of biodiesel from methanol and PFAD was optimised by varying catalyst loading (2.5, 5, 10 and 15wt. %) and time (2, 4, 6 and 8 hours) at 100 °C oil bath with PFAD/methanol ratio of 1:20. Results showed that when the catalyst sulfonated with 30 ml of 10 w/v% ammonium sulfate solution, heated to 235 °C for 30 minutes was used, the optimum esterification conditions achieved with the highest FAME yield was 48.87% at the reaction condition of 15 wt% catalyst loading, esterification time of 8 hours, methanol to PFAD molar ratio of 20:1 at 100 °C oil bath.

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LIST OF SYMBOLS / ABBREVIATIONS

AC	Activated Carbon
AV	Acid Value
BET	Brunauer-Emmet-Teller
EDX	Energy Dispersive X-ray
FAME	Fatty Acid Methyl Esters
FFA	Free Fatty Acid
FT-IR	Fourier-transform Infrared
GC-FID	Gas Chromatography – Flame Ionisation Detector
MWCNT	Multi Walled Carbon Nano Tubes
PFAD	Palm Fatty Acid Distillate
SEM	Scanning Electron Microscope
SWAC	Seaweed Activated Carbon
TPD	Temperature Programmed Desorption
TG	Triglyceride
TGA	Thermogravimetric Analysis
XRD	X-ray Diffractometer

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CHAPTER 1

INTRODUCTION

1.1 Overview of World Energy Consumption

In the modern days now, energy has become the most fundamental requirement in human life. It is the most basic necessity and essential to perform work. The global energy consumption is increasing gradually over the years. World energy consumed that is used to generate power has increased by 0.9% in 2014 (British Petroleum, 2015). The increase of global energy consumption is due to the increase of world population was just part of the reasons that contributes to the increase of energy consumption. The main reason is due to the development of the countries. Developed countries like United States is one of the highest energy consumption countries even though it does not have the most population among other countries.

The energy consumption is divided into four major energy end-use sectors, which are residential, commercial, transportation and industrial. Taking a developed country as example, U.S had increased the consumption of energy every year. In year 2014, according to the statistic of U.S. total energy consumption, residential sector has consumed total energy of 21,618 Trillion Btu, increased by about 400 Trillion Btu from 2013. Commercial sector consumed about 18,394 Trillion Btu of total energy, increased by about 300 Trillion Btu from 2013 as well. As for industrial, sector that consumed the most energy at about 31,308 Trillion Btu, remained almost constant from 2013. And lastly, the transportation sector consumed 27,142 Trillion Btu in year 2014 (U.S. Energy Information Administration, 2015). Figure 1.1 shows that in 2014, industrial sector consumed the most energy with the reason mentioned above.

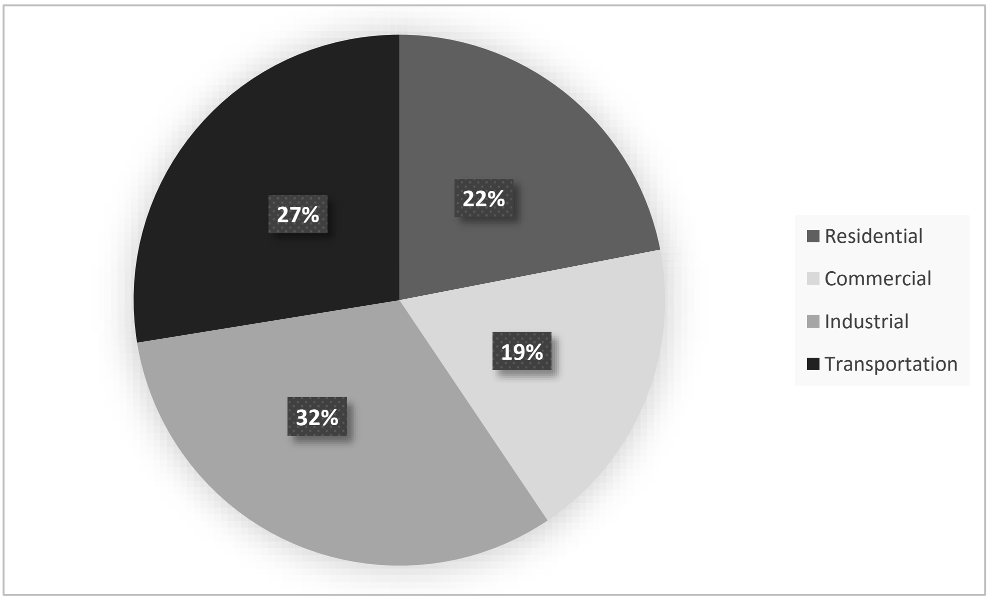


Figure 1.1: World Energy Consumption by Four Major Sectors in 2014 (U.S. Energy Information Administration, 2015)

The sources of energy are divided into two major groups, renewable energy and non-renewable energy. Non-renewable energy is generally defined as energy that cannot be replenished in a short period of time once consumed. In contrast, renewable energy is generally defined as the infinite energy source that can replenished rapidly after consumed. The most common type of non-renewable energy is fossil fuels which consist of petroleum, natural gas and coal. Nuclear energy is also one of the non-renewable energy. Whereas renewable energy researches include hydro power, wind energy technology, solar energy technology, geothermal energy, biomass conversion, wave, tidal and ocean thermal energy and many more.

Non-renewable energy resource is currently the world main source of energy. Fossil fuels contribute for about 80% of the total primary energy supply by resource (World Energy Council, 2013). Fossil fuels are very important source of energy as a large amount of energy can be produced by just simple combustion. Oil has become much more important after the invention of combustion engine which require oil as burning fuel. The invention of combustion engines then led to the creation of combustion engine driven motor vehicles which consume high amount of oil on a daily basis. Besides that, it has also become the main pillar of the industry sectors that are very important in developing the economics of a country.

However, non-renewable energy is facing two major problems. One of the major problems is that the usage of non-renewable energy like fossil fuels and nuclear energy gives a large impact to the environment. The burning of fossil fuels like oil and coal tends to produce abundance of greenhouse gas like carbon dioxide that will lead to global warming. These gases will tend to trap heat radiation from the sun on the earth surface causing the rise of global temperature. Global warming will bring consequences like melting of ice glacial at north and south poles of the earth, flood and submerged of low land city that cause by the rise of sea level. Besides that, incomplete combustion of these fuels will produce carbon monoxide that is harmful to human health once inhaled. Carbon particles will also produce from incomplete combustion which will then cause air pollution due to the suspension of these particulate matters in the air which will cause respiratory problem to human as well as animals.

Besides environmental impact that is caused by burning of fossil fuels, nuclear energy will also give a large impact to the environment, ecosystems and human beings as a non-renewable source of energy. There are more than one hundred units of nuclear power plants operating in United States. Approximately 20% of the energy source in United States originates from nuclear energy (U.S. Energy Protection Agency, 2013). Nuclear powered energy which involves the process from mining of uranium ore, process of uranium to be enriched fuel, nuclear reactions to production of radioactive by-product will cause all types of pollution to the environment. Moreover, uranium is extracted from the earth crust through various mining techniques and cannot be replenished in human time scale.

As mentioned, nuclear energy gives only finite supply of energy that will reach the limit once the raw materials are used up. Same goes to fossil fuels, which can only sustain for about 60 years based on the unproduced oil and gas in discovered reservoirs. These fuels are also known as the reserves (Carbon Counted, 2015). Although the undiscovered oil and gas are estimated to be able to sustain for more than 100 years, but there are still uncertainties and might require more resources in terms of financial and labour to be invested in the projects as the left over oil and gas are mostly trapped in the area that require higher technology and equipment to be drilled into.

The introduction of renewable energy has become the alternative for non-renewable energy and has a very big potential to replace the position of fossil fuel as the main source of energy in power generation. As shown in Figure 1.2, the production of renewable energy (other than hydro power) had increased from 10% at year 1993 to 11% in 2011 and it is estimated that is will increase to 16% in the year of 2020 (World Energy Council, 2013). The implement of renewable energy can act as a solution for the two major problems that is faced by sourcing non-renewable energy. Renewable energy harnesses the natural resource to convert them into energy. Natural resources are able to reproduce infinitely within human time frame which is known as the sustainable development. Renewable energy like solar, wind and wave energy cause relatively little environmental pollution. Although the burning of biomass produces carbon dioxide like how fossil fuel do, the amount of carbon dioxide produced from combustion of biomass is same as the amount of carbon dioxide will be consumed by the plants for photosynthesis reaction. This will ended up with the zero net production of carbon dioxide from burning of biomass, known as the carbon neutral materials.

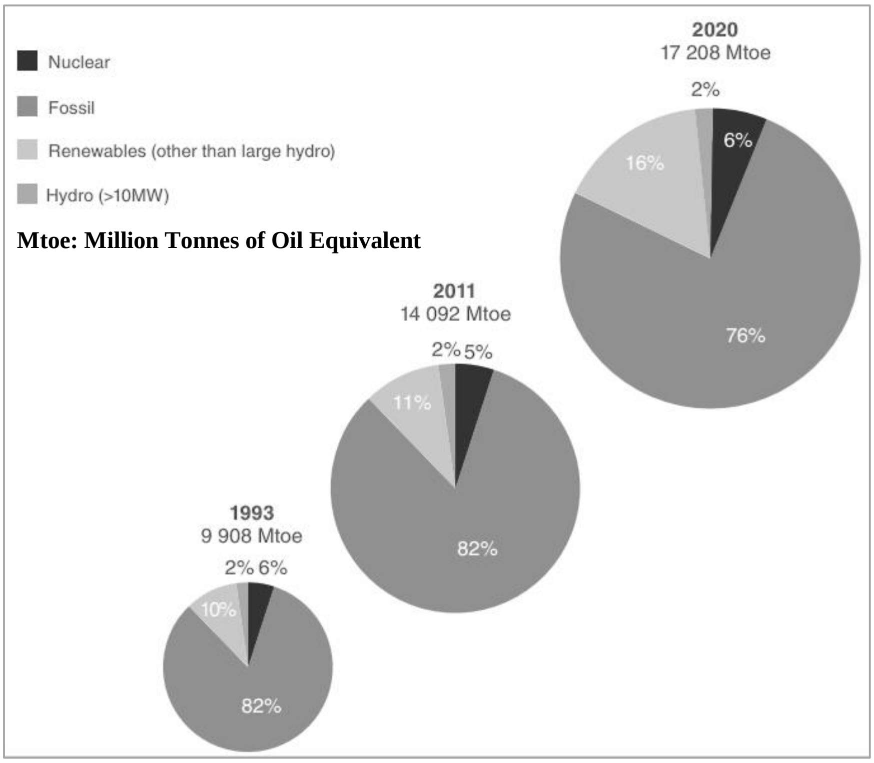


Figure 1.2: Primary Energy Supply in 1993, 2011 and Prediction on 2020 (World Energy Council, 2013)

1.2 Biofuels

Biofuels can be defined as the biological materials derived fuels. Although the working principle of biofuels is similar to fossil fuel, which is to generate energy through combustion from fuel source, biofuels are categorized as renewable energy. Biofuels are said to be renewable because it uses natural materials from plant and animal as the source for combustion. These biological materials are able to be reproduced in a very short time frame and are sustainable and renewable. Biofuels can be categorized into 3 types, which are solid biofuel (biomass), liquid biofuels and gaseous biofuel (Biogas). The production methods and forms of appearance of these 3 types of biofuels are different.

Solid biofuels are basically known as biofuel that appears in solid forms. Wood, leaves, animal dung and energy crops are examples of solid biofuels. Solid biofuels is the primary biofuel that require no production steps to be generated, it always appears in convenient form that is readily to be used. Biomass is usually burnt directly to generate heat without any prior conversion to any form. But sometimes, biomass like wood will be processed into pellet form. In 2014, the production of wood pellets has risen by 9%, at about 24 million tonnes (REN21, 2015). Energy crops like Switchgrass (*Parnicum virgatum*) and elephant grass (*Pennisetum purpuream*) are planted especially for bioenergy production by burning and conversion to other form of biofuels, which will be discussed later sections.

On the other hand, gaseous biofuels or biogas is produced through the anaerobic activity of bacteria in breaking down the animal dung, sewage and crops. Europe has the highest production of biomethane worldwide at approximately 9.4 TWh per year with 154 production plants set-up in Germany, 54 in Sweden and 23 plants in Netherland (REN21, 2015). Biogases produced from fermentation by bacteria are composed of several chemicals which include 50-75% of methane (main and desired product) and the rest are carbon dioxide, oxygen, water, hydrogen and nitrogen. These gases are then refined and purified into biomethane for use.

Next, biofuels are also available in liquid form. These liquid biofuels can be used for transportation vehicles which made it different from the other types of biofuels.

Liquid biofuels is a potential source of energy that could replace the petroleum as automotive fuel and has more advantages at the current high-oil-price-market. Liquid biofuels is known as the secondary biofuel which is produced from processing of biomass. Secondary biofuels are evolving day by day from the first generation to fourth generation:

i. **First Generation biofuel** is mainly produced from food crops like wheat and sugarcane. The feed stocks of first generation biofuel are edible crops which were then lead to the fuel vs. food crisis. The usage of food crops in biofuel production has increased the demand of food crops and became competitive with the global food market. For some period the food price rose due to the limitation of food supply. Besides that, first generation biofuel were also facing problem like negative net energy produced by certain crops (Naik, et al., 2010).

ii. **Second generation biofuel** is improved to resolve the problem encountered by the first generation biofuel. Instead of edible crops, non-edible biomass is used in producing the biofuel. Examples of second generation biofuel feedstock are crop waste, wood, straw, organic waste and many more. Life cycle assessment of second generation has also been done and proven that the net energy gain has also increased from the previous generation of biofuel (Sims, et al., 2010).

iii. **Third generation biofuels** is implemented based on the improvement in producing biomass. Engineered energy crop like algae are being cultivated and to be used as the feedstock for biofuel production. Algae are renewable source and easily to be grown at any environment at very low cost. Biofuels derived from engineered energy crops have the potential of producing larger amount of energy when combusted than the conventional crops derived biofuels (Maity, et al., 2015).

iv. **Fourth generation biofuels** focus not only in the sustainable energy but also targeted to capture and store carbon dioxide from atmosphere. Carbon dioxide are being captured and stored in all stages of biofuel production process. This biofuel production is aim to be carbon negative rather than just carbon neutral to reduce the amount of carbon dioxide in the atmosphere (Biopact, 2007).

There are several types of liquid biofuel produced from biomass. Figure 1.3 shows the production trend of liquid biofuels like hydrotreated vegetable oil (HVO), bioethanol and biodiesel. Methanol is produced from the feedstock with high amount of sugar, for example, sugarcane and starch (wheat and maize). Starch will be first converted into sugar and then followed by fermentation of sugar to produce bioethanol. Pure ethanol will then be obtained through distillation process. Bioethanol can be burnt in pure form or mix with petrol to improve the combustion performance and reduce emission of carbon monoxide from vehicles. Energy produced by bioethanol can be up to two third the energy produced by petrol (Bell Performance, 2014).

Other than bioethanol, biodiesel is also a liquid biofuel produced from biomass. Biodiesel is produced from the transesterification and esterification of plant oil and animal fats in the presence of alcohol. Similar to bioethanol, biodiesel can mix with petroleum derived diesel to improve combustion performance by reducing carbon monoxide emission or to be burnt at pure form. Biodiesel releases up to 93% of the energy release by the same amount of petroleum diesel (C2ES, 2013.).

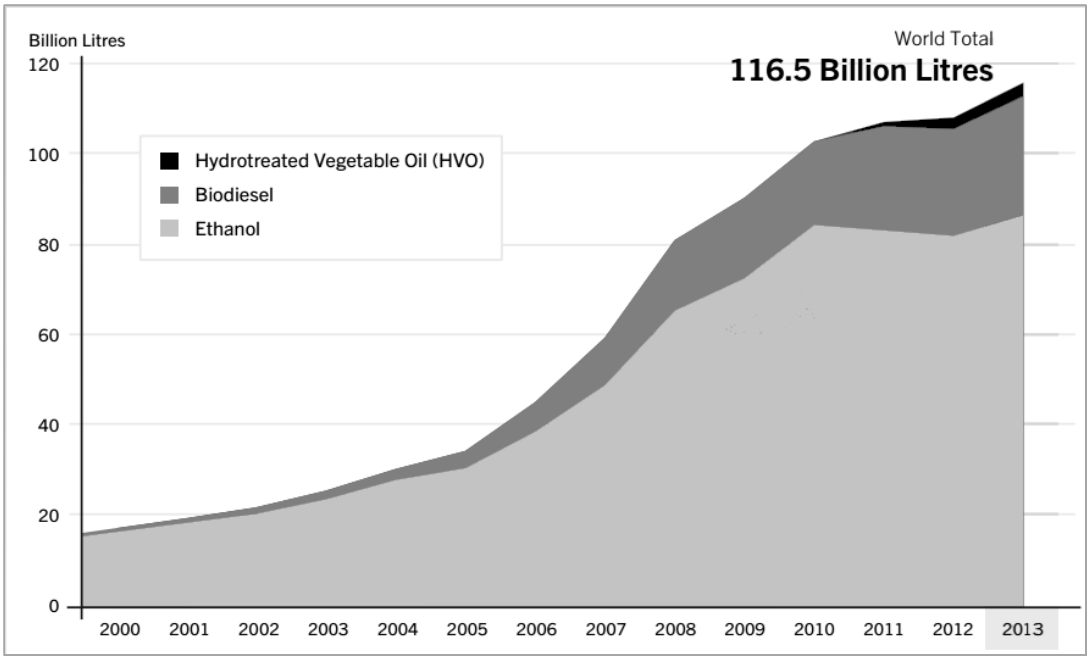


Figure 1.3: Global Production of Bioethanol, Biodiesel and HVO from 2000 to 2014 (REN21, 2015)

1.3 Biodiesel

The transesterification of vegetable and plant oil to produce biodiesel started at the year of 1853 by scientists E. Duffy and J. Patrick (Ayhan, 2009). This process had begun very long before the invention of diesel engine. In the year of 1893, Dr. Rudolf Diesel, the German inventor had invented the diesel engine which was named after him (Ayhan, 2009). The design of diesel engine was originally powered by biomass fuel. The invention of biodiesel was before the available of petroleum. In the 20th century, the discovery of petroleum has made oil companies to refine crude oil in large quantity leaving surplus of distillate, which was then found to be excellent diesel fuel at much lower cost. However, in 1921, Dr. Diesel confidently claimed that the use of non-flammable biodiesel to power diesel engine will be the real future of his diesel engine although biofuels seems to be insignificant during that time (Ayhan, 2009).

According to the monthly biodiesel production report from United States Energy Information Administration, the production of biodiesel in United States has gradually increased over the month. Production of biodiesel has increased for 10 million gallons from March to about 108 million gallons in April 2015 (EIA, 2015). The increase of biodiesel production has shown that biodiesel is becoming more important in the fuel market with a very high potential to take over petroleum-derived diesel especially during high oil price period.

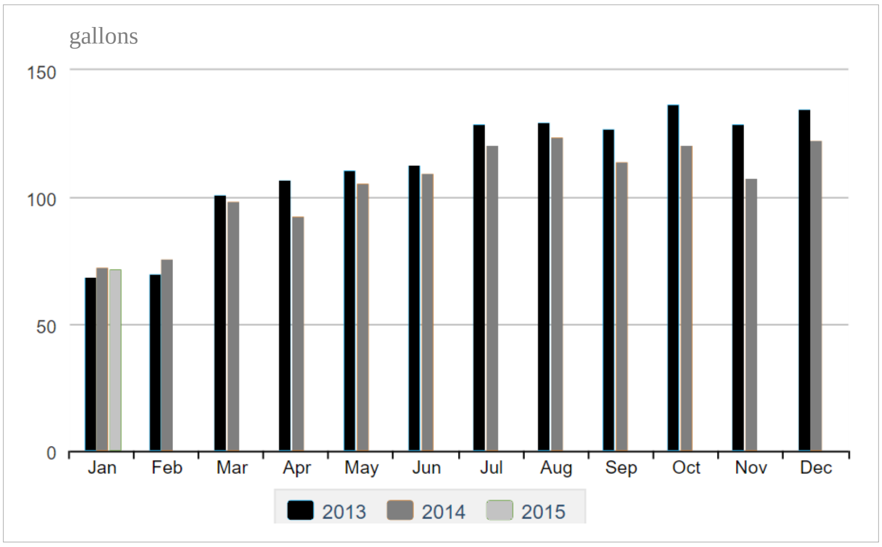


Figure 1.4: U.S. Monthly Biodiesel Production from 2013 to 2015 (EIA, 2015)

Biodiesel gives several advantages over the petroleum diesel including:

i. Biodiesel can be made from renewable resources that are non-toxic and biodegradable (Bozbas, 2008).
ii. Biodiesel released far lesser amount of pollutants than petroleum based diesel (Ayhan, 2007).
iii. Biodiesel has the potential to show higher efficiency than petroleum biodiesel as a fuel to power compression-ignition engines (Ayhan, 2007).
iv. Biodiesel has lower sulfur and aromatic content (Dennis, Xuan and Leung, 2010).

1.4 Production Pathways of Biodiesel

There are 4 methods available in the production of biodiesel which are all associated with pros and cons (Dennis, Xuan and Leung, 2010).

i. **Direct use and Blending**. In this method, the extracted oils are mixed with diesel fuel or to be used directly. However, when this type of biodiesel is used in engines, several problems will occur like formation of coking and trumpet deposits of carbon and gelling and thickening of lubricating oil.

ii. **Micro-emulsions**. When there are two immiscible liquids and ionic or non-ionic amphiphiles, a colloidal equilibrium dispersion of optically isotropic fluid with dimension of 1 -150 nm will occur. This will decrease the viscosity level of the fuel but also release lower energy. When used in engines, the viscosity of lubricant oil will rise and heavy carbon will be deposited.

iii. **Thermal Cracking (Pyrolysis)**. Heat is applied to convert the long-chain saturated substance derived from biomass into biodiesel. The biodiesel produced from pyrolysis has the similar chemical properties with the petroleum diesel.

iv. **Transesterification**. This is the most common method used in the production of biodiesel. Biodiesel is formed by the catalytic transesterification process of plant oil or animal fat with alcohol to form esters and glycerol. The biodiesel formed by this method is found to have higher combustion efficiency.

1.5 Catalytic Transesterification of Biodiesel

As mentioned in Section 1.4.4, triglycerides will react with alcohol through transesterification process to produce biodiesel and glycerol in the presence of catalyst. The reaction can be written as shown in Figure 1.5.

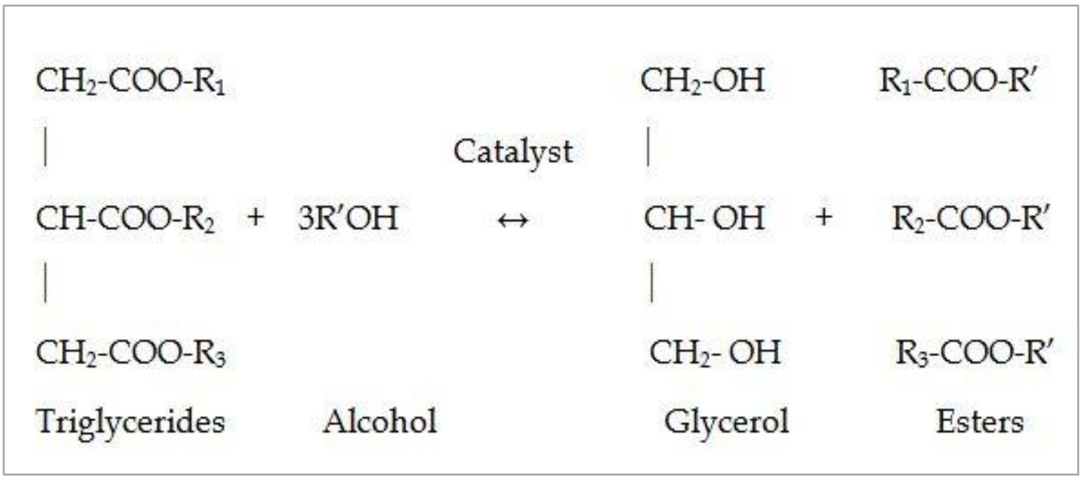


Figure 1.5: Transesterification Process of Biodiesel Production

There are various types of catalyst that can be used in the biodiesel production through transesterification process. Homogeneous base catalyst like NaOH, KOH and $NaOCH_3$ are commonly used as the catalyst due to the higher activity rate. However, most of the oil and fat contain certain amount of free fatty acid (FFA) that act as a barrier for the base-catalysed transesterification process. Plant oil or animal fats have to contain no more than 0.5 wt% of FFA else formation of soap will occur in the reaction (Shu, et al., 2010). Figure 1.6 shows that the base catalyst will react with the FFA content in the oil to form soap and water. Table 1.1 shows estimated FFA composition of edible and non-edible oil which contributes to the formation of soap.

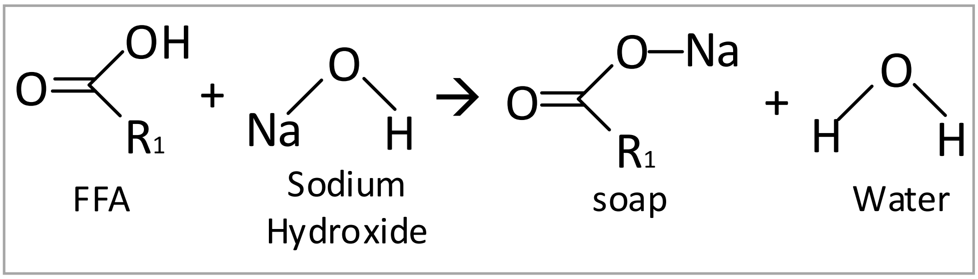


Figure 1.6: Saponification Reaction in the Presence of Base Catalyst

Table 1.1: Estimated FFA Composition in Edible and Non-edible Plant Oil/ Fats (Robles, et al., 2009)

Plant Oil and Fats	Free Fatty Acid Composition, % by weight						
	Lauric 12:00	Myristic 14:00	Palmitic 16:00	Stearic 18:00	Oleic 18:1	Linoleic 18:2	Linolenic 18:3
Soybean	0.1	0.1	10.2	3.7	22.8	53.7	8.6
Cottonseed	0.1	0.7	20.1	2.6	19.2	55.2	0.6
Palm	0.1	1.0	42.8	4.5	40.5	10.1	0.2
Lard	0.1	1.4	23.6	14.2	44.2	10.7	0.4
Tallow	0.1	2.8	23.3	19.4	42.4	2.9	0.9
J. curcas	0.0	0.0	12.8	6.2	35.58	45.4	0.0

Saponification occurs as a side reaction that yields soap and water which give plenty of drawbacks as below:

i. Yield of biodiesel decreases.
ii. Water hydrolyses triglyceride to diglyceride and forming more FFA.
iii. Binding of soap with catalyst increases the amount of catalyst required and results in higher cost.

One of the reasons of biodiesel not being commercialized in the market is due to the relatively high raw material cost (Antonio, et al., 2014). The usage of cheap feedstock like waste cooking oil and non-edible oil are a very good way to mitigate the problem associated with the high material cost. Nonetheless, the FFA contents in the cheap feedstock are high and making base-catalyst not suitable to be use in the production. Problems associated with based-catalyst may be overcome as below:

i. Pre-treatment of feedstock in removing FFA contained in the oil or fat.
ii. Used of alternative catalysts in the reaction.

In this case, homogeneous acid catalysts are proven to be a solution for the high FFA content problem faced by base catalyst. At the presence of acid catalyst, the FFA in feedstock will react with methanol to form fatty acid ester (FAME), which is the biodiesel through esterification process as shown in Figure 1.7. Normally, sulfuric acid, H_2SO_4 is used as the acid catalyst. Although homogeneous acid catalyst shows a better performance than base catalyst, it has some limitation that denied it to be the best choice of catalyst in biodiesel production. The usage of homogeneous acid catalyst (H_2SO_4) will cause the corrosion of equipment in the production plant (Shu, et al., 2010). Besides that, the catalyst is hard to be separated from the product to be recovered and may consume high energy.

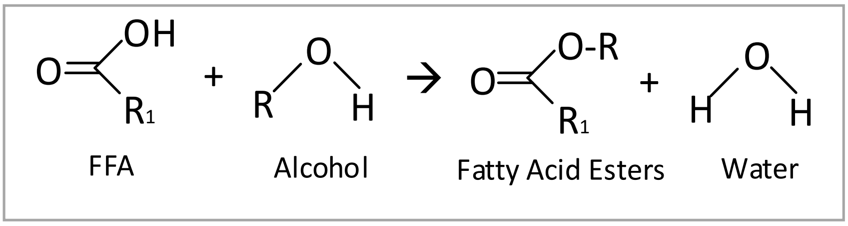


Figure 1.7: Esterification of FFA in the Presence of Acid Catalyst

1.6 Types of Heterogeneous Acid Catalyst

By using heterogeneous acid catalyst, both transesterification of triglyceride and esterification of FFA can undergo simultaneously, achieving the one step catalytic conversion of low cost feedstock into biodiesel. Table 1.2 shows various types of solid acid catalyst have been discovered by researchers obtaining from different materials.

Table 1.2: Various Types of Heterogeneous Catalyst (Adam, et al., 2014)

Types of Heterogeneous Catalyst	Description	Examples
Mesoporous Silica	Belongs to the Santa Barbara Amorphous (SBA) family where sulfonic groups or SO_4/ZrO_2 are coated on the porous surface.	Phenyl SBA-15, Propyl SBA-15
Heteropolyacids	Large group of complex oxygen-containing acid formed from dehydration of two or more inorganic acids containing flexible structure.	$H_3PW_{12}O_{40}$ supported on magnetic iron oxide
Acidic Polymer and Resins	Mesoporous organic polymer that contains high absorption capacity and are easily recovered.	Sulfonated Mesoporous Polydivinylbenzene (PDVB-SO_3H)
Waste Carbon	Biomass-derived catalyst through sulfonation. Residue of biomass after oil extraction is carbonized and sulfonated.	Sulfonated Carbonaceous algal residues, crop waste.
Miscellaneous	Other solid acid catalyst researched by scientist.	Ferric Hydrogen Sulfate [$Fe(HSO_4)_3$], Supported Tungsten Oxides (WO_3/SnO_2)

.

1.7 Biomass Heterogeneous Acid Catalyst Synthesis Method

Solid acid catalyst derived from carbonized biomass followed by sulfonation is introduced by Toda and his research team from sugar (Folasegun, et al., 2014). From there onwards, various types of organic waste material were then used as the raw material for the synthesis of biomass acid catalyst for esterification of FFA to biodiesel. Several synthesis methods are discovered and used to produce these catalysts. Some examples of sulfonation are shown in Table 1.3.

Table 1.3: Examples of Sulfonation Methods

Literature	Method	Description
Du, Zhao and Liang (2008)	Sulfonation by Thermal Decomposition of Ammonium Sulfate	When heat is supplied, ammonium sulfate $(NH_4)_2SO_4$ decomposed to form sulfur trioxide, SO_3 which will then graft on the mesoporous material.
Du, Zhao and Liang (2008)	Sulfonation by in situ polymerisation of poly(sodium4-styrenesulfonate)	This method is first started with vigorous stirring of the deionised water, poly(sodium4-styrenesulfonate) (PSS) and the treated carbonised material and followed by addition of ammonium persulfate, $(NH_4)_2SO_8$ and heat to initiate polymerisation then added with large amount of concentrated sulfuric acid.
Shuit and Tan (2014)	Sulfonation by in situ polymerisation of acetic anhydride and sulfuric acid	A mixture consists of treated carbonised materials, concentrated sulfuric acid and acetic anhydride, $(CH_3CO)_2O$ is stirred and heated for certain duration.
Shuit and Tan (2014)	Direct Sulfonation with concentrated sulfuric acid, H_2SO_4	In this method, carbonised biomass and sulfuric acid is directly treated with heat for a period of time to allow the sulfuric acid to be attached onto the carbon pores.

1.8 Problem Statement

In order to amplify the potentials of the biodiesel as the alternative fuel to power automotive engines, the yield of biodiesel should be improved without increasing the production cost. There are several researches done on the factors affecting the biodiesel production like alcohol quantity, reaction time, reaction temperature and catalyst concentration. Nevertheless, the type of catalyst used in the production is also an important element that should be taken into account. The creation of effective catalyst enables the production of biodiesel to be more cost effective and viable.

However, not all types of catalyst are suitable to be used on all types of oil feedstock. Base catalyst has the largest limitation dealing with the high FFA content although it shows to have better activity rate in the biodiesel production than acid catalyst. When homogeneous acid catalyst like sulfuric acid is used, the performance was shown to be good. However, the usage of homogeneous acid catalyst asserts a problem where the separation of liquid catalyst from the product is difficult and required large amount of energy for separation.

In this case, heterogeneous acid catalyst seems to be a very potential catalyst to be used in the biodiesel process. Researches are being done to obtain the optimum conditions to synthesize the good quality and economic biomass catalyst by using different biomass material, synthesizing method and parameters. Not all types of biomass are suitable to be used as the precursor for catalyst and it is very depending on the structure of the biomass. The synthesizing method should also be studied on whether it is suitable to be used on the biomass selected as the carbon precursor from all aspects, for example, whether the biomass can withstand the synthesising temperature, the acidity of sulfonating agent used and so on.

1.9 Scope of Study

The research focus on the method used to synthesis the solid acid catalyst from the biomass. There are plenty types of biomass available that the capability to be used as catalyst support after carbonised can be studied. Thus, selection of biomass to be carbonised to the precursor of catalyst is the earliest stage in this study. Carbonisation of biomass was a process to form carbon material to be sulfonate to form acid catalyst.

Sulfonation of carbon material was the most important stage in the research. Different sulfonation methods yield different production outcome. This study was to investigate the results outcome of the selected synthesis method (sulfonation by thermal decomposition of ammonium sulfate). During the sulfonation process, the reaction parameters will be varied so that the optimum synthesis conditions can be achieved.

Production of biodiesel by using the catalyst synthesised was done to study the efficiency of catalyst based on the biodiesel yield. Production reaction conditions was also varied to obtain the optimum reaction conditions that is when the synthesised catalyst is used so that the performance of catalyst is optimised.

1.10 Research Objective

This research project focuses on discovering the better alternative of fuels for the next generation by creating a simpler and feasible biodiesel production pathway. The objectives of this study includes:

i. To study the feasibility of seaweed to be used for synthesis of solid catalyst by using the method thermal decomposition of ammonium sulfate for biodiesel production.
ii. To investigate the optimum ammonium sulfate concentration and time used in the catalyst synthesis process.
iii. To study the optimum catalyst loading and the reaction time in esterification.

CHAPTER 2

LITERATURE REVIEW

2.1 Reaction Mechanisms of Biodiesel Production

Base-catalysed transesterification is the most common biodiesel synthesis method used. However, there is limitation on using a base catalyst in the reaction which is the formation of soap when oil with high free fatty acid (FFA) content is used as the feedstock of the biodiesel production. Usually, low quality oil contains higher amount of FFA but it is cheaper than the low FFA content oil.

Thus, acid catalyst is used to overcome the soap formation problem by converting FFA to biodiesel through esterification reaction. Following shows the mechanism of biodiesel production of both base and acid catalysed reaction.

2.1.1 Transesterification Reaction Mechanism

In this reaction, one mole of triglyceride (TG) will first react with one mole of alcohol (methanol is usually used) and converted to one mole of diglyceride and one mole of ester (biodiesel). Diglyceride will then be converted to monoglyceride and finally to glycerol. During each conversion, one mole of ester will be formed. The chemical pathway of the full reaction is shown in Figure 2.1.

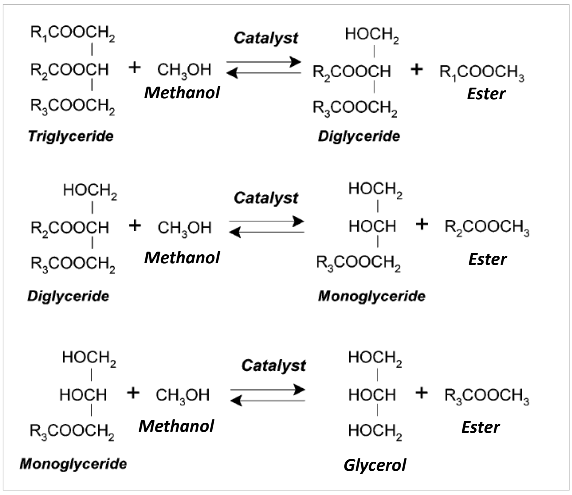
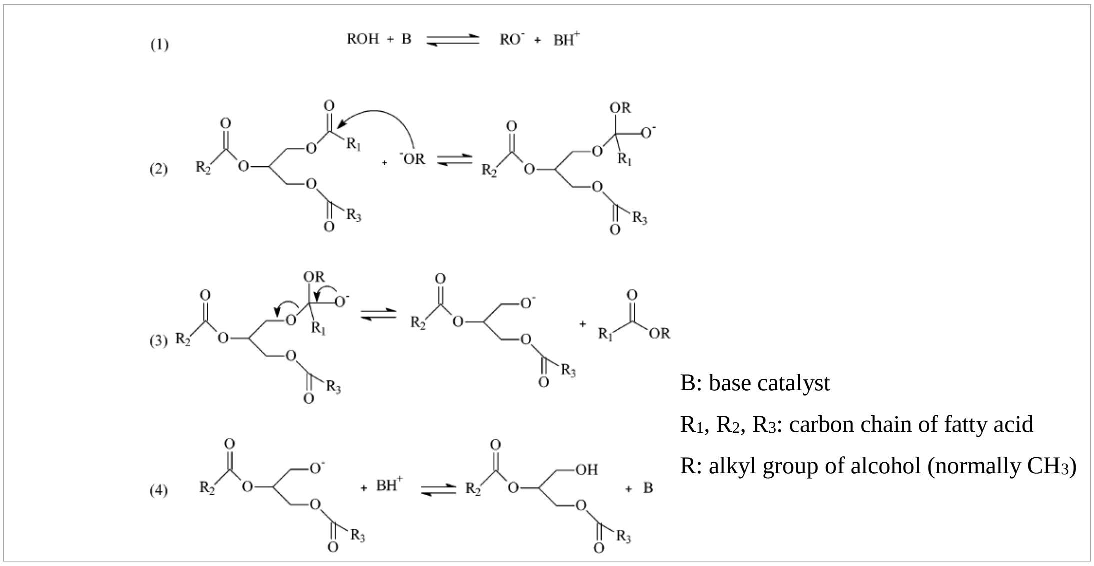


Figure 2.1: Transesterification of Triglyceride and Methanol (Edgar, et al., 2005)

The reaction mechanism of the base-catalysed transesterification reaction of triglyceride is shown in Figure 2.2. At step (1), alkoxide ions, RO^- are formed when alcohol is reacted with hydroxyl ions from the base catalyst. Next, in step (2), the alkoxide ions, which are the strong nucleophiles, attack the carbonyl group on the triglyceride forming a tetrahedral intermediate. Then in step (3), the tetrahedral intermediate breaks down and produce one mole of ester. And lastly in step (4), the base catalyst will be regenerated and form diglyceride. This sequence will repeat twice until 1 mole of glycerol and 3 moles of esters (biodiesel) is formed.



B: base catalyst

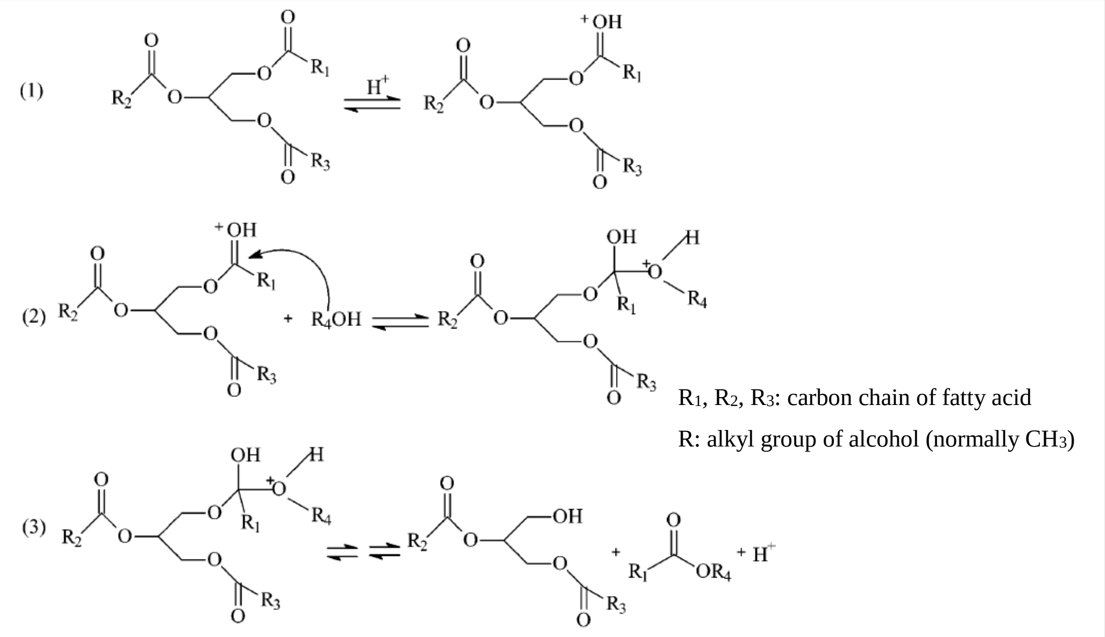
R_1, R_2, R_3: carbon chain of fatty acid

R: alkyl group of alcohol (normally CH_3)

Figure 2.2: Reaction Mechanism for Homogeneous Base Catalysed Transesterification of TGs (Edgar, et al., 2005)

The usage of base catalyst is to promote the soap formation process in the reaction. The chemical equation of the saponification process is shown in Figure 1.6. The products of the saponification reaction include soap and water. The formation of water has created another problem, which is the promotion of FFAs formation which will then deactivate the catalyst and produce more soap (Edgar, et al., 2005). The usage of acid catalyst in the biodiesel production is introduced to resolve the soap formation problem. Thus, transesterification of TGs can also be done in the presence of acid catalyst instead of base catalyst. Figure 2.3 shows the reaction mechanism for homogeneous acid catalysed transesterification process.

According to Figure 2.3, in step (1), the carbonyl group on the triglyceride is protonated by the hydrogen ions from the acid catalyst. Next in step (2), the alcohol gives a nucleophilic attack to the carbon hydroxyl double bond of protonated triglyceride, forming a tetrahedral intermediate. And lastly in step (3), the tetrahedral intermediate will be broken down and the hydrogen ion will be migrated from the intermediate. Then, one mole of esters and diglyceride is formed. This sequence will be repeated twice until one mole of glycerol and 3 moles of esters (biodiesel) is formed.



R_1, R_2, R_3: carbon chain of fatty acid
R: alkyl group of alcohol (normally CH_3)

Figure 2.3: Reaction Mechanism for Homogeneous Acid Catalysed Transesterification of TGs (Edgar, et al., 2005)

Both the reaction mechanism for base and acid catalysed transesterification of triglycerides show the different chemical pathways for the formation of glycerol and esters. For the base catalysed transesterification reaction, the reaction route is more direct which forms alkoxides to act as strong nucleophiles. In contrast, the key step for acid catalysed transesterification is the protonation of carbonyl oxygen which makes the adjoining carbon atom to be more susceptible to nucleophilic attack by increasing the electrophilicity of it. In short, base catalysed reaction forms a strong nucleophile while acid catalysed reaction forms a more electrophilic species.

2.1.2 Esterification Reaction Mechanism

Vegetable oil or animal fats that contain more than 0.5 wt. % of FFAs is not suitable to be used as feedstock for base catalysed reaction to produce biodiesel (Shu, et al., 2010). When the FFAs content in the oil feedstock is high, acid catalyst is suitable to be used in the biodiesel production reaction. The presence of acid catalyst will convert the FFAs into useful biodiesel through esterification reaction. Thus, transesterification of triglycerides and esterification of FFAs will occurs simultaneously when acid catalyst is used.

Unlike transesterification reaction mentioned that uses homogeneous acid catalyst, the esterification reaction that will be described at the following is a heterogeneous solid acid catalysed esterification reaction. The difference between homogeneous and heterogeneous acid catalysed reaction is that when homogeneous acid is used, FFA will supply hydroxide ions whereas alcohol will supply proton in the esterification without involving intermediate process. On the other hand, heterogeneous acid catalysed esterification follows a carbonium ion mechanism which involves intermediate process (Stoytcheva and Montero, 2011).

Figure 2.4 shows the reaction mechanism for esterification of FFAs. Firstly, carbonyl carbon of the FFA will be protonated by the protons from solid acid catalyst, forming a carbonium ion. Then, alcohol (or methanol) will give a nucleophilic attack on the carbonium ion to form a tetrahedral intermediate. Lastly, the intermediate will break down after the proton migrated resulted in water and fatty acid ester, FAME (biodiesel). The proton is then reformed and ready to be used for next reaction.

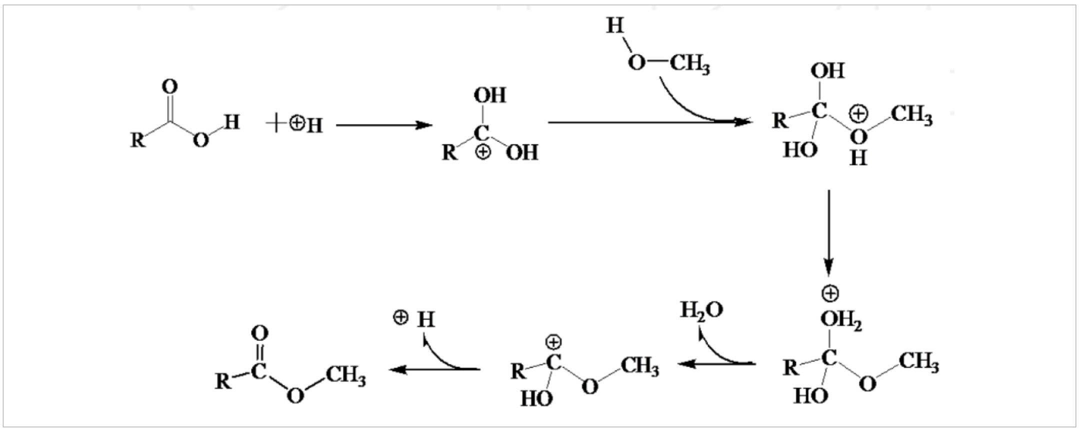


Figure 2.4: Reaction Mechanism for Solid Acid Catalysed Esterification of FFA (Stoytcheva and Montero, 2011)

2.2 Biomass Derived Carbon-based Solid Acid Catalyst

Biomass residues can be found in abundance after various kind of human activities like agriculture, oil extraction and many more. In this study, brown algae (seaweed) are selected to be used as the raw material for the derivation of carbon material for the solid acid catalyst. Figure 2.5 shows the overall procedure for the synthesis of solid acid catalyst from biomass.

Firstly, the collected biomass will be cut into smaller pieces and dried in the oven at temperature around 100 °C. Then, dried biomass will be pyrolysed under high temperature around 200-600 °C to turn into carbon materials. The surface morphology of the produced carbon material will be studied to know the capability of this biomass as a catalyst support. Carbon materials will then be sulfonated via different types of synthesis methods to become sulfonated carbon catalyst. In Figure 2.5, the sulfonated carbon contains functional groups like $–SO_3$, –COOH and –OH. The functional group –SO3 acts as the active site for the chemical reaction. –OH attached absorbs β-1, 4 glycosidic bonds and provides good access for the reactants towards the SO_3H groups in the carbon material (Stoytcheva and Montero, 2011).

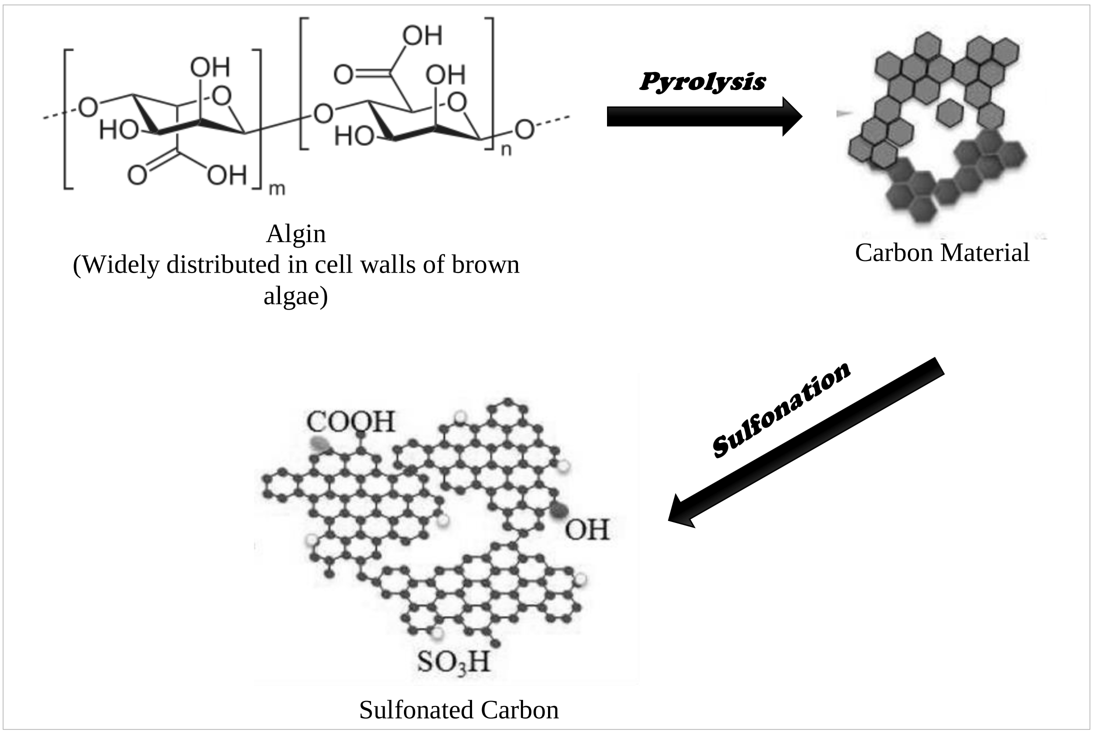


Figure 2.5: Summary for Synthesis Method of Brown Algae Derived Carbon Solid Acid Catalyst

2.3 Carbonisation and Pre-treatment of Biomass

As mentioned in Section 2.2, collected biomass is required to be treated before proceed to sulfonation process. Biomass will be converted to carbon materials like amorphous carbon, biochar or activated carbon through carbonisation process. Resulted carbon materials will normally be grounded into powder form and the size of the powder can be controlled with the usage of sieving equipment.

The biomass selected as raw material in this study was the brown algae (seaweed). According to Janaun, Abang and Anwar (2013), the brown algae obtained was cut into smaller size and dried in oven at 105 °C overnight. Dried seaweed was pyrolysed in a tube furnace at 400 °C for 4 hours. Pyrolysis system was purged with nitrogen prior to heating. The resulted black materials was then grounded with pestle and mortar. Sulfonated carbon is noted with the term SBC (seaweed-based catalyst). FT-IR analysis had investigated that SBC consisted of aromatic carbon sheets with SO_3H, COOH and OH groups attached along with inorganics and metals binding.

2.3.1 Effect of Carbonisation Variables

The parameters used in the carbonisation process are also important factors that would affect the activity of the catalyst produced. When different reaction conditions are employed in the carbonisation process, the resulted outcome will be different as well. Several researches had studied for the effects of synthesis reaction conditions on the catalyst by varying the reaction parameters like temperature and time.

Folasegun, et al. (2014) had selected glucose as the raw material for the synthesising of catalyst. About 200 g of glucose had undergone incomplete combustion in a tube furnace at 400 °C at constant nitrogen atmosphere. The temperature was ramped up at 2 °C /min until 400 °C and kept constant for 1, 5 and 10 hours. Figure 2.6 shows the example of surface morphology of the sulfonated catalyst. The black solid obtained was passed through a 0.5 mm sieving equipment and resulted in regular size powder. Amorphous carbon composed of aromatic sheets having with random orientation formed.

The highest acid content of the catalyst was achieved with 1 hour carbonisation time at about 1.0 mmol/g of SO_3H, followed by 0.8 mmol/g of SO_3H by both 5 and 10 hours carbonisation time. Thus, the trend was that shorter carbonization time poses higher number of smaller carbons sheets which in turn, having higher SO_3H densities. In the transesterification reaction at the conditions (C. inophyllum oil = 0.5 g, methanol = 5.5 g, carbon material = 0.3 g, time = 5 hours, temperature = 150 °C), FAME yield obtained was 64.4%.

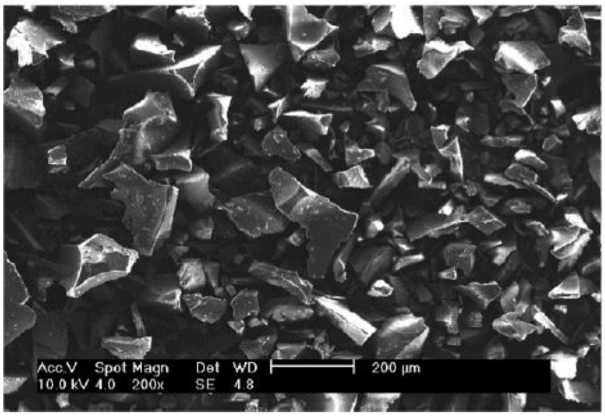


Figure 2.6: Morphology of Sulfonated Catalyst at Carbonised Temperature 400 ℃ at Time 1 hour (Folasegun, et al., 2014)

Liu, et al. (2013) had studied the effect on the carbonisation time and temperature on the performance and characters of catalyst synthesised. 2 g of corn straw was heated for 0.5, 1, 2 and 3 hour(s) at different temperatures of 250, 300, 350, 400, 450, 500 °C under the flow of nitrogen in a tube reactor. As shown in Figure 2.7, carbonisation of corn straw at 300 °C (573 K) for 1 hour has the highest FAME yield of 92% by esterification (temperature = 60 °C, time = 4 hours, molar ratio methanol/oleic = 3:1 and 3 wt. % catalyst) and total acid density of 2.64 mmol/g. Table 2.1 summarised the carbonisation conditions of various biomass material.

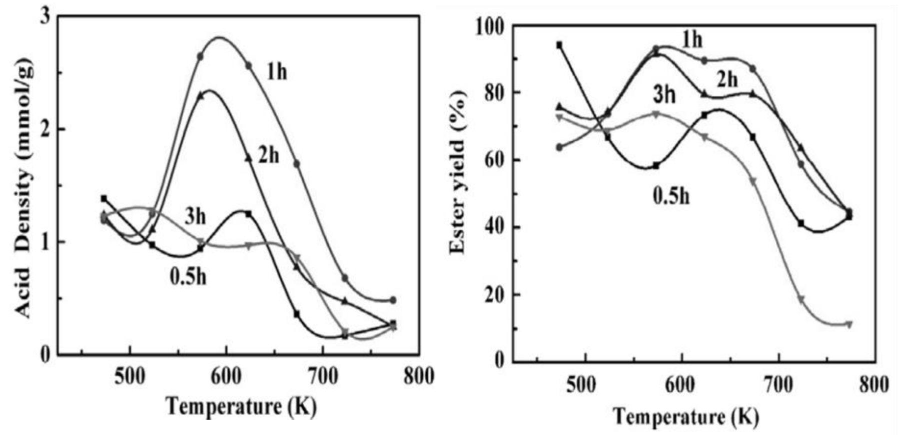


Figure 2.7: Effect of Carbonisation Time and Temperature on Catalyst Acid Density and Ester Yield (Liu, et al., 2013)

Table 2.1: Raw Materials Selected and Carbonisation Conditions of Several Literatures

Literature	**Raw Material**	**Conditions**	
		Temperature (°C)	**Time (hours)**
Ezebor, et al. (2014)	Sugarcane Bagasse and Oil Palm Trunk	400	15
Folasegun, et al. (2014)	C. inophyllum oil seed cake	400	5
Janaun, Abang and Anwar (2013)	Seaweed	400	4
Konwar, et al. (2015)	Deoiled Waste Cake (DOWC) - J. curcas - P. pinnata	500	1
Liu, et al. (2013)	Corn Straw	300	1
Mar and Somsook (2012)	Vermicelli made from starch of Mung Bean	300	1
Shu, et al. (2010)	Vegetable oil asphalt	500-700	1

2.4 Catalyst Synthesis Methods

The synthesis method of carbon acid catalyst is the main focus of the study in this project. Carbon acid catalyst is usually synthesised by sulfonation of carbon materials. Researches are investigating on different carbon sulfonation methods to achieve optimum performance for the synthesised solid acid catalyst. The purpose of sulfonation is to graft the $–SO_3$ group on the carbon support. This can be done by several pathways with different starting chemicals and operating procedures.

Folasegun, et al. (2014) has studied two types of sulfonation methods. These two methods include the direct sulfonation with sulfuric acid, H_2SO_4 and sulfonation by using p-toluenesulfonic acid (PTSA). In this study, glucose will be carbonised to form carbon material. For direct sulfonation with H_2SO_4, 5 g of pyrolysed carbon and 50 cm^3 of concentrated H_2SO_4 was heated with nitrogen flow at 150 °C for 10 hours. Next, the mixture was cooled at room temperature and washed with distilled water until no more impurities detected. Synthesised catalyst was then dried in vacuum oven for 10 hours at 60 °C. On the other hand, for sulfonation with PTSA, 5 g of carbon material, 2.5 g of PTSA and 20 cm^3 of de-ionized water was mixed in Teflon-lined autoclave at 150 °C for 5 hours. Catalyst produced was filtered, washed with distilled water and dried in vacuum at 100 °C for 4 hours. Catalyst synthesised from H_2SO_4 and PTSA will be noted as GBC_{SA} and GBC_{PTSA} respectively.

After sulfonation process, SO_3H groups was attached on the polycyclic aromatic carbon sheets of the carbon structure. Characterisation of catalyst showed that the sulfur content and acid density of GBC_{SA} was higher than GBC_{PTSA}. The SO_3H density of GBC_{SA} was about 1.0 mmol/g but GBC_{PTSA} contained only 0.1 mmol/g of SO_3H. Since the SO_3H density has direct relationship with the FAME yield, it is obvious that using GBC_{SA} has higher FAME yield (65-75%) than GBC_{PTSA} of FAME yield (8 – 11 %) in esterification (reaction conditions: C. inophyllum oil = 0.5 g, methanol = 5.5 g, carbon material = 0.3 g, reaction time = 5 hours, temperature = 150 °C). Both of these catalysts are thermally stable until 400 °C. By comparing these two methods, direct sulfonation with sulfuric acid was proved to be a better sulfonation method and can be employed in the future study.

Dehkhoda, West and Ellis (2010) had also studied the direct sulfonation method by concentrated sulfuric acid. 20 g of hardwood biochar was mixed with 200 mL of concentrated H_2SO_4 and then heated to 150 °C for 24 hours. Heated mixture was filtered and placed in cool distilled water. It was then washed with 80 °C distilled water until it was neutralised and dried in the oven at 70 °C for 1 hour. Resulted sulfonic group density was 0.65 mmol/g. Desorption of acid group occurred at around 650 °C which indicated a strong sulfonic acid sites on the catalyst.

Janaun, Abang and Anwar (2013) reported a sulfonation by fuming sulfuric acid. Fuming sulfuric acid, or also known as Oleum is a chemical with different composition of free sulfur trioxide dissolved in sulfuric acid. In this study, black carbon carbonised from seaweed was heated with fuming sulfuric acid (20 wt. % free SO_3) at 210 °C for 4 hours. After sulfonation, mixture was washed with distilled water until the washing water neutralised. Filtered sample was then dried in the oven at 110 °C. Total acidity of sample was measured to be 2.01 ± 0.03 mmol/g and SO_3H content of 0.28 mmol/g. The catalyst is thermal stable until the 240 °C.

Sulfonation by fuming sulfuric acid was also investigated by Liu, et al. (2013). Sulfonation was done by mixing 0.8 g of carbonized mater (corn straw) and 10 mL of fuming sulfuric acid (50 wt. % SO3) in a round bottom flask and heated in an oil bath at 80 °C for 4 hours. Mixture was diluted with distilled water after cooled to room temperature. Water-circulating pump was used to filter the sample and then washed thoroughly with hot distilled water to remove impurities like sulfate ions. Sample was then dried at the temperature 60 °C in vacuo for 4 hours. The total acid density of the catalyst synthesised was 2.64 mmol/g. It had a FAME yield of 92% at reaction temperature of 60 °C for 4 hours with methanol: oil molar ratio of 3 and catalyst of 3 wt. % (carbonised at 300 °C for 1 hour).

Malins, et al. (2015) and Konwar, et al. (2015) had reported the catalyst synthesis method of sulfonation by arylation using 4-sulfobenzenediazonium salts. According to Malins, et al. (2015), Activated carbon (AC) grains were first dried at 100 °C for 6 hours. Then, 1 g of AC, sulfanilic acid, NaOH and deionized water (50 - 200 mL), depending on the sulfanilic/AC ratio) was stirred and heated or cooled to temperature from 20 – 85 °C. NaNO2, NaOH and HCl were added with molar ratio of sulfanilic acid to NaNO2, NaOH and HCl of 1:05, 1:0 and 3:0 respectively. Various amount of water were used to completely solubilised reagents depending on the reaction temperature. NaOH was used to maintain pH of reaction mixture at 7 to 8. Reaction time (10 minutes) of arylation of AC was measured. Activated carbon attached with 4-sulfophenyl group (ACPhSO$_3$H) was obtained and washed with DI water to neutral pH and refluxed with acetone for 3 hours. ACPhSO$_3$H was dried at 65 °C for 6 hours in vacuum oven after separation and purification. Varying of reaction conditions had affected the character of the catalyst. The resulted characters of the catalyst will be discussed in Section 2.4.1.

Konwar, et al. (2015) had also studied on the sulfonation of activated carbon formed from de-oiled waste cake (DOWC) of Jatropha curcas (J), P. pinnata (P) and M. ferrea L. (M) by using 4-benzenediazoniumsulfonate (4-BDS), which is also known as the radical sulfonation process. Similarly, sulfonation occurred when there were covalent attachment of aryl radicals generated from the reduction of 4-BDS in the presence of hypophosphorus acid, H_3PO_2 as the reducing agent. In the sulfonating reaction, 15.2 g of sulfanilic acid was dispersed in 300 mL of 1 M HCl aqueous solution in a three necked flask. The flask was then placed into ice water bath which the temperature was controlled at 3 – 5 °C and the mixture stirred continuously. Then, 90 mL of 10% excess of 1 M $NaNO_2$ aqueous solution was added and resulted in a clear solution. About 16 g white precipitate of 4-BDS was formed and filtered after stirring for another 1 hour at the same temperature. The white precipitate was transferred into a beaker that contained 200 mL of deionised water and 60 mL of ethanol. 1.5 g of activated carbon (AC) was then added and the temperature was maintained at 3 – 5 °C, followed by addition of 30 – 32 % H_3PO_2 aqueous solution subsequently. After stirred for another 30 minutes, 50 mL of H_3PO_2 was added and mixture was stood for another 1 hour with occasional stirring. Sulfonated carbons obtained were wash with acetone and dried in the vacuum. The total density catalyst derived from J. curcas seed was 3.24 mmol H^+/g.

Shuit and Tan (2014) had compared four different catalyst synthesis methods. The sulfonation methods employed were in situ polymerisation of poly(sodium4-styrenesulfonate) (PSS), in situ polymerisation of acetic anhydride and sulfuric acid, thermal decomposition of ammonium sulfate and thermal treatment with concentrated sulfuric acid. In this studied, multi-walled carbon nanotubes (MWCNTs) were used as the catalyst support where SO_3H groups will be attached to. MWCNTs was ultrasonic treated with HNO_3 to purify the nanotubes.

For the sulfonation by in situ polymerisation of PSS, 0.4 g of purified MWCNTs was stirred in a mixture of 0.8 g PSS and 100 mL of deionised water for 10 hours at room temperature. The mixture was added with 1.6 g of $(NH_4)_2S_2O_8$ and then stirred and heated for 48 hours at 65 °C. The mixture was diluted with deionised water after it was cooled to room temperature and followed by sonication for 1 hour. Next, mixture was filtered and mixed with 50 mL of 4 M H_2SO_4 and stirred for 24 hours at room temperature and finally, the mixture was then wash with deionised water and dried for 12 hours at 120 °C. Density of SO_3H was 0.061 mmol/g. Desorption occurred at around 300 °C, which is stable at reaction temperature. Palm fatty acid distillate (PFAD) was use as the feedstock of the esterification reaction. It has the FAME yield of 93.4% at reaction temperature of 170 °C for 3 hours with methanol/ PFAD ratio of 20 and 2 wt. % catalyst.

As for sulfonation by in situ polymerisation of acetic anhydride and sulfuric acid, 0.2 g of purified MWCNT was mixed with 300 mL of acetic anhydride and 20 mL of concentrated H_2SO_4. Then, the mixture was then stirred and heated to temperature of 70 °C for 2 hours and then continued to stir until it reached room temperature. Sample was then filtered, washed and dried for 12 hours at 120 °C. Synthesised catalyst was undergone several characterisation. The SO_3H density of the catalyst is 0.03 mmol/g. Desorption occurred at around 250 °C, which was proven to be stable at reaction temperature. FAME yield of 85.8% was achieved at reaction temperature of 170 °C for 3 hours with methanol/PFAD ratio of 20 and 2 wt. % catalyst.

Another method reported by Shuit and Tan (2014) was sulfonation by thermal decomposition of ammonium sulfate. 0.4 g of purified MWCNTs were mixed with 30 mL of 10% ammonium sulfate solution. The mixture was then sonicated for 10 minutes and then followed with heating it to 235 °C for 30 minutes. Sample was then washed with distilled water and dried for 12 hours at 120 °C. With this method, desorption occurred at around 250 °C, which was considered stable at reaction temperature.

Catalyst synthesised by thermal decomposition of ammonium sulfate had the FAME yield of 88.0 % at reaction temperature of 170 °C for 3 hours with methanol/PFAD ratio of 20 and 2 wt. % catalyst.

The fourth method studied by Shuit and Tan (2014) was sulfonation by thermal treatment with concentrated sulfuric acid, similar to those mentioned in earlier phase. The outcomes of these four catalyst synthesis sulfonation methods were compared and in situ polymerisation of PSS was shown to be the method that had the highest FAME yield and with highest density of SO_3H groups in the catalyst. However, the sulfonation by this method involved a series of processing steps that used many types of chemicals and also required a relatively long reaction time of about 4 days. Thus, sulfonation by thermal decomposition may be a better solution due to less time consuming as well as involving less acidic chemicals. And the most important thing is that the catalyst activity does not has big different with the sulfonation in situ polymerisation of PSS.

The characterisation results and catalytic activity of the catalysts from synthesis methods discussed was summarised in Table 2.2.

Table 2.2: Various Synthesis Method for Sulfonation of Carbon Catalyst

Literature	Synthesis Method	Conditions	Acid Density of Catalyst, SO_3H (mmol/g)
Folasegun et al. (2014)	Direct sulfonation with sulfuric acid, H_2SO_4	T: 150 ℃ Time: 10 hours	1.0
	Sulfonation by using p-toluenesulfonic acid (PTSA)	T: 150 ℃ Time: 5 hours	0.1
Dehkhoda, West and Ellis (2010)	Direct sulfonation with sulfuric acid, H_2SO_4	T: 150 ℃ Time: 24 hours	0.65

Table 2.2 (continued): Various Synthesis Method for Sulfonation of Carbon Catalyst

Literature	Synthesis Method	Conditions	Acid Density of Catalyst, SO_3H (mmol/g)
Janaun, Abang and Anwar (2013)	Sulfonation by fuming sulfuric acid (20 wt. % free SO_3)	T: 210 ℃ Time: 4 hours	0.28
Liu et al. (2013)	Sulfonation by fuming sulfuric acid (50 wt. % free SO_3)	T: 80 ℃ Time: 4 hours	Total acid: 2.64 mmol/g S content: 7.81%
Kristap et al. (2015)	sulfonation by arylation using 4-sulfobenzenediazonium salts	Without H_3PO_2 T: 70 ℃ Time: 10 minutes	Total acid: 0.22 mmol/g
Konwar, et al. (2015)	sulfonation by arylation using 4-benzenediazoniumsulfonate (4-BDS)	With H_3PO_2 T: 3 - 5 ℃ Time: 1 hour	Total acid: 3.24 mmol/g S content and SO_3H density not measured
Shuit et al. (2014)	In situ polymerisation of poly(sodium4-styrenesulfonate) (PSS)	T: 65 ℃ Step1: 10 hours Step1: 48 hours Step1: 24 hours	0.61
	In situ polymerisation of acetic anhydride and sulfuric acid	T: 70 ℃ Time: 2 hours	0.03
	Thermal decomposition of ammonium sulfate	T: 235 ℃ Time: 30 minutes	0.029
	Thermal treatment with concentrated sulfuric acid	T: 250 ℃ Time: 12 hours	0.016

2.4.1 Effect of Synthesis Variables

For the synthesis method selected in one study, reaction conditions can be varied to obtain the optimum conditions that are able to produce the catalyst with highest acid density which correspond to the FAME yield. Synthesis variables like weight ratio of acid to carbon, reaction temperature and reaction time can be studied.

As mentioned, Malins, et al. (2015) that employed arylation of activated carbon grains (AC) with 4-sulfobenzenediazonium salt from sulfalinic acid to obtain $ACPhSO_3H$ has varied the catalyst synthesis parameters to study the effect of these parameters on the resulted catalyst synthesised. This study was also conducted in order to optimise the synthesis conditions that are able to maximise the catalyst performance and properties. Experiment parameters of weight ratio sulfanilic acid to AC and reaction temperature were varied. This research acts as an example in varying the synthesis parameters for the future researches.

Different weight ratio of sulfanilic acid to AC (0.14/1, 0.70/1, 1.4/1, 3.5/7, 7/1, 14/1) were used. The effect of these different ratios on the S content on ACPhSO3H was investigated. As shown in Figure 2.8, weight ratio of sulfanilic acid to AC of 7/1 has achieved the maximum $PhSO_3H$ density attached (0.59 mmol H+/g). Section 2.4 had mentioned that the reaction was carried out from temperature of 20 to 85 °C. So, temperature of 20, 30, 50, 70, 85 °C were employed when conducting the catalyst synthesis reaction without the presence of H_3PO_2 as reducing agent. According to Figure 2.9, the density of $PhSO_3H$ on AC increased with the increase of temperature until 70 °C was reached. Further increase in temperature will reduce the efficiency. Reaction temperature of 70 °C gave $PhSO_3H$ density of 0.72 mmol H+/g.

Weight ratio of chemical to carbon material and temperature were just some of the examples of parameters can be varied. The effect of different molar ratio of chemicals used in the synthesis, reaction time, concentration of chemicals and many more other parameters can also be studied by preparing a number of samples synthesised with varying parameters and compared the properties of catalyst and the catalyst activity between these samples.

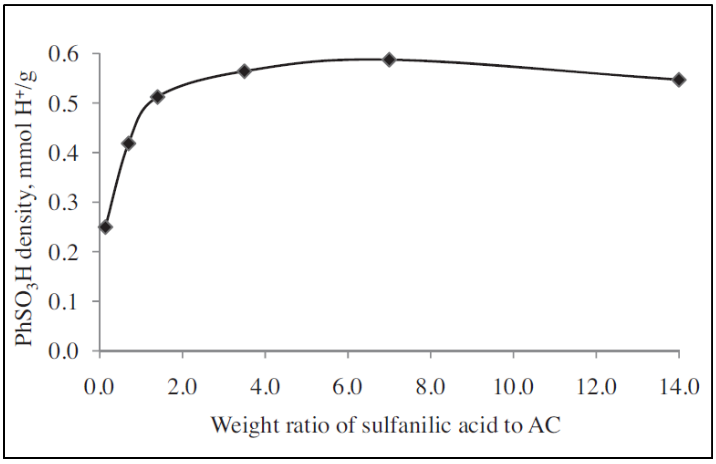


Figure 2.8: Effect of Weight Ratio of Sulfanilic Acid to AC on PhSO$_3$H Density (Malins, et al., 2015)

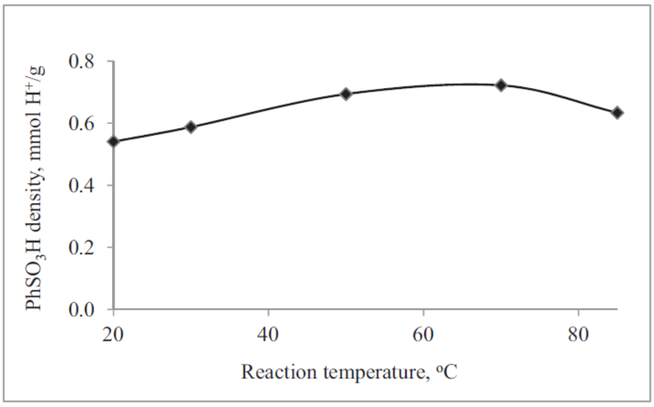


Figure 2.9: Effect of Reaction Temperature of Sulfanilic Acid to AC on PhSO$_3$H Density (Malins, et al., 2015)

2.5 Characterisation of Synthesised Catalyst

Characterisation of catalyst is done to study the properties of the catalyst synthesised. Properties like surface morphology, thermal stability, acid density, functional groups attached and many more are studied to verify whether or not the synthesis method is suitable to be used to produce the catalyst. Characterisation of catalyst can be carried out by using different types of instrument available in the laboratory. Table 2.3 shows several examples of catalyst characterisation completed by researches. The most common characterisation done includes Scanning Electron

Microscopy (SEM), FT-IR spectra analysis, back titration for acid density and Thermal gravimetric analysis (TGA).

Table 2.3: Catalyst Characterisation

Literature	Instrument/ Method	Description
Folasegun, et al. (2014)	Nitrogen adsorption/desorption conducted at -196 ℃ by using Automatic Surface Analyzer and Porosity	To determine surface area of carbon catalyst obtained
	Scanning Electron Microscopy (SEM) connected to Energy-Dispersive X-ray Spectroscopy (EDX)	To obtain structural information and amount of sulfur on catalyst
	X-ray Diffractometer (XRD) with Cu Kα radiation - λ = 0.1540 nm - 40 kV and 40 mA - Range = 2Θ of 10° to 90° - Scanning Speed: 0.05°/min	To study the structure and crystallinity of the carbon catalyst
	FT-IR with KBr pellets and Raman spectroscopy	To determine the functional groups attached
	Differential Thermal Analysis/ Simultaneous Thermogravimetric (DTA-TG) - Temperature: 900 °C - Rate: 10 °C/min	To determine the thermal stability of catalyst
Janaun, Abang and Anwar (2013)	Back titration method by first mixing catalyst with 0.008 M NaOH - Titrant: 0.02 M HCl	To measure total acidity of the catalyst
	FT-IR equipped with Attenuated Total Reflectance (ATR)	To determine functional groups

Table 2.3 (continued): Catalyst Characterisation

Literature	Instrument/ Method	Description
Janaun, Abang and Anwar (2013)	Scanning Electron Microscopy (SEM) connected to EDX	To study the surface morphology and percentage of carbon, oxygen and sulfur in the catalyst
	Thermal gravimetric analysis (TGA) - Temperature range: 30 to 400 °C ramped at 10 °C/min - Nitrogen flow: 100 mL/min	To study the thermal stability of the catalyst
Shuit and Tan (2014)	Zetasizer Nano-ZS	To determine the zeta potential of MWCNT
	FT-IR spectra analysis	To determine the presence of SO_3H group in sample
Konwar, et al. (2015)	Transmission Electron Micrograph (TEM) - Voltage: 200 kV - Resolution: 0.4 nm	To obtain the TEM of catalyst
	Carlo Erba Sorptomatic 1990 - BET equation (P/P_o = 0.05-0.3) - Barrett-Joyner-Halenda (BJH) method	BET was used to determine the specific area whereas BJH method was used to determine the pore size distribution of the catalyst
	Temperature-programmed Adsorption-desorption of Ammonia (TPD) - Temperature: 100 to 500 °C - Heating rate: 10 °C/min	To determine the strength and acid sites of the catalyst

2.6 Characterisation of Feedstock and Products

Feedstock are vegetable oil or animal fats that will react with alcohol (normally methanol) to form biodiesel. When free fatty acids (FFA) content of the oil is high, the feedstock will undergo esterification to form fatty acid methyl ester (FAME). Acid density of the oil feedstock and the composition of the acids in the feedstock will be determine prior to or after the reaction to ensure that acid catalyst is used when FFA content of feedstock is high.

The FFAs contained in the oil are the saturated and unsaturated fatty acid with different carbon to double ratio (C: D). Palmitic acid (16: 0), stearic acid (18:0) and lauric acid are some examples of saturated fatty acids. Oleic (18: 1), linoleic acid (18: 2) and linolenic acid (18: 3) are some example of free fatty acids present in the oil. Composition (%) of these fatty acids are determined in the experiment.

Malins, et al. (2015) followed the standard ISO 5509 whereby the fatty acid composition in the Rapeseed oil was determined by using rapeseed oil fatty acid methyl ester with gas chromatography (GC) analysis equipped with FID and a capillary column of dimension 30 m × 250 µm × 0.25 µm. Detector temperature was programmed at 390 °C and column temperature of 200 °C for 25 minutes. Helium was flow at the rate of 2 mL/min as the carrier gas where 1 µL of sample was injected. Acid composition of the rapeseed oil fatty acid was also determined by GC analysis according to the standard EN 14103.

The yield of FAME was determined by using gas chromatography equipped with FID and polar capillary column (30 m × 0.25 mm i.d. × 0.25 µm) with methyl heptadeconoate as internal standard according to (Ezebor, et at., 2014). European regulation procedure EN 14103 was followed to analyse and calculate the FAME content of the samples. FAME yield was calculated with equation 2.1.

$$\text{FAME yield (\%)} = \frac{\sum \mathrm{A} - \mathrm{A_{IS}}}{\mathrm{A_{IS}}} \times \frac{\mathrm{C_{IS}} \times \mathrm{V_{IS}}}{\mathrm{m_{sample}}} \times 100\% \qquad (2.1)$$

where

$\sum A$ = total peak area

A_{IS} = methyl heptadeconoate peak

C_{IS} = concentration of methyl heptadeconoate solution (mg/mL)

V_{IS} = volume of methyl heptadeconoate solution used (mL)

m_{sample} = mass of sample used (mg)

Shu, et al. (2010) claimed that the FFA and FAME have very close molecular size that may lead to overlapping of peak when these two material was detected by high performance liquid chromatography (HPLC) and resulting in peak area calculation error. Thus, the conversion of FFA in the feedstock can be determined by calculating the acid value of both feedstock and products. According to ISO 1242:1999 the measurement of acid value (mg KOH/g) can be measured by using titration method. Potassium hydroxide, KOH was used as the titrant and the amount of KOH used to neutralise the feedstock and products was recorded. Then, conversion of FFA was determined by calculating the difference of acid value between feedstock and product.

2.7 Biodiesel Production Experiment

Liu, et al. (2013) had reported the catalytic reaction procedure. A 100 mL flask that was equipped with magnetic stirrer was used for the esterification reaction. Reaction temperature of 60 °C was maintained. Reaction mixture consisted of 10 g of oleic acid, 4.3 mL of methanol with 3 wt. % of catalyst. The reaction mixture was stirred at the speed of 100 rpm for 4 hours. After completed reaction, the catalyst was filtered and washed. Reaction products was transferred to three necked flask to remove water and methanol by reduced pressure distillation.

Shu, et al. (2010) had carried out the reaction in an autoclave reactor equipped with magnetic stirrer. Mixed oil (rapeseed, cottonseed and soybean acidified oils) and synthesised catalyst were charged into the autoclave reactor by a pump. The reaction mixture was stirred at the rotation speed of 240 rpm at 140 °C. When the reaction is completed reduced pressure distillation was used to remove the FAME from the reaction mixture. After the reaction mixture was cooled, it was reduced to pressure of about 3 mm Hg and heated to 240 °C and maintained for 90 minutes. The reaction mixture was cooled and filtered after 90 minutes. Filtrate was then allowed to settle and it will be separated into two layers. The aqueous phase consisted of water, methanol and glycerol whereas FAME is contained in the oil phase.

2.7.1 Stability and Regeneration Test

Stability test is important to be carried out for the catalyst synthesised. After each time catalyst is used in the biodiesel production process, there is possibility that the SO_3 grafted on catalyst will be leached during the reaction reducing the activity of the catalyst in the next cycle of reaction. Thus, the activity of the catalyst after several consecutive cycles with and without regeneration is studied.

Folasegun, et al. (2014) had studied on the stability of the catalyst synthesised from C. inophyllum seed cake derived carbon with sulfonation by heat treatment with concentrated H_2SO_4. Operation stability was compared between catalyst with 1 hour (cat -1) and 5 hours (cat – 2) carbonization time. Catalyst with 1 hour carbonization time has smaller carbon sheets and shows significant leaching. The yield of FAME at 5th cycle is 38.9% and 50.3% for 1 hour and 5 hours carbonization time respectively. Regeneration of catalyst can be achieve by washing with tetrahydrofuran (THF). Table 2.4 showed the FAME yield after several recycling cycles of catalyst.

Table 2.4: Effect of Catalyst Recycling on the Yield of FAME (Folasegun, et al., 2014)

Cycles	Yield (%)	
	Cat – 1 [a]	Cat – 2 [b]
Fresh	99.0	99.0
1	96.2	97.0
2	90.8	93.5
3	75.1	82.8
4	65.4	72.4
5	38.9	50.3

(Reaction condition: vegetable oil 5 g, methanol = 5.5 g, catalyst = 0.38 g, temperature = 180 °C, reaction time [a] = 4 hours, reaction time [b] = 5 hours)

Malins, et al. (2015) claimed that leaching of $PhSO_3H$ group acts as the main problem of the AC based catalyst. $PhSO_3H$ groups in the catalyst ($ACPhSO_3H$ catalyst synthesised by Arylation of activated carbon grains (AC) with 4-sulfobenzenediaonium salt from sulfalinic acid) had decreased by about 32% (0.49 mmol H^+/ g) after seven reaction cycles (Reaction condition: molar ratio rapeseed oil/methanol = 1/20, 10 wt. % catalyst, temperature = 65 °C, reaction time = 2 hours). As shown in Figure 2.10, regeneration of catalyst enable it to achieve and increment of $PhSO_3H$ groups to about 0.7 mmol H^+/ g (close to freshly prepared catalyst).

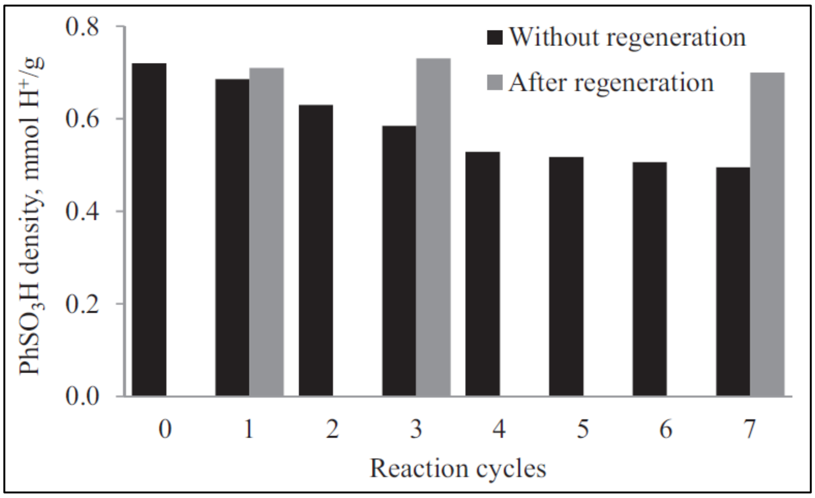


Figure 2.10: Comparison between Catalytic Reaction Cycles With and Without Regeneration of Catalyst (Malins, et al., 2015)

Shuit and Tan (2014) has compared the reusability of catalyst synthesised from four different methods through five consecutive cycles of esterification. Catalyst separated from reaction mixture was sonicated in methanol for 20 minutes and dried at 120 °C for 12 hours. FAME yield after each cycles of reaction by catalysts sulfonated with in situ polymerisation of poly(sodium4-styrenesulfonate), in situ polymerisation of acetic anhydride and H_2SO_4, thermal decomposition of ammonium sulfate and thermal treatment with concentrated sulfuric acid is shown in Figure 2.11 and compared. The results showed that after 5 cycles of catalytic reaction, the FAME yield was not dropped significantly and resulted to be at the range to 70 to 80%. Regeneration of catalyst could be employed to achieve higher yield of FAME.

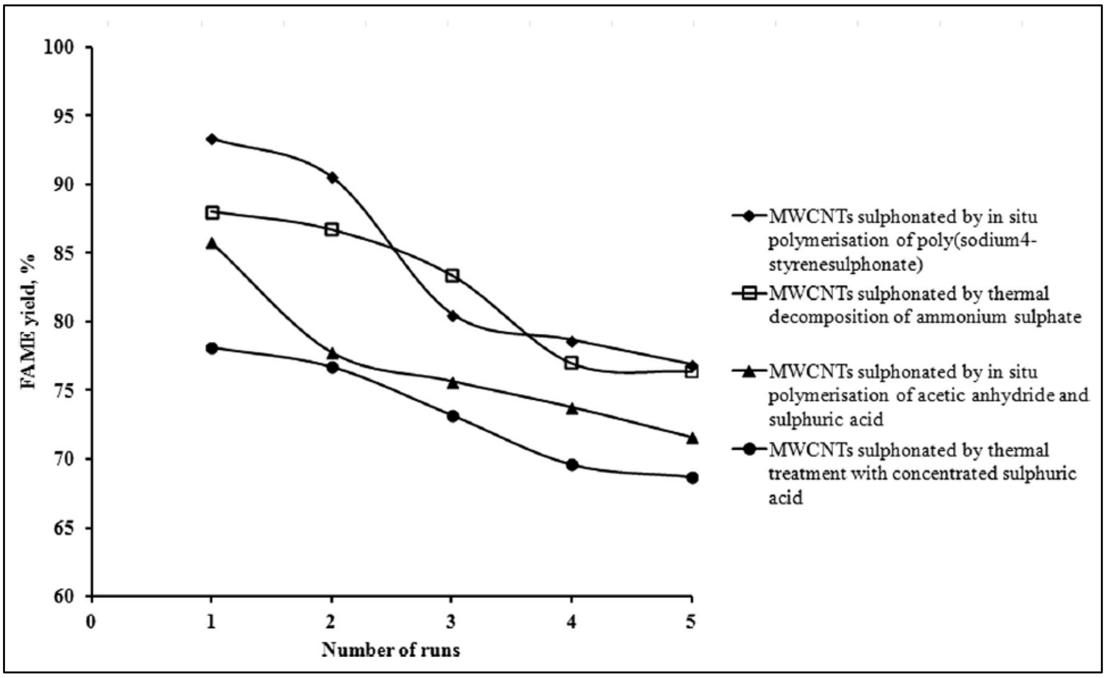


Figure 2.11: Reusability of the Sulfonated MWCNT in the Esterification of PFAD (Shuit and Tan, 2014)

2.7.2 Optimisation Study

Although the reaction conditions stated in Section 2.7 are feasible for the catalytic reaction, determination of the optimum conditions is still important to ensure that the performance of catalyst in esterification and transesterification process is optimised. In this study, the optimum conditions for the reaction of biodiesel production are obtained by varying the reaction conditions until the highest FAME yield is achieved. Variables like molar ratio of oil to methanol, catalyst concentration, reaction time and reaction temperature are investigated by researchers.

Folasegun, et al. (2014) had investigated on the effect of molar ratio of C. inophyllum oil (15% FFA) to methanol (1:12 to 1:45), catalyst loading (1.5 – 7.5 wt. %), temperature (130 – 200 °C) and time (1 – 5 hour(s)) on the FAME yield. As shown in Figure 2.12, the increase of molar ratio of C.inophyllum oil to methanol showed positive response towards the yield of FAME until it reaches the ratio of 1:30. Further increase of molar ratio after 1:30 give no significant effect to the FAME yield and this is probably because the excess dilution that lead to the reduce of collision frequency and flooding of small surface area of catalyst.

The FAME yield increases with the increase of catalyst wt. %. Optimum catalyst concentration was achieved at about 7.5 wt. %. No significant increase of FAME yield is observed at higher than 7.5 wt. % catalyst concentration. On the other hand, increase of temperature increases the yield of FAME 99% yield of FAME was achieved at the temperature of 180 °C. However, further increment of reaction energy may cause reverse production according to Figure 2.12. Then, FAME yield increase gradually with time. 99% yield of FAME was achieved with the reaction time of 5 hours.

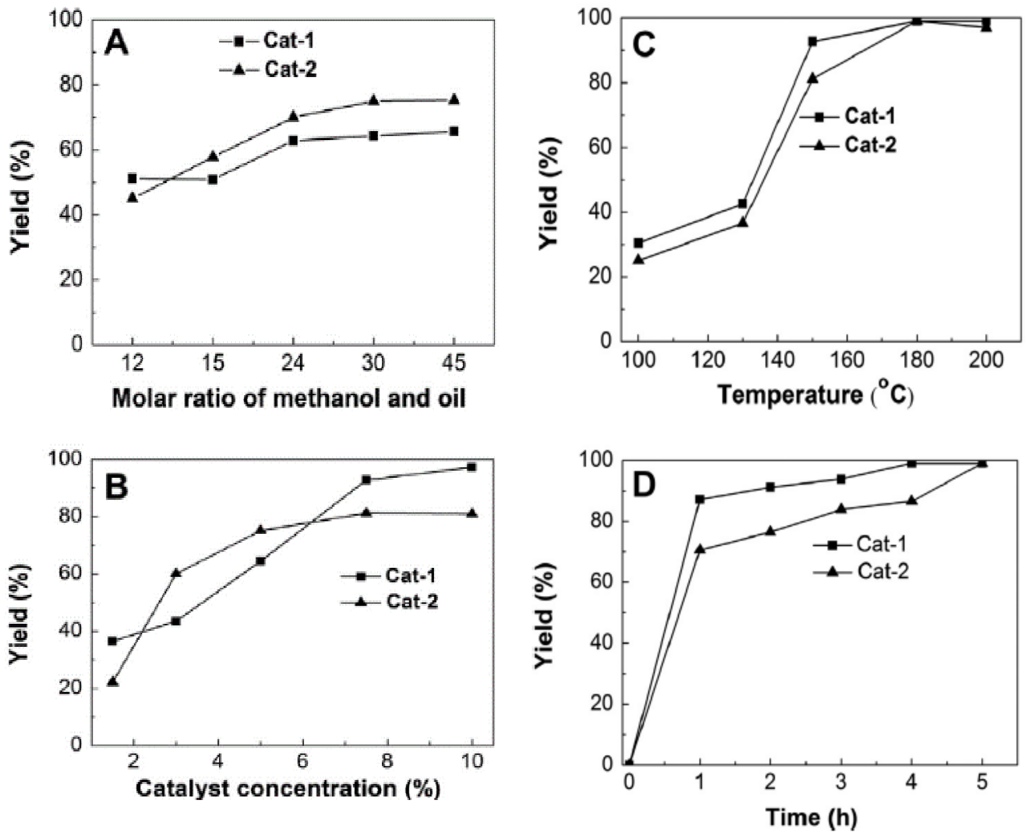


Figure 2.12: **Effect of (A) Molar ratio of methanol and oil (B) Catalyst Concentration (C) Temperature and (D) Time on the FAME Yield (Folasegun, et al., 2014)**

Liu, et al. (2013) which reported the corn straw derived carbon based acid catalyst sulfonated by fuming H_2SO_4 had studied on the effect of molar ratio of oleic acid to methanol and catalyst concentration. Molar ratio of methanol to oleic acid at 4, 5, 6, 7 and 8 was tested. Highest FAME yield was obtained at molar ratio 7:1 of methanol/oleic acid. Then, catalyst weight percentage of 3, 4, 5, 6, 7 and 8 wt. % was studied and compared. Highest FAME yield was achieved when catalyst concentration of 7 wt. % was used.

Table 2.5 summarised the optimum catalytic reaction conditions obtained through the optimisation study from several literatures. This is very useful when deciding the reaction conditions in the future to achieve the maximum FAME yield and optimised the catalytic activity of the catalyst synthesised.

Table 2.5: Summary of Optimum Reaction Conditions from Several Literatures

Literature	Feedstock Used	Optimum Conditions			
		Feedstock/ Methanol Molar Ratio	**Catalyst Loading (wt. %)**	**Temperature (°C)**	**Time (hours)**
Dehkhoda, West and Ellis (2010)	Canola Oil	1/18	5	60	3
Folasgun, et al. (2014)	C. inophyllum oil	1/30	7.5	180	5
Ezebor, et al. (2014)	Palmitic Acid	1/18	9	65	5
Liu, et al. (2013)	Oleic acid	1/7	7	60	4
Shu, et al. (2010)	Mixed vegetable Oil	1/17	0.2	220	4.5
Shu, et al. (2009)	Cottonseed oil	1/18	1.5	260	3

CHAPTER 3

METHODOLOGY

3.1 List of Materials and Apparatus

The following sections are the list of materials, apparatus and equipment required to run the whole research. All of the things listed below were prepared prior to the start of the experiments for further studies and investigation.

3.1.1 Materials and Chemicals

This research involves various types of chemicals and raw materials that have to be prepared prior to the start of experiment. Seaweed (brown algae) is selected as the raw material to synthesise biomass-based carbon acid catalyst. Sulfonation of carbon will be done by thermal decomposition of ammonium sulfate. The types, sources, amount and usage of materials and chemicals required throughout the whole experiment in the study are listed in Table 3.1, 3.2 and 3.3.

Table 3.1: List of Chemicals and Materials Required for the Experiments

Chemicals/Materials	Source	Quantity	Usage
Seaweed (brown algae)	Beach at Labuan	5 kg	Raw material for carbon support of the catalyst
Palm Fatty Acid Distillate (PFAD)	Malaysia	1 L	Feedstock for the synthesis of biodiesel
10 %(w/v) Ammonium Sulfate	Salt Crystal from OmniPur	2 L	Chemical for synthesis of catalyst
Methanol	Fisher Scientific	2 L	Reactant for the synthesis of biodiesel
Potassium Hydroxide	Pellet form Friendemann Schmidt	1 kg	Titrant for determination of acid value
Phenolphthalein	R & M Chemical	50 mL	pH indicator
Hexane	Synerlab	2 L	To be used as a solvent for FAME
0.1 M NaOH	GENE Chemicals	2 L	To determine acid density of catalyst
0.2 M HCl	Reagents DUKSAN	2 L	To determine acid density of catalyst
30 v/v% Phosphoric Acid	Reagent DUKSAN		To activate biomass
Distilled Water	-	-	To wash of excess reactant from catalyst after reaction
Oil	Saji Cooking Oil	500 mL	To use as the oil bath for heating

3.1.2 Apparatus and Equipment

The whole experiment throughout the whole study involves various types of apparatus and equipment with different usages. They are important to be used in the preparation, reactions and analysis process in the whole experiment. Table 3.2 shows the apparatus and equipment required for different sections of the experiment.

Table 3.2: List of Apparatus and Equipment Used in Preparation of Catalyst

Apparatus and Equipment	Specifications	Usage
Oven	Memmert	To dry the seaweed and synthesised catalyst
Furnace	Carbolite	For pyrolysis of raw materials into carbon material
Grinder	Deer	To grind seaweed biomass into powder form
Water Bath Ultrasonicator	Wisd	Mix activated carbon with sulfonating agent
Pestle and Mortar	-	To ground carbon material into powder form
Hot Plate	IKA RH basic 2	To heat up reaction mixture to desired temperature
Reflux Column	Flavorit 300 mm Graham Condenser	Reflux methanol during biodiesel production
Filter Paper	Double Rings	To filter catalyst from other liquid mixture

Table 3.3: List of Instrument and Apparatus Required for Characterisation of Catalyst and Feedstock and Product Analysis

Instrument and Apparatus	Specifications	Usage
Scanning Electron Microscope (SEM)	Hitachi Model S-3400N coupled with EDX	To obtain surface morphology of catalyst
Energy Dispersive X-ray Spectroscopy	Ametek	To study the sulfur content in the catalyst
Fourier Transform-infrared (FT-IR)	Nicholet IS10	To study the functional groups on the catalyst
Gas Chromatography	GC-FID Perkin Elmer Clarus 500	To determine acid composition in oil feedstock and FAME yield in the reaction products
Thermogravimetric Analysis (TGA)	STA 2500 Regulus	To determine the thermal stability of catalyst

3.2 Overall Research Methodology

This study involves a series of methodology steps throughout the whole experiment with the synthesis of carbon based solid acid catalyst as the main focus of the research. The research methodology can separated into several sections and summarised as show in Figure 3.1 below.

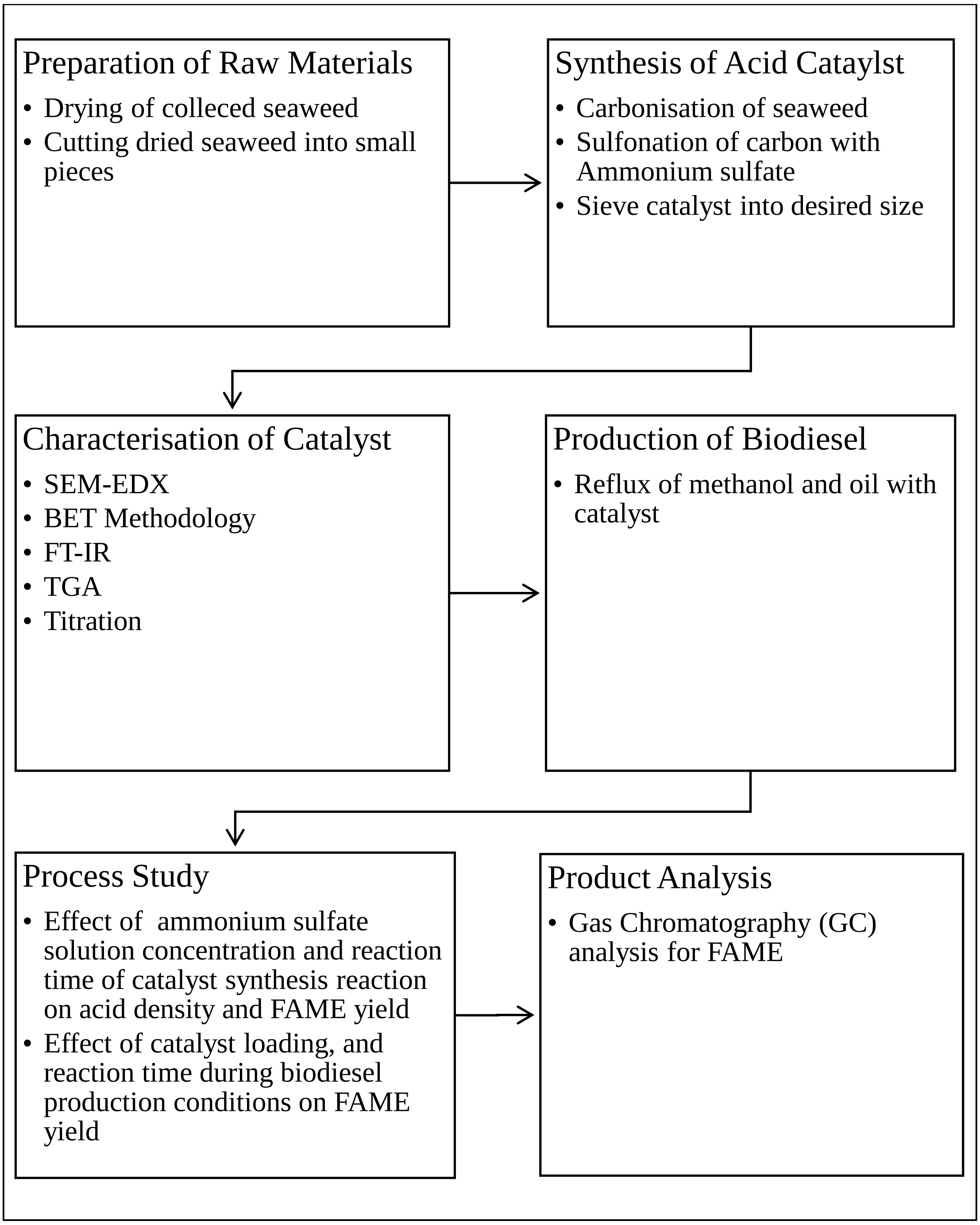


Figure 3.1: Summary Procedures of the Experiment

3.3 Synthesis of Catalyst

3.3.1 Carbonisation of Seaweed

The collected seaweed was washed and dried in the oven at 80 °C for overnight. Next, the dried seaweed pieces was crushed into smaller piece and grinded into powder form by using grinder. Then, the seaweed powder will be added with 30 v/v% phosphoric acid solution with the ratio of 1 to 3 powder to solution ratio and left for overnight. Activated seaweed powder was then be wash with distilled water and dried in the oven at 80 °C for overnight. The activated seaweed was sent to tube furnace for pyrolysis process. Pyrolysis of seaweed was done at the rate of 5 °C/min until the desired temperature (200, 300, 400, 500 and 600 °C) is reached and kept constant for 2.5 hours. The summary of the seaweed carbon preparation process are shown in Figure 3.2. The resulted brown to black materials was then grounded into powder form by using pestle and mortar. Carbon materials will then be analysed by using Brunauer-Emmett-Teller method and Scanning Electron Microscopy (SEM) which the procedures will be explained at the following sections.

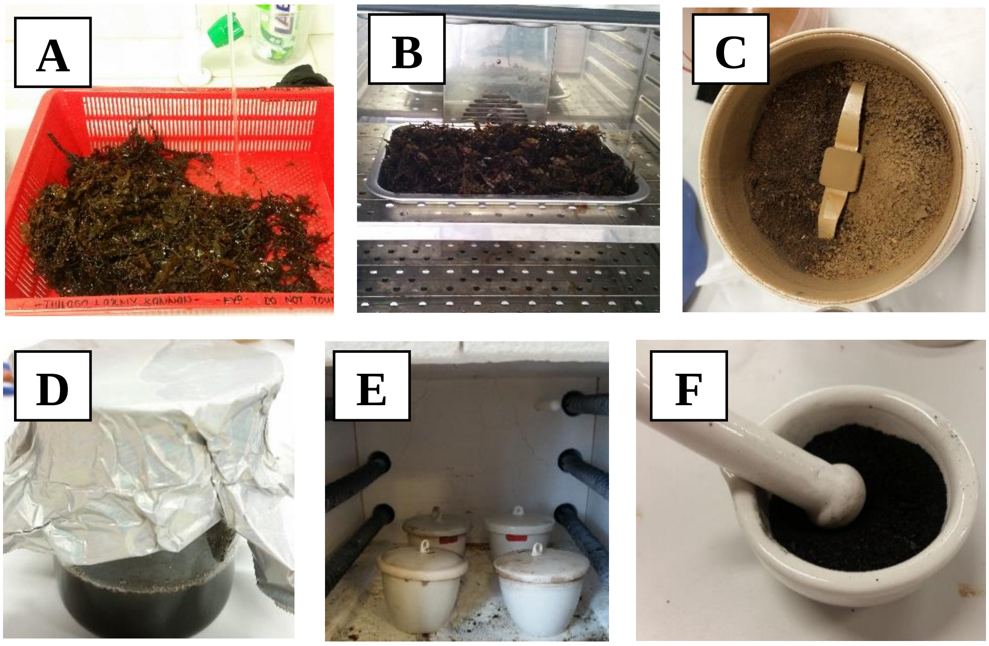


Figure 3.2: (A) Washing of Collected Fresh Seaweed (B) Drying of Seaweed (C) Grinding of Seaweed into Powder Form (D) Activation of Seaweed in 30 v/v% Phosphoric Acid (E) Pyrolysis of Seaweed in Furnace (F) Grounding of Carbon

3.3.2 Sulfonation of Carbon

The sulfonation of carbon was done by the method thermal decomposition of ammonium sulfate, $(NH_4)_2SO_4$. In this experiment, different concentration of $(NH_4)_2SO_4$ (5, 10, 20, 30 and 40 w/v%) and carbon material was mixed and ultrasonicated with water bath ultrasonicator for 10 minutes. The mixture was then heated to the temperature of 235°C in a furnace and for various durations (15, 30, 60 and 90 minutes). After cooled, the sample was washed with distilled water to remove excess $(NH_4)_2SO_4$ and filtered. Filtered sample was then dried in an oven at 80 °C overnight. Figure 3.3 shows the summarised procedure for sulfonation of seaweed carbon.

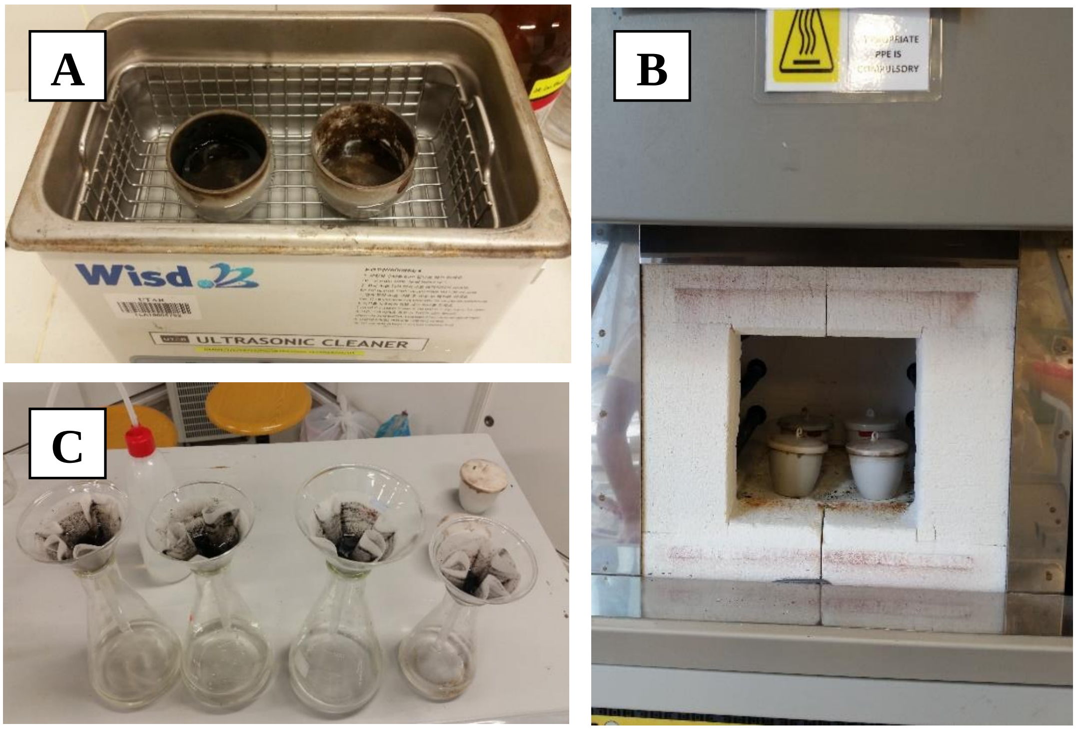


Figure 3.3: (A) Water bath Ultrasonication of Carbon and Ammonium Sulfate Mixture (B) Heating to 235 °C in Furnace (C) Washing and Filtration of Catalyst

The variation of parameters was studied to obtain the optimum parameters so that the synthesised solid acid catalyst is grafted with maximum acid density and thus, the FAME yield is maximised. When experiment was done at different heating duration, the condition was kept constant at 10 minutes ultrasonication, temperature of 235 °C by using 30 ml of different concentration of ammonium sulfate solution. Experiment was repeated with the heating duration of 15, 30, 60 and 90 minutes and each of the heating duration, 30 ml of $(NH_4)_2SO_4$ solution with different concentration at 5, 10, 20, 30 and 40 w/v% was used as the sulfonating agent with other conditions remained constant at 10 minutes ultrasonication and heating temperature of 235 °C.

3.4 Catalyst Characterisation

Characterisation of catalyst was done on all the seaweed-based acid catalyst synthesised previously at different synthesis parameters. Characterisation was carried out to study the effect of various synthesis parameters on the chemical and physical properties of the catalyst by using different equipment to study on different properties. The catalyst with the best properties in overall will be selected to be used in the process study on biodiesel production. Normally, the quality of the catalyst was determined with the SO_3H density attached as the main criteria.

3.4.1 Surface Morphology

The surface morphology of catalyst was observed under Scanning Electron Microscopy (SEM) (Hitachi Model S-3400N). The sulfonated carbon catalysts were scanned at the magnification of 500x, 2000x and 10,000x. When the scanning was done, the diameter of the pore size can be estimated by measuring the length of pores on the micrographs manually referring to the scale provided on the images. The SEM connect to Energy Dispersive X-ray Spectroscopy (EDX) was used to obtain the sulfur (S), carbon (C) and oxygen (O) content in the catalyst.

3.4.2 Brunauer-Emmet-Teller Methodology

Brunauer-Emmet-Teller (BET), surface area of catalyst was analysed with the Sorptomatic 1990 by using inert Nitrogen liquid at temperature -196 °C as the coolant. For this surface analysis, two types of analysis were carried out, which were the blank analysis and the sample analysis. Blank analysis was carried out by using Helium gas to determine the dead volume of the measurement cell. Then, sample analysis was done by using Nitrogen gas as the adsorbate and it will be absorbed into the sample for the measurement of surface area.

3.4.3 Fourier Transform - Infrared Spectroscopy

Fourier transform-infrared spectroscopy (FT-IR) (Nicholet IS10) was used to study the functional groups attached in the catalyst. This study was done by putting the catalyst on top of the diamond sample platform and fixed by the pressure tower and compression tip. The component on the spectroscopy is shown in Figure 3.4. Scanning by FT-IR spectroscopy was done in the range of 500 to 4000 cm^{-1}. The FT-IR absorbance spectra of the unsulfonated carbon and sulfonated carbon (catalyst) were recorded.

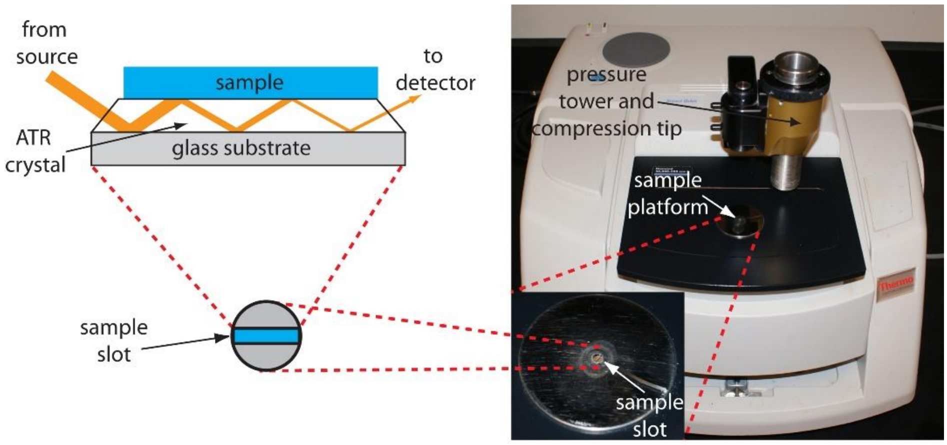


Figure 3.4: FT-IR Spectroscopy Component (ChemWiki, 2013)

3.4.4 Acid Density

The total acid density of the catalyst was determined by the back titration method. In this method, 0.02 M of aqueous HCl solution was used as the titrant with phenolphthalein as the pH indicator. 0.1 g of catalyst sample was mixed with 60 mL of 0.01 M aqueous NaOH solution in a conical flask and agitated with magnetic agitator at 300 rpm for 30 minutes at room temperature. The mixture was then filtered and the filtrate was then titrated with 0.02 M HCl.

The concept of this method is to mix the acid catalyst with excess 0.01 M NaOH solution. The alkali NaOH solution will then react with the acid catalyst. The remaining unreacted NaOH will then be titrated with 0.02 M of HCl. The volume of HCl used will be recorded and used to calculate the acid density of catalyst in mmol/g. Figure 3.5 explains the calculation of acid density from back titration method to obtain Equation 3.1.

Let V = volume of 0.02 M HCl titrated (Litre)

Number of mol of HCl used (mol) = 0.02 × V

After 30 minutes of reaction of 0.01 M NaOH with acid catalyst, the excess unreacted will then be titrated by 0.02 M of HCl.

Number of mol of NaOH remaining is equivalent to number of mol of HCl used
= 0.02v mol

Initially,

60 mL of 0.01 M or 0.01 mol/Litre NaOH solution is equivalent to 0.0006 mol NaOH

Number of mol of NaOH reacted with acid in catalyst = 0.0006 mol – 0.02V mol

Thus,

$$\text{Acid Density}\ \left(\frac{\text{mmol}}{\text{g}}\right) = \frac{0.0006\ \text{mol} - 0.02\text{V mol}}{0.1\ \text{g}} \times 1000 \qquad (3.1)$$

Figure 3.5: Derivation of Acid Density Formula

3.4.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was done to study the thermal stability of catalyst. The temperature of which the functional group will be detached from the carbon support will be determined. This analysis was conducted by STA 2500 Regulus. Sample of mass 5.308 g was placed in alumina crucible before transferring into the thermal analyser and the temperature was ramped from room temperature to 100 °C at the heating rate of 5 °C/min under nitrogen atmosphere at room temperature to 900 °C and synthetic air atmosphere at temperature 900 °C to 1000 °C.

3.5 Feedstock Analysis

3.5.1 Acid Value Test

The acid value of the palm fatty acid distillate (PFAD) was determined by using titration method. In this experiment, potassium hydroxide, KOH is used as the titrant with propanol as solvent and phenolphthalein as pH indicator. 0.1 N of potassium hydroxide solution was prepared by adding 1 L of water into 5.6 g of potassium hydroxide pellet. Next, 1 g of biodiesel sample was added into the conical flask, followed by 5 mL of propanol solvent and 1 mL of phenolphthalein. The mixture in conical flask was titrated with KOH solution until a clear pink colour solution is formed. The volume of KOH solution used in the titration was recorded. Acid value was calculated by Equation 3.2:

$$\text{Acid Value, AV (mg KOH/ g)} = \frac{V \times N \times MW_{KOH}}{W_s} \tag{3.2}$$

where

V = Volume of KOH solution used

N = Normality of KOH solution; 0.1 N

MW_{KOH} = Molecular Weight of KOH; 56.11 g/mol

The FFA% can be converted from the acid value through Equation 3.3:

$$\text{FFA\%} = \frac{\text{Acid Value}}{1.99} \tag{3.3}$$

3.6 Biodiesel Production

PFAD and methanol are used as the reactant in the reaction of producing biodiesel (FAME). This experiment was set up as shown in Figure 3.6. 10 g of PFAD was mixed with the amount of methanol equal to the methanol/oil molar ratio of 20:1 and then added with 5 wt% of catalyst loading. The mixture was poured into a round bottom flask and was immersed in an oil bath of 100 °C with methanol reflux for 4 hours at rotation speed of 300 rpm by using magnetic stirring. When the reaction was completed, the catalyst was then filtered out from the liquid product by using filter paper and filter funnel.

The experiment was repeated with different esterification time of 2, 6 and 8 hours with catalyst loading of 5 wt%. Also, the effect of different catalyst loadings of 2.5, 10 and 15 wt% at 8 hours was studied. When experiment is repeated with different catalyst loading and esterification time, other than the varying parameter, methanol to oil molar ratio of 20:1 and oil bath temperature of 100 °C was remained constant for all sets of experiment. The FAME yield was then recorded and compared between different reaction conditions.

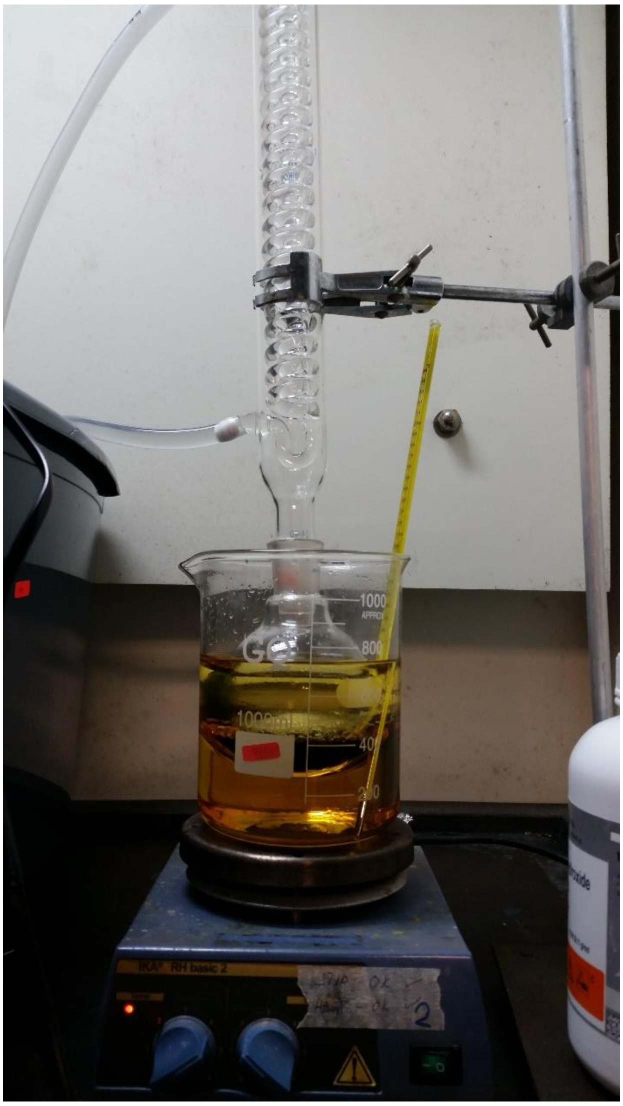


Figure 3.6: Esterification Reaction Set-up

3.7 Gas Chromatography Analysis

Gas chromatography Perkin Elmer Claurus 500) equipped with FID was used in the study. In this GC analysis, Helium gas was used as the carrier gas with the flowrate of 2 ml/min at pressure 24.7 psi. The detector temperature was set to 220°C. Then, the injector temperature and flame ionization temperature was set to 250 °C and 270 °C respectively. ZB-FFAP GC biodiesel column (60 m × 0.25 mm × 0.25 µm) was used. The analysis sample was prepared by diluting the oil sample with hexane as the solvent according to the pre-determined dilution factor.

3.7.1 Determination of Acid Composition

The composition of acids in the PFAD like palmitic acid, stearic acid, oleic acid, linoleic acid and other acids components were measured by using gas chromatography (Perkin Elmer Claurus 500) equipped with FID. Homogeneous sulfuric acid was used as the catalyst for the esterification reaction with methanol. The FAME yield obtained was assumed to be 100% so that the concentration of methyl esters produced are associated with the free fatty acid composition of the PFAD. For the GC analysis, 1.0 µL of FAME sample was injected into the ZB-FFAP GC biodiesel column to run the analysis.

3.7.2 Biodiesel Yield Analysis

Biodiesel produced from esterification between methanol and PFAD in the presence of synthesised catalyst was analysed with gas chromatography (GC) to determine the yield of FAME produced in the product. 1.0 µL of oil sample was injected into the ZB-FFAP GC biodiesel column to run the analysis. There are two types of analysis method to determine the FAME yield, by using the internal standard or external standard. The usage of external standard required the plot of external standard calibration curve in order to determine the FAME yield.

To obtain the calibration curve for the methyl esters, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate was diluted with different amount of hexane as the solvent to obtain the peak area on GC. Then, the graph of peak area of different methyl esters concentration was plotted against the methyl esters concentration as shown in Figure 3.7. An equation was obtained from each of the plotted calibration curve and it was used to calculate the concentration of methyl esters in the product. The total methyl esters that composed of methyl palmitate, methyl stearate, methyl oleate and methyl linoleate of one sample will be used to calculate the FAME yield by Equation 3.4.

$$\text{Yield (\%)} = \frac{(\sum \text{Concentration of each methyl esters})(\frac{g}{g\ sample}) \times (\text{mass of product produced})(\text{g sample})}{10\ \text{g PFAD}} \tag{3.4}$$

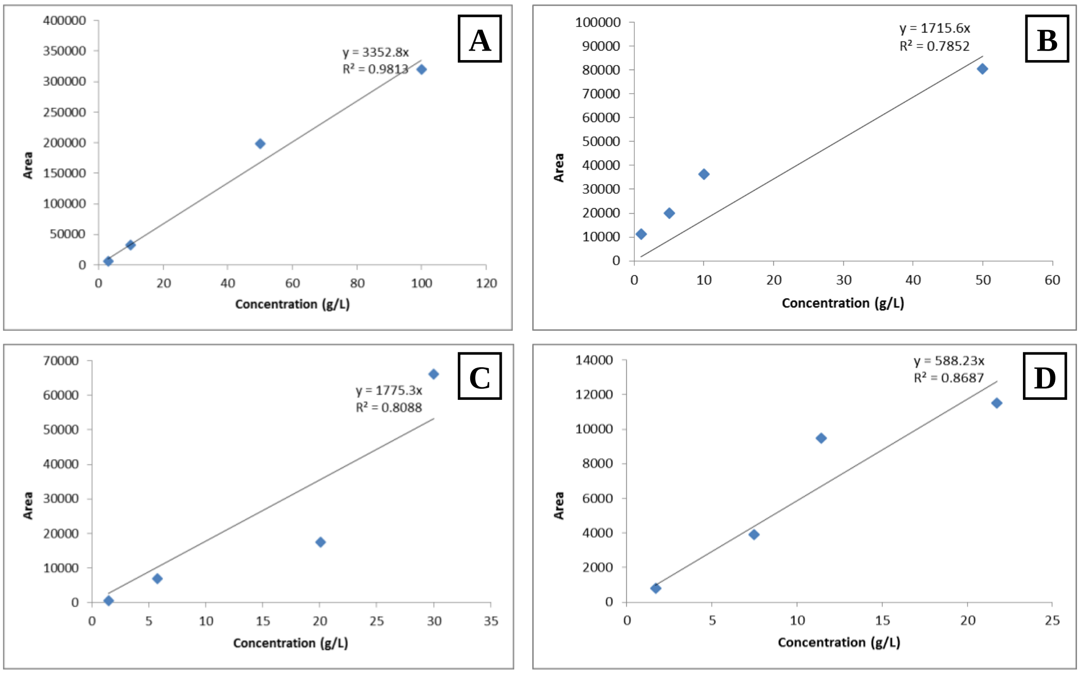


Figure 3.7: Calibration Curves for (A) Methyl Palmitate (B) Methyl Stearate (C) Methyl Oleate (D) Methyl Linoleate

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Preliminary Stage Observation

Catalyst are prepared by different carbonisation temperatures, different sulfonation durations and different concentrations of ammonium sulfate as sulfonating agent with other conditions kept constant. Table 4.1 shows the preparation of seaweed based activated carbon, SWAC at different temperatures. All carbonisation was done at the duration of 2.5 hours with ramping rate of 5 °C/min. Figure 4.1(A) shows the carbonised seaweed appeared as black powder. Table 4.2 shows the catalyst annotation and the preparation conditions. Besides sulfonation duration and concentration of ammonium sulfate, all sulfonation was done at 10 minutes sonication by using 30 ml of ammonium sulfate as sulfonating agent at 235 °C. Figure 4.1(B) shows the sulfonated catalyst and all catalyst present in black powder form.

Table 4.1: Carbon Samples and the Preparation Conditions

Carbon Sample	Carbonisation Conditions	
	Duration (hours)	Temperature (°C)
SWAC200	2.5	200
SWAC300	2.5	300
SWAC400	2.5	400
SWAC500	2.5	500
SWAC600	2.5	600

Table 4.2: Catalysts Samples and the Preparation Conditions

Catalyst Sample	Carbonisation Conditions	Sulfonation Conditions Variables	
	Temperature (°C)	Duration (minutes)	Ammonium Sulfate Solution Concentration (w/v %)
Cat-A	200	30	10
Cat-B	300	30	10
Cat-C	400	30	10
Cat-D	500	30	10
Cat-E	600	30	10
Cat-A1	200	15	5
Cat-A2	200	15	10
Cat-A3	200	15	20
Cat-A4	200	15	30
Cat-A5	200	15	40
Cat-A6	200	30	5
Cat-A7	200	30	10
Cat-A8	200	30	20
Cat-A9	200	30	30
Cat-A10	200	30	40
Cat-A11	200	60	5
Cat-A12	200	60	10
Cat-A13	200	60	20
Cat-A14	200	60	30
Cat-A15	200	60	40
Cat-A16	200	90	5
Cat-A17	200	90	10
Cat-A18	200	90	20
Cat-A19	200	90	40

Carbonisation Conditions: Fixed at 2.5 hours at 5 °C/min

Sulfonation Conditions: 1.5 g of carbon, 10 minutes ultrasonication, 30 ml ammonium sulfate solution at 235 °C

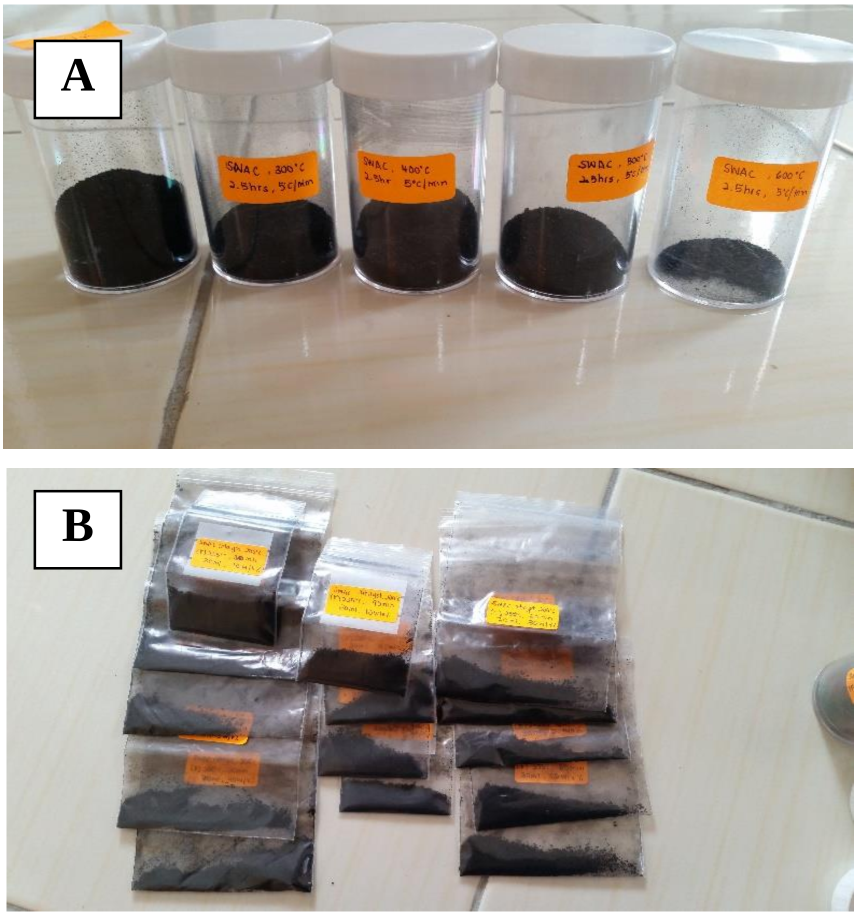


Figure 4.1: (A) SWAC Samples and (B) Catalyst Samples

4.2 Characterisation of Catalyst

In this study, catalysts that were synthesised through various sulfonation conditions. Basically, catalysts were synthesised at different sulfonation duration with different concentration of ammonium sulfate solution used as the sulfonating agent. Characterisation of catalyst was done study the difference between the catalyst produced from different sulfonation conditions. Characterisation of the catalyst was done by 4 types of characterisation test, which are SEM, FT-IR, BET and TGA.

4.2.1 Scanning Electron Microscope

Scanning Electron Microscope was used to obtain the surface morphology of the seaweed derived catalyst. Figure 4.2 has shown the SEM image of seaweed biomass before carbonisation where Figure 4.3 shows the SEM images of seaweed carbon carbonised at different temperature for 2.5 hours from seaweed biomass.

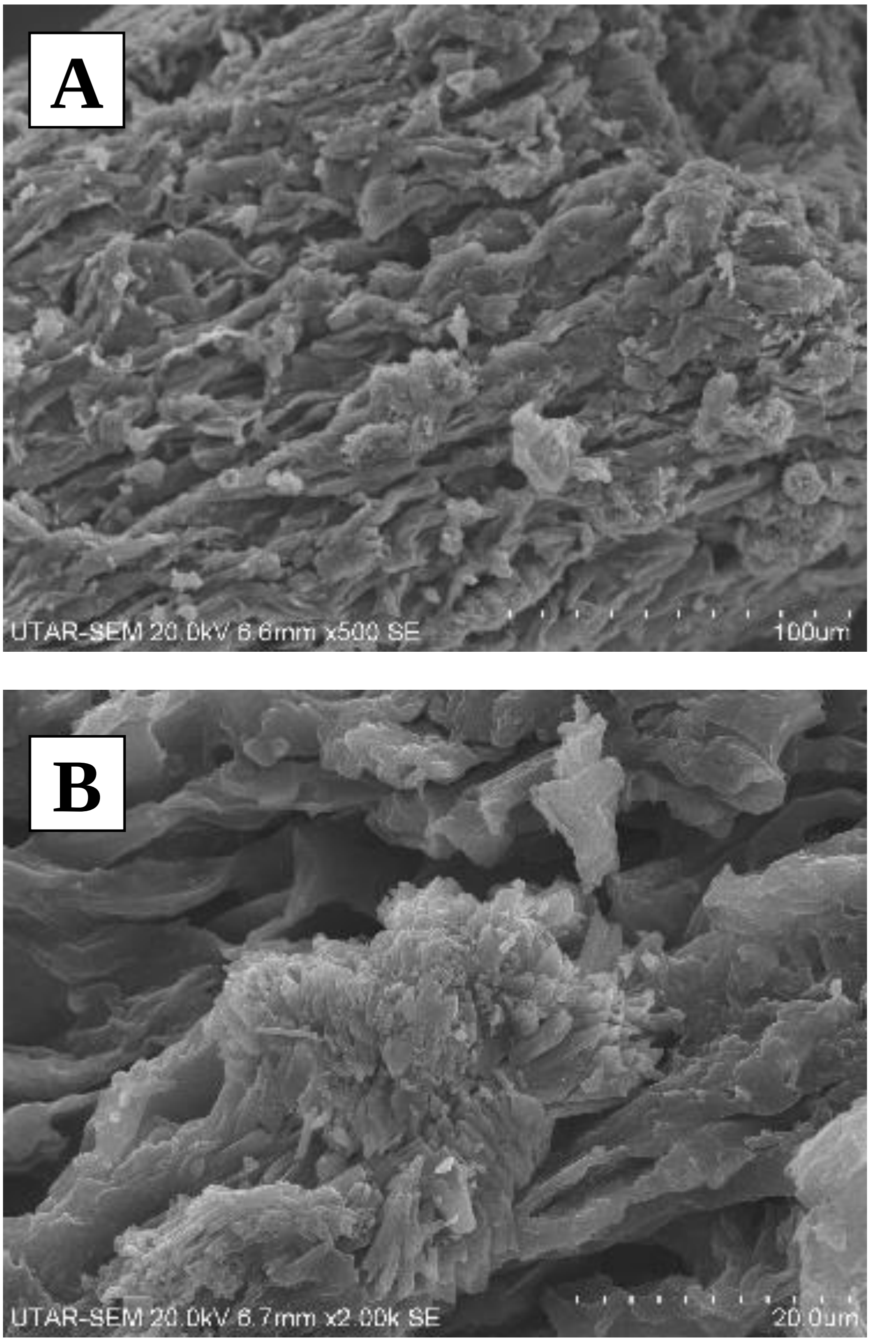


Figure 4.2: SEM Images of Seaweed Biomass Before Carbonisation at Magnification (A) x500 and (B) x2000

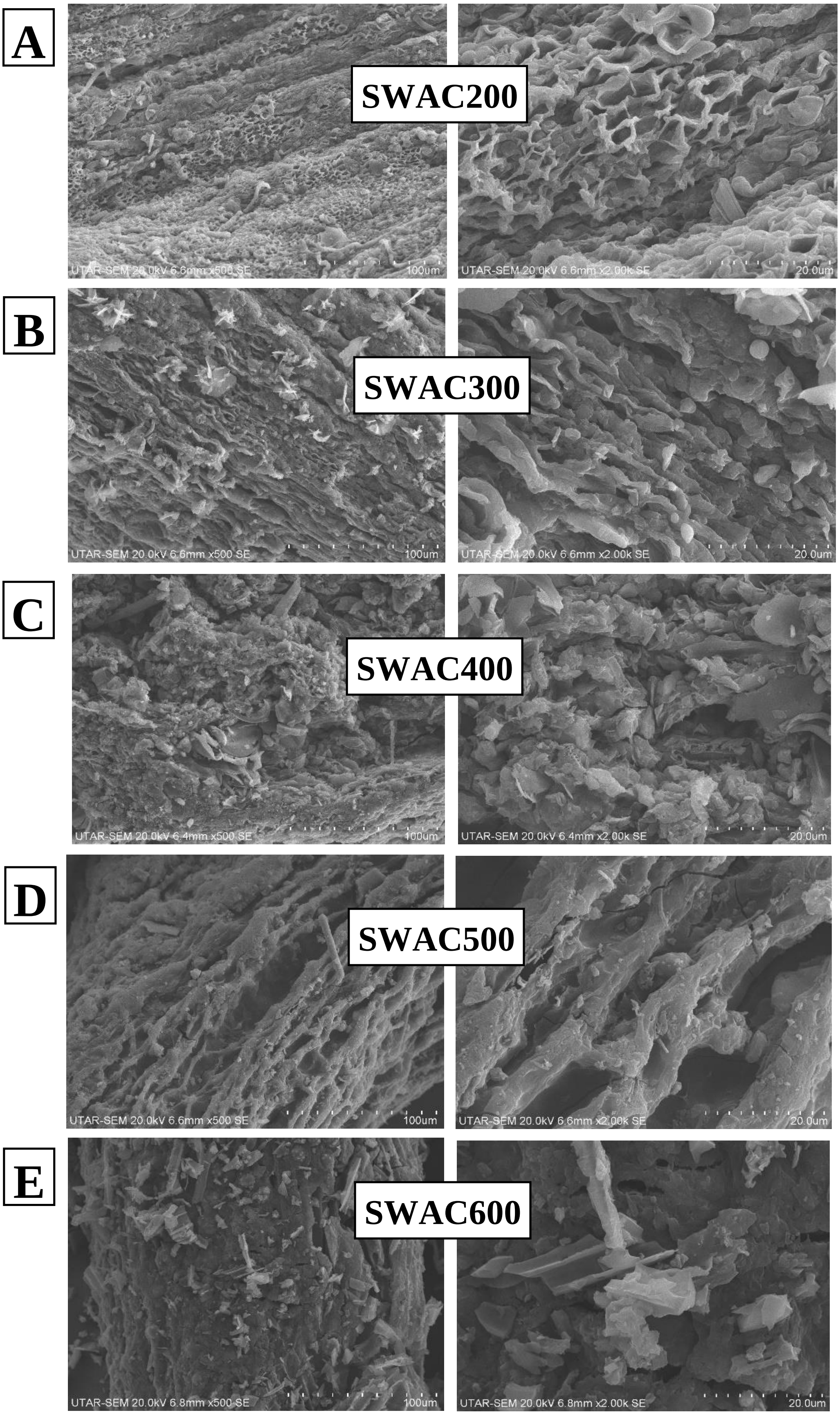


Figure 4.3: SEM Images of Seaweed After Carbonisation at (A) 200 °C (B) 300 °C (C) 400 °C (D) 500 °C (E) 600 °C at 500x and 2000x Magnification

Figure 4.2 shows the surface morphology of seaweed biomass before carbonisation. The seaweed derived carbon will be noted with the term SWAC which stands for seaweed activated carbon in the following. SWAC produced from carbonisation of 200, 300, 400, 500 and 600 °C will be noted as SWAC200, SWAC300, SWAC400, SWAC500 and SWAC600 respectively. Through the process of carbonisation, the algin in the seaweed was transformed into carbon structure. The seaweed biomass before carbonisation shows an irregular and uneven surface. The surface morphology of seaweed derived carbon in Figure 4.3 shows the presence of pores after carbonisation which serve as the site for the sulfonic group attachment.

Figure 4.3(A) showed the SWAC produced for 2.5 hours at carbonisation temperature of 200 °C. Uniform irregular surface was observed in SWAC200. SWAC200 was shown to be very porous and the black holes are observed on the surface. According to Janaun, Abang and Anwar (2013), the black hole could be associated as the pores formed. The pore size of SWAC 200 is observed at about 6 µm. The uniform uneven surface of the SWAC200 made it a potential precursor to be sulfonated to the solid acid catalyst.

At carbonisation temperature of 300 °C, less pores was observed on the surface of SWAC300 compared to of SWAC200. The surface of SWAC300 has many uniform but irregular lumps and a larger pore size was observed as larger black holes are shown in Figure 4.3 (B). Sun, et al. (2008) claimed that the number of pores increase with the carbonisation temperature. According to Gaber, et al. (2013), when biomass was treated with high temperature, volatiles material will escape from the biomass leaving plenty of pores on the carbon. However, when the temperature increases, more materials escape from the biomass where the pores tend to agglomerate together leaving larger pore size due to the sintering of pores (Gaber, et al., 2013).

SWAC400 shows a similar structure with SWAC 300 at the SEM magnification of 500x. The surface was rough with large pore observed. There are a lot of dented site observed on. It can be seen that the pore size increase from SWAC400 to SWAC500 that has the largest pore size. The large pores of SWAC600 was not obvious in as shown in Figure 4.3 (E). Instead, the surface of SWAC600 was smoother than the others. Gaber, et al. (2013) reported that the increase of pore size will reduce the surface area of the carbon. This will then result in lower active sites being attached on the carbon surface and reducing the FAME yield.

Figure 4.4 shows the sulfonated SWAC200, by using 30 ml of 10w/v% ammonium sulfate solution for 30 minutes at 235 °C (Cat-A7). It shows that there are pieces of material covering on the surface of the catalyst. These materials may be the ammonium sulfate solid that was still remained on the catalyst because the catalyst was not washed properly after sulfonation. After all, the surface morphology of the samples did not change much after sulfonation compared to the activated carbon in Figure 4.3(A). According to Okamura, et al. (2006), the surface morphology has not much difference on the carbon material after sulfonation. All SEM images of catalyst synthesised at different conditions are attached in Appendix A.

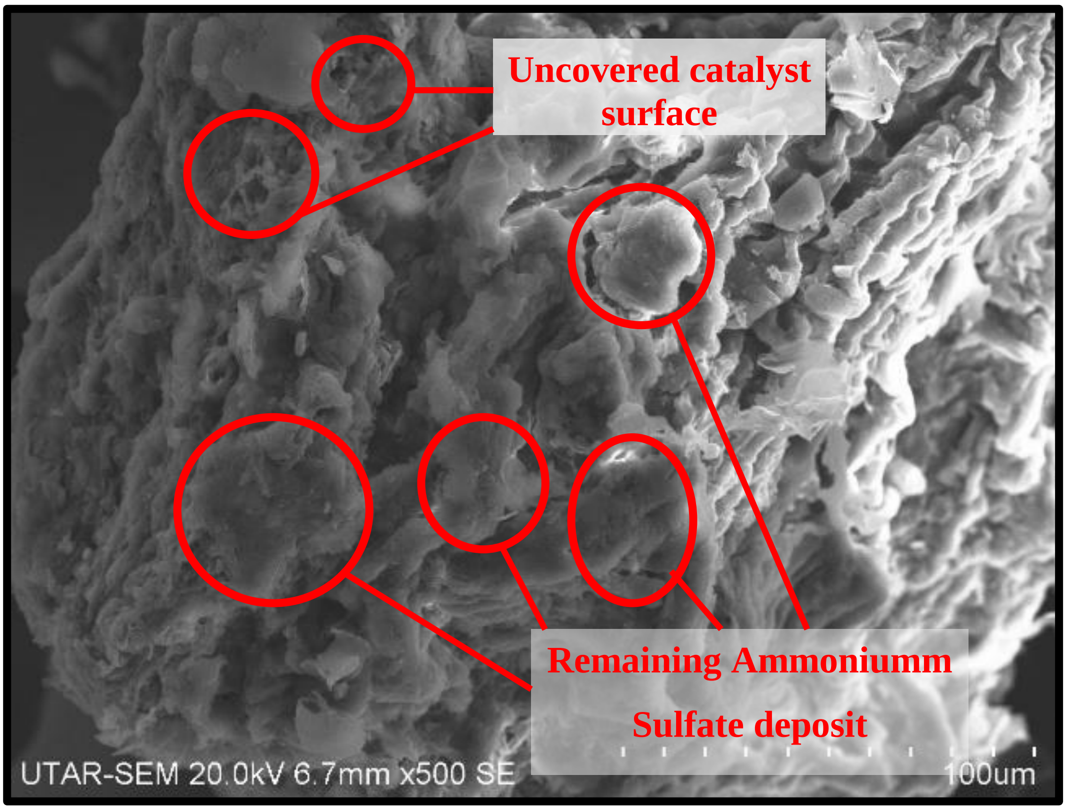


Figure 4.4: SEM Image of Cat-A7

4.2.2 Brunauer-Emmet-Teller Analysis

Brunauer-Emmet-Teller (BET) was done to determine the surface area of pyrolysed activated carbon. Since Cat-A synthesised from SWAC200 exhibits the highest acid density, activated carbon SWAC200 was selected to study on the surface area. Result showed that the surface area of SWAC200 is shown to be 5.1767 m^2/g. Literature Folasegun, et al., 2014 reported that activated carbon produced from glucose has 0.2 m^2/g of surface area based on the BET analysis and was successfully produced biodiesel at 99% FAME yield. It will be better if the activated carbon exhibits higher surface area because the present of surface area enables the attachment of functional group SO_3H as active site for esterification on to the carbon. Thus, seaweed based activated carbon is a suitable biomass was to be used as the precursor for solid acid catalyst to be used in the production of biodiesel.

4.2.3 Fourier Transform - Infrared Spectroscopy

Fourier Transform – Infrared Spectroscopy analysis was done to determine the functional group present on the catalyst. This test was performed to confirm the presence of sulfonic group, SO_3H- attaching on the catalyst because the sulfonic group is the active site for the esterification reaction between PFAD and methanol to form FAME. Most of the catalyst shows a peak at wavenumbers around 1040 cm^{-1}, 1200 cm^{-1}, 1600 and 1700 cm^{-1}.

According to Lambert (1989), SO_3H group in sulfonic acids is represented by wavenumbers 1040 to 1080 cm^{-1} with SO_3 symmetric stretch and wavelength 1155 to 1245 cm^{-1} with S=O stretch. Then, the wavenumber of 2400 to 3100 cm^{-1} is related to the –OH in carboxylic acids of H bonded OH stretch. Ezebor, et al. (2014) reported that wavenumber at around 1600 and 1700 cm^{-1} are indicating the C=C aromatic stretching and C=O stretching vibrations respectively.

Figure 4.5 shows the results of FT-IR analysis of catalyst sulfonated with difference concentrations of ammonium sulfate solution for 15 minutes. Peaks was observed at wavenumber 1050 and 1190 cm^{-1} that are related to the SO_3H group for sulfonic acid of SO_3H symmetric stretch and S=O stretching vibrations for catalyst CAT-A1, CAT-A2, CAT-A3, CAT-A4 and CAT-A5 at different intensity. Also, aromatic C=C stretching was observed with an obvious peak at 1600 cm^{-1}, C=O stretching at wavenumber about 1700 cm^{-1} and peak at 2930 cm^{-1} that is assigned to –OH group for all catalysts in Figure 4.6 including the SWAC200. This explained that the –OH and –COOH groups were present even before sulfonation was carried out.

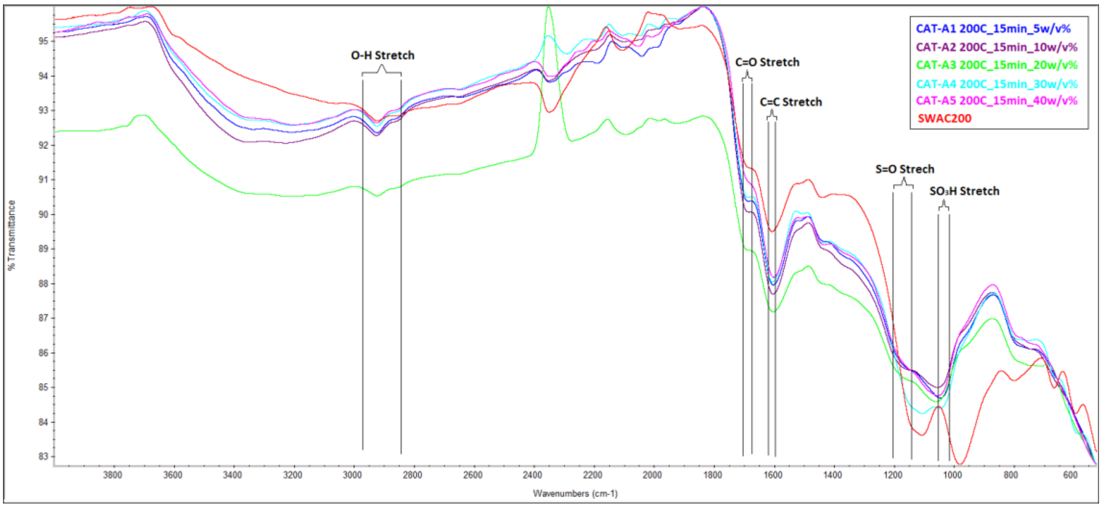


Figure 4.5: FT-IR Spectra for Catalysts Sulfonated for 15 minutes in Different Ammonium Sulfate Solution Concentration

Next, Figure 4.6 shows the FT-IR spectra for catalysts sulfonated for 30 minutes. These catalysts showed the highest intensity of SO_3H group at wavenumber 1040 cm^{-1} and 1200 cm^{-1}. SO_3H is the significant functional group that have to be present in the catalyst to act as the active site for esterification reaction to carry out to produce biodiesel. High intensity of SO_3H group observed through FT-IR meaning that catalysts sulfonated for 30 minutes could provide the best performance among the catalysts sulfonated for other durations. Similarly, CAT-A6, CAT-A7, CAT-A8, CAT-A9 and CAT-A10 exhibited peak at 1620 and 2950 cm^{-1} for the C=C aromatic stretching and –OH group vibrations showing that –OH and –COOH group that was originally attached on the catalyst precursor was still present in the catalyst.

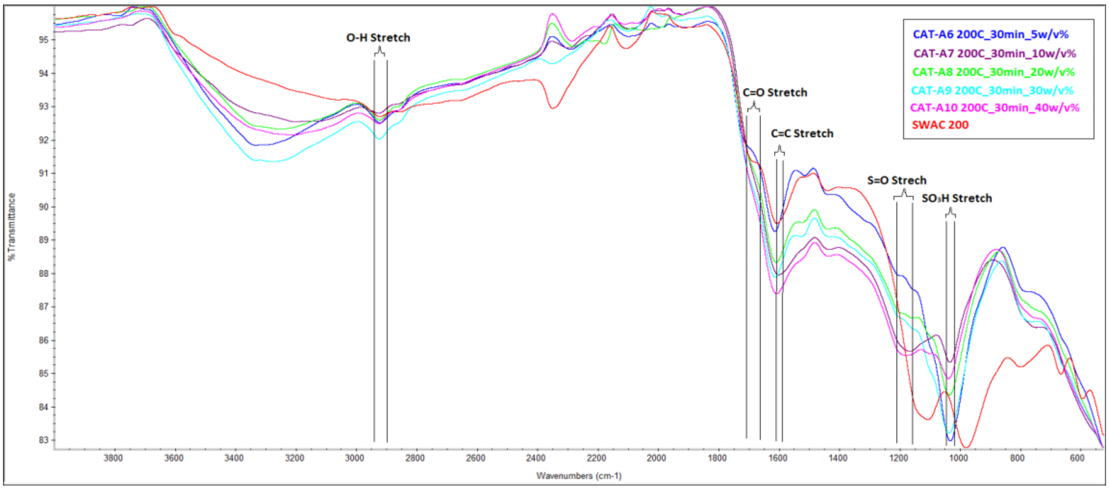


Figure 4.6: FT-IR Spectra for Catalysts Sulfonated for 30 minutes in Different Ammonium Sulfate Solution Concentration

Figure 4.7 and Figure 4.8 shows similar trend with others catalyst. The catalysts sulfonated for 60 and 90 minutes exhibit SO_3H group with S=O stretching and SO_3 symmetric stretch but at a lower intensity compared to catalyst sulfonated for 30 minutes. Lower intensity of SO_3H group is indicating the catalyst will have lower performance which will exhibit lower biodiesel yield. Zhang, Liu and Liu (2015) indicated that the loss of volatile component are associated with the increase of heating duration. Due to the high temperature sulfonation reaction, the volatiles materials in the carbon will be further escape and the surface for sulfonation attachment is reduced. Also, wavenumber 1630, 1730 and 2930 cm^{-1} that was assignment to the C=C aromatic stretch, C=O stretch and –OH group vibrations appeared at very low intensity as the peak was not obvious and deep.

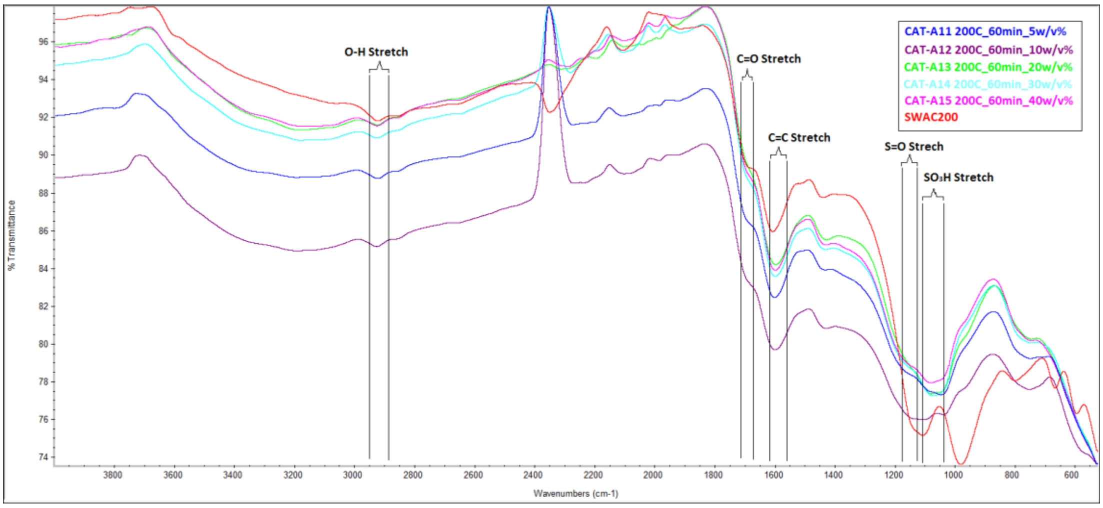


Figure 4.7: FT-IR Spectra for Catalysts Sulfonated for 60 minutes in Different Ammonium Sulfate Solution Concentration

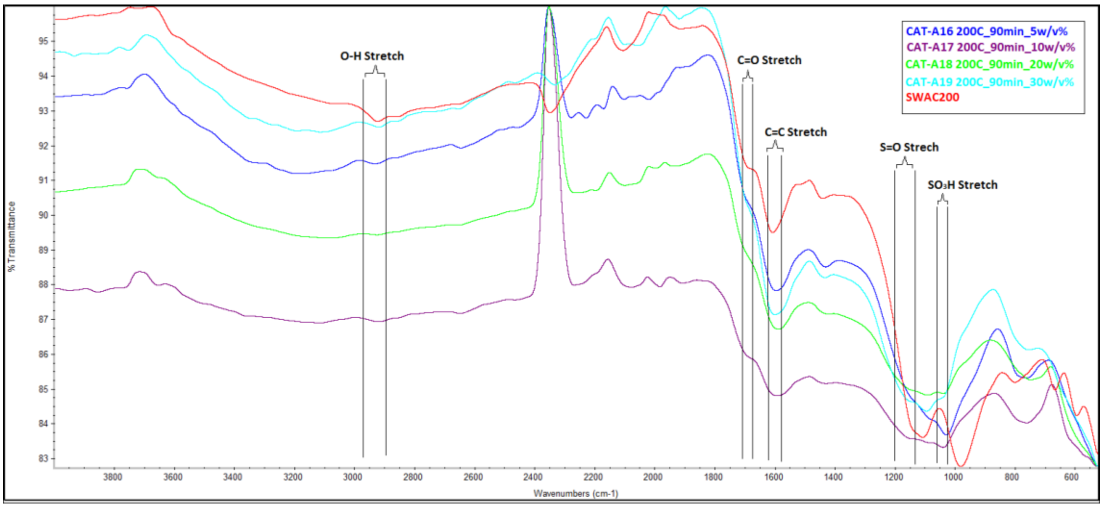


Figure 4.8: FT-IR Spectra for Catalysts Sulfonated for 90 minutes in Different Ammonium Sulfate Solution Concentration

4.2.4 Acid Density

Acid density test was carried out to determine the total acid density of catalyst where the acidity comes from $–SO_3H$, -OH and –COOH group present in the catalyst. Janaun, Abang and Anwar (2013) claimed that total acid density mainly came from the $–SO_3H$ and this functional group is the only active site involved in the esterification reaction. The total acid density of catalyst synthesised from different carbonisation conditions was tabulated in Table 4.3.

Figure 4.9 shows the total acid density trend of catalyst sample Cat-A, Cat-B, Cat-C, Cat-D and Cat-E. Carbonisation temperature of 200 °C poses the highest acid density at 2.48 mmol/g among the catalyst synthesis from other carbonisation temperatures. The total acid density decreases from 200 to 500 °C but slightly increase at 600 °C carbonisation temperature. The decreasing of total acid density from 200 °C to 500°C may be due to the increase of pore size that leads to the sintering effect. Gaber, et al. (2013) claimed that increase of number of pores resulting in pores combining together and reducing the surface area for the attachment of SO_3H group. It was noted that there were slight increase of total acid density from 500 to 600 °C which may be due to the inconsistency of back titration done to determine the total acid density of catalyst.

Table 4.3: Total Acid Density of Catalyst Samples at Different Carbonisation Temperature

Catalyst Sample	**Carbonisation Conditions**		**Total Acid Density (mmol/g)**
	Duration (hours)	**Temperature (°C)**	
Cat-A	2.5	200	2.48
Cat-B	2.5	300	1.32
Cat-C	2.5	400	1.24
Cat-D	2.5	500	0.88
Cat-E	2.5	600	1.4

1 g of SWAC sulfonated in 30 ml of 10 w/v% Ammonium Sulfate solution for 30 minutes at 235 °C

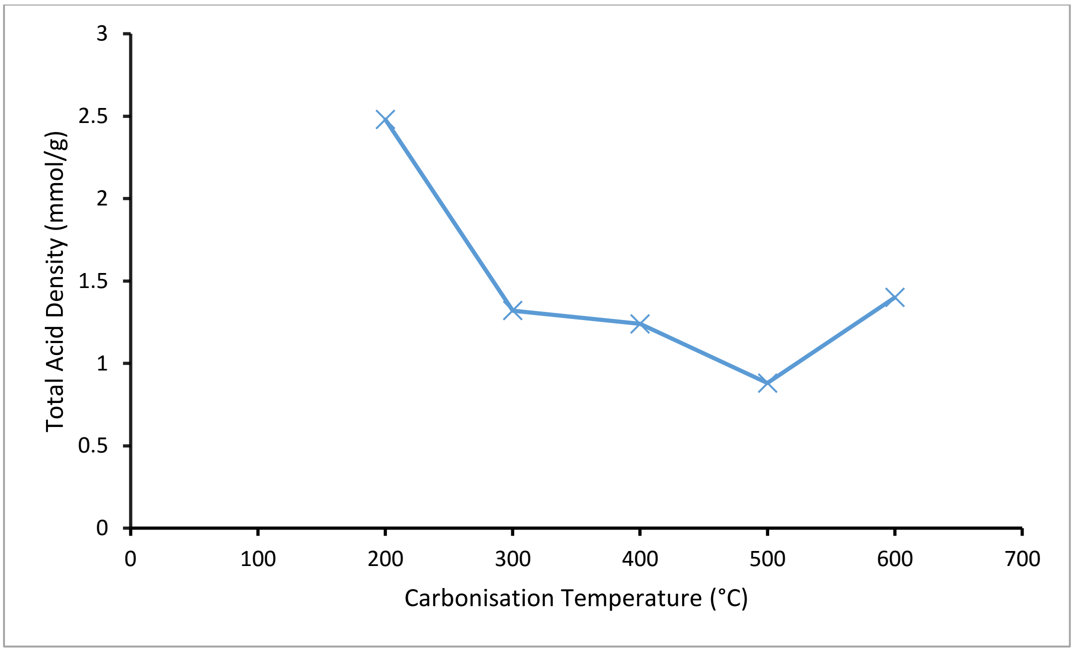


Figure 4.9: Total Acid Density of Catalysts Synthesised from Different Carbonisation Temperature, Sulfonated in 30 ml of 10 w/v% Ammonium Sulfat Solution for 30 Minutes at 235 °C

The catalyst with highest total acid density was then used to further study the sulfonation parameters. Thus, catalyst was synthesised with 200 °C carbonisation was sulfonated with different concentrations of ammonium sulfate solution at different sulfonation durations. Table 4.4 shows the catalysts total acid density that was synthesised at various conditions.

Table 4.4: Total Acid Density of Catalyst Samples at Different Sulfonation Conditions

Total Acid Density (mmol/g)				
Concentration (w/v%)	**Duration (minutes)**			
	15	**30**	**60**	**90**
5	1.64	1.84	1.28	1.12
10	1.68	3.32	1.52	1.24
20	1.76	3.2	1.8	1.52
30	1.84	2.6	1.4	-
40	1.4	2.2	1.12	1.12

1.5 g of SWAC200 sulfonated in 30 ml of Ammonium Sulfate solution at 235 °C

Figure 4.10 shows the graph of total acid density trend of catalyst sulfonated from different conditions. By comparing the total acid density of catalyst synthesised at different sulfonation durations, catalyst that was sulfonated for 30 minutes poses the highest total acid density as an overall, followed by 15 minutes, then to 60 minutes and sulfonation for 90 minutes gives the lowest overall total acid density. On the other word, total acid density increases from sulfonation duration of 15 minutes to 30 minutes, then decreases after reaching the optimum sulfonation duration of 30 minutes. The decrease of total acid density at longer sulfonation time may be due to the escape of volatile substance in the catalyst as the sulfonation was carried out at high temperature of 235 °C thus the catalyst surface area will be further decreased resulting in less SO_3H group grafted on the seaweed based carbon.

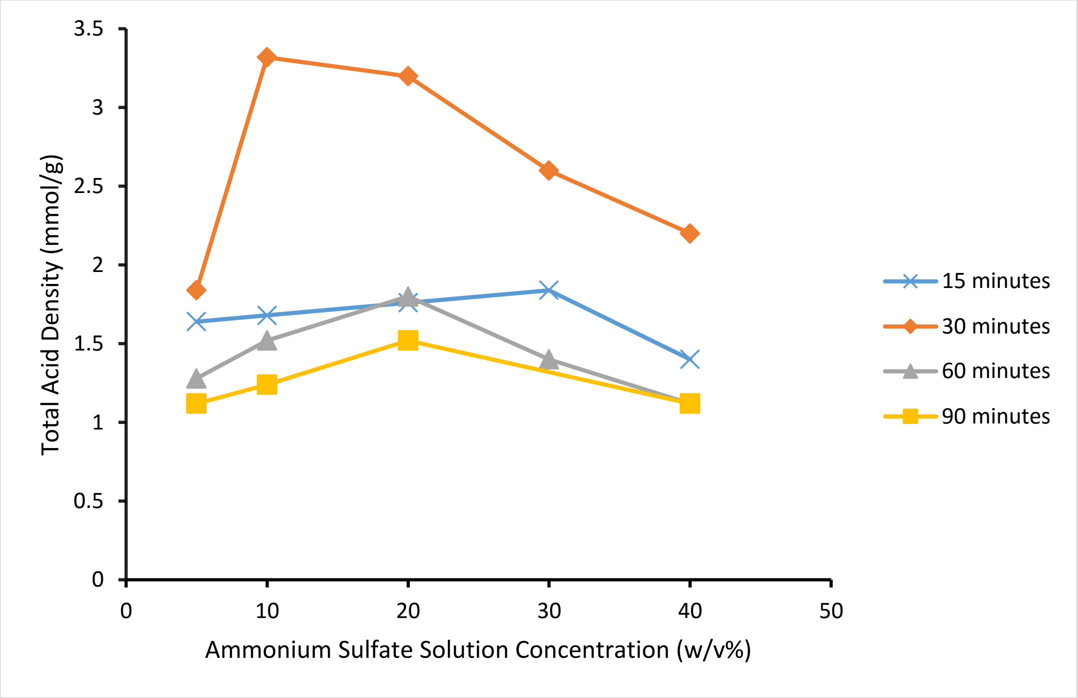


Figure 4.10: Graph of Total Acid Density of Catalysts Synthesised from Different Sulfonation Temperature

In each of the sulfonation duration, different optimum ammonium sulfate concentration was resulted according to the total acid density. For 15 minutes sulfonation duration, 30 w/v% of ammonium sulfate solution gives the highest total acid density at 1.84 mmol/g and the high total acid density of 3.32 mmol/g was achieved for sulfonation duration of 30 minutes. As for 60 and 90 minutes sulfonation duration, the highest total acid density was obtained at 1.8 and 1.52 mmol/g respectively, when 20 w/v% of ammonium sulfate solution was used. Generally, high concentration of ammonium sulfate solution will increase the acid density as the amount SO_3H will also be high. However, too high concentration of ammonium sulfate solution may give adverse effect to the catalyst. Shuit, Ng and Tan (2015) reported that at high concentration, the solution will appear in higher viscosity and this will affect the dispersion of seaweed carbon in the solution. Therefore, seaweed carbon will still remained in lump and not all of the carbon are being exposed to the solution.

Janaun, Abang and Anwar (2013) reported the total acid density of 2.01 mmol/g for the seaweed based catalyst that was sulfonated by using fuming sulfuric acid (20 wt% free SO_3). Compared to this research, a higher total acid density was achieved in this research at 3.32mmol/g. within the range of parameters studied, the sulfonation carried out by mixing 30ml of 10 w/v% ammonium sulfate solution with 1.5 g of SWAC200 that was ultrasonicated for 10 minutes and heated to 235 °C for 30 minutes will be the condition to achieve the optimum total acid density.

Yu, Dehkhoda and Ellis (2010) reported that the FAME yield is dependent on the total acid density of catalyst. Thus, the catalyst with highest total acid density may produce the highest FAME yield among other catalyst.

4.2.5 Energy-Dispersive X-ray Spectroscopy

EDX is an analytical method for surface elemental analysis. The elemental composition of carbon, C, oxygen, O and sulfur of catalyst was tabulated in Table 4.5

Table 4.5: Elemental Composition on Catalyst

Catalyst Sample	**Elemental Composition (wt %)**		
	C	**O**	**S**
Cat-A	53.22	25.03	9.36
Cat-B	52.94	12.89	4.58
Cat-C	36.82	36.36	0.81
Cat-D	32.32	25.21	00.00
Cat-E	22.89	25.45	0.70
Cat-A1	21.78	36.88	00.91
Cat-A2	31.71	31.55	2.94
Cat-A3	51.62	29.98	3.04
Cat-A4	64.27	28.87	2.92
Cat-A5	59.41	33.33	2.38
Cat-A6	47.03	42.48	2.59
Cat-A7	36.99	31.62	9.70
Cat-A8	49.46	35.89	3.08
Cat-A9	55.00	40.19	2.12
Cat-A10	27.93	45.60	1.35
Cat-A11	39.70	38.22	4.27
Cat-A12	42.95	32.87	9.02
Cat-A13	53.23	27.70	9.36
Cat-A14	40.05	35.65	6.52
Cat-A15	53.94	33.73	1.01
Cat-A16	41.40	32.41	5.29
Cat-A17	42.26	36.72	5.60
Cat-A18	54.96	31.50	8.66
Cat-A19	53.22	25.03	9.36

As shown in Table 4.5, Cat-A7 has the highest S content in the catalyst. Zhang, et al. (2010) reported that all S content can be assumed to be correspond to the SO_3H present in the catalyst. Thus, when Cat-A7 was used as the catalyst for esterification, is exhibits the highest FAME yield. Figure 4.11 shows the EDX analysis result for catalyst Cat-A7. The generated report for EDX results of Cat-A6, Cat-A7, Cat-A8, Cat-A9 and Cat-A10 is attached in Appendix B as reference. Several catalysts exhibit very low C, O and S composition and some exhibits a very high. One of the reasons was due to the different sulfonation conditions that affect that result. Besides that, it may due to the inconsistency of analysis. Janaun, Abang and Anwar (2013) claimed that the EDX analysis is only able to analyse the surface of one small piece of catalyst instead of the bulk material. Thus, EDX may not give accurate result as some functional group may be away from the surface where the analysis done.

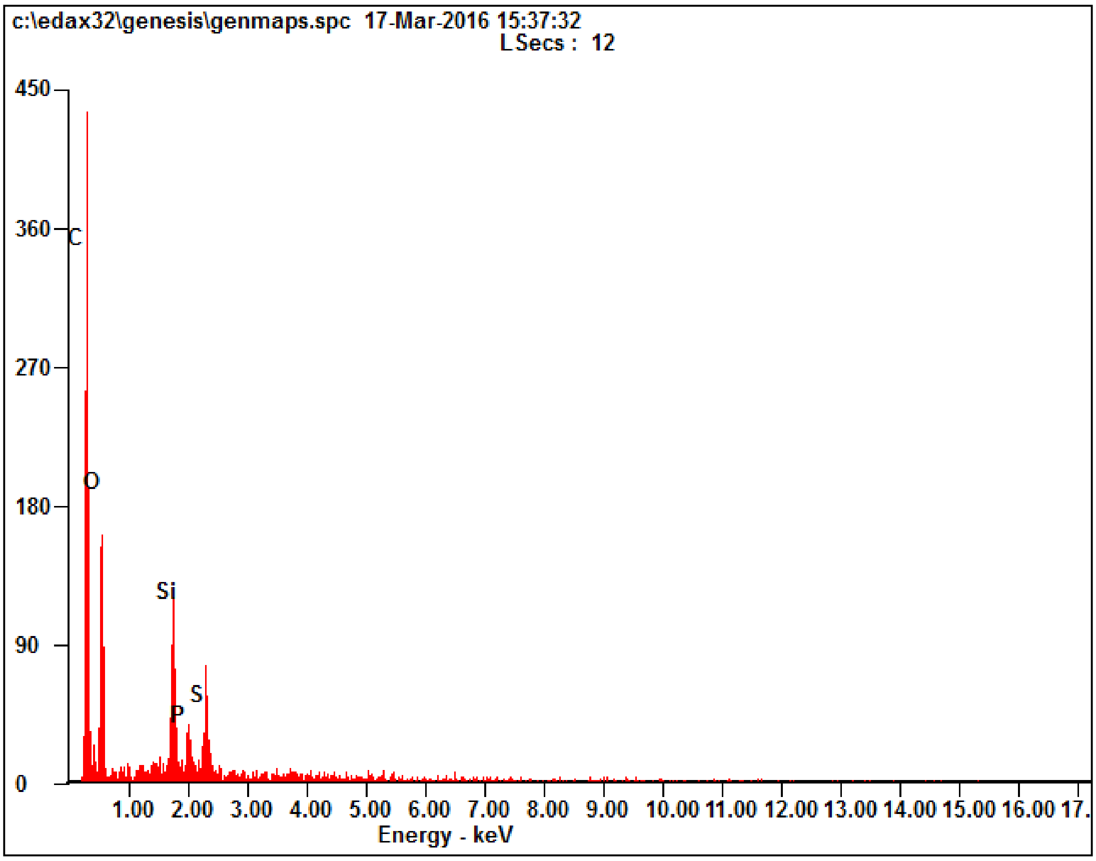


Figure 4.11: EDX Analysis for Catalyst Cat-A7

4.2.6 Thermogravimetric Analysis

Sample Cat-A7 which was carbonised at temperature of 200 °C, sulfonated with 10 w/v% ammonium sulfate solution at 235 °C for 30 minutes was sent for the thermogravimetric analysis (TGA). The result obtained was showed in Figure 4.12. The green curve on the line shows the mass loss for the sample. It was observed that there were two mass loss steps under inert condition (nitrogen atmosphere) and one mass loss step under oxidative condition (synthetic air atmosphere).

The sample were relatively stable until the temperature of 70.8 °C, a significant weight reduction was observed. The observed mass loss at this stage was mostly likely due to the release of volatile materials or moisture content in the sample. Then, the samples was slightly stable until the temperature of 537.9 °C which was associated with the second mass loss step at inert atmosphere. The mass reduction observed at this temperature can be related to the decomposition of functional group, which is the SO_3H group in the sample. The oxidative mass loss at 928.1 °C is associated as the burn-up of the carbon component in the sample.

Lee (2013) reported the synthesis of acid catalyst from lignosulfonate with concentrated sulfuric acid as the sulfonating agent. The results shows that the weight loss was significant at around 230 °C due to the decomposition of SO_3H group in the catalyst. On the other hand, Kastner, et al. (2012) claimed that activated sulfonated by using concentrated sulfuric acid has lower thermal stability where the SO_3H group decomposed at 250 to 300 °C compared to the activated carbon which was sulfonated by using gaseous SO_3 that was decomposed at 500 to 550 °C. This has indicated that the seaweed based activated carbon that was sulfonated by thermal decomposition of ammonium sulfate has a comparable thermal stability.

In addition, the DTA signal shows the characterization of the observed effects. Mass loss was observed under the inert condition associated with the endothermic effect while exothermic signal was observed under the oxidative condition.

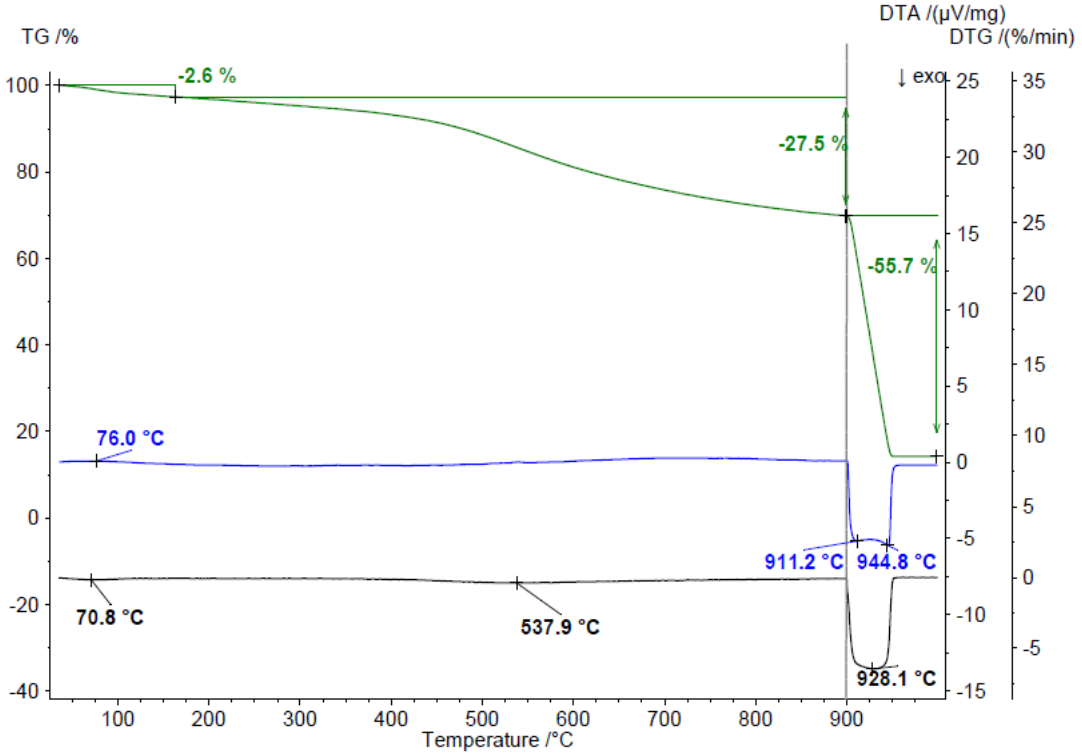


Figure 4.12: Temperature-Dependent Mass Loss (TG, green), Mass Loss Rate (DTG, black) and DTA-Curve (blue) for Cat-A7

4.3 Analysis of Feedstock

Palm fatty acid distillate (PFAD) was used as the feedstock that will react with methanol in the presence of catalyst synthesised to produce fatty acid methyl esters (FAME) which is the biodiesel. The free fatty acid content, FFA% contained in the PFAD and the fatty acid composition of PFAD was analysed. The FFA% in the PFAD was determined by the method as mentioned in Section 3.6.1. Table 4.6 shows the acid value and FFA% calculated for the PFAD used as the feedstock. Result shows that the FPAD has the FFA content of 64.95%.

On the other hand, free fatty acid composition in the PFAD was obtained by analysing the FAME produced from using homogeneous concentrated sulfuric acid as catalyst by assuming 100% yield of FAME and the result is shown in Table 4.7.

Table 4.6: Acid Value and FFA content of Feedstock

Sample	Sample Mass (g)	Normality of KOH (N)	Volume of KOH used (ml)	Acid Value	FFA content (%)
PFAD	1	0.1	23	129.26	64.95

Table 4.7: Free Fatty Acid Composition of Feedstock

Sample	Free Fatty Acid Composition, % by weight				
	Palmitic C16:00	Stearic C18:00	Oleic C18:1	Linoleic C18:2	Others
PFAD	40.71	3.72	36.428	17.18	1.96

4.4 Analysis of Biodiesel Produced

4.4.1 Optimisation Study for Sulfonation Conditions

Sulfonation was carried out with the objective to graft the SO_3H group onto the carbon to serve as a catalyst for biodiesel production through esterification reaction between PFAD and methanol. In this study, the sulfonation method employed was the thermal decomposition of ammonium sulfate method. This method was conducted by Shuit and Tan (2014) by using multi-walled carbon nanotube (MWCNT). 0.4 g MWCNT was ultrasonicated with 30 ml of 10 w/v% ammonium sulfate solution for 10 minutes, the ultrasonicated mixture was then heated to 235 °C for 30 minutes.

In this study, the concentration of ammonium sulfate solution and the temperature holding time was varied to investigate the optimum condition for these 2 parameters. Thus, 1.5 g of SWAC200 was added with 30 ml of 5, 10, 20, 30 and 40 w/v% ammonium sulfate solution and ultrasonicated for 10 minutes. The ultrasonicated mixture was then heated to 235 °C for 15, 30, 60 and 90 minutes. The catalyst synthesised was then used in the esterification reaction to produce FAME. The FAME yield (%) will then be used as a reference to determine the efficiency of the catalyst and the condition that was used to synthesis catalyst that exhibits the highest FAME yield will be recorded as the optimum condition. The product of the esterification is as shown in Figure 4.13.

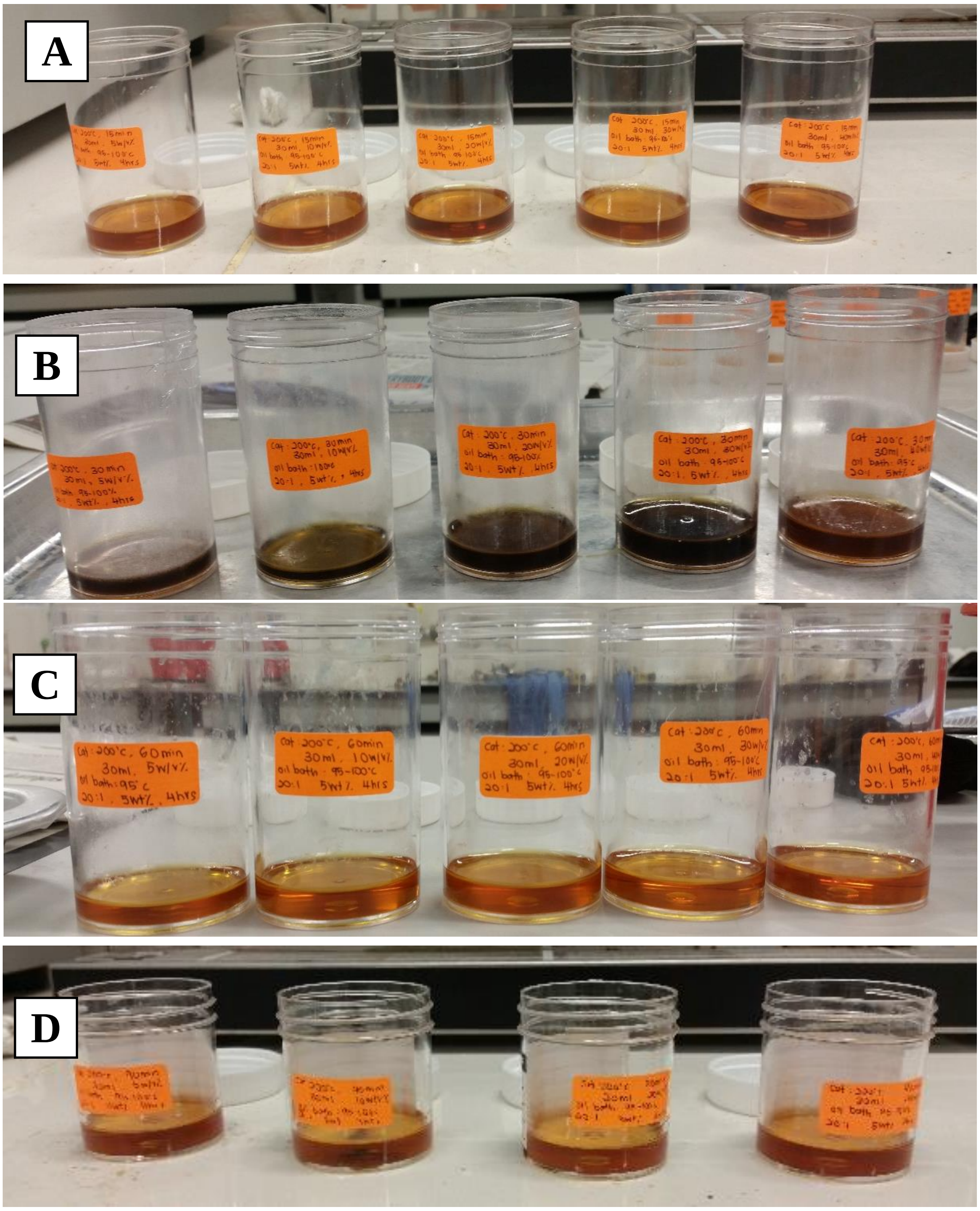


Figure 4.13: Product of Esterification by Catalyst Sulfonated for (A) 15minutes and (B) 30 minutes (C) 60 minutes (D) 90 minutes with Different Concentration of Ammonium Sulfate Solution

Other esterification reaction conditions were remained constant throughout the whole optimization study so that the efficiency of each catalyst sulfonated at different conditions can be studied. The esterification reaction was conducted at the oil bath temperature of 100 °C for 4 hours with 5wt% of catalyst loading and molar ratio of methanol to PFAD at 20: 1.

The FAME yields are assumed to be composed of the major methyl esters like methyl palmitate, methyl stearate, methyl oleate and methyl linoate. Other minor methyl esters components were ignored because those only consist of very small amount in the FAME yield. FAME yield was obtained by using gas chromatography with external standard. Table 4.8 shows the concentrations of each major methyl esters and the final yield calculated by using the external standard curve. The sulfonation conditions of each of the catalyst samples were all tabulated in Table 4.2 for reference. The gas chromatography report for Cat-A1 will be attached is Appendix C as a sample.

Figure 4.14 shows the graph of FAME yield obtained from catalyst sulfonated with by using different concentration of ammonium sulfate solution at different holding time. Overall, sulfonation for 30 minutes gives the highest yield than all other sulfonation time. However, sulfonation duration of 15, 60 and 90 minutes did not show a clear picture on which durations gives the highest overall yield because the yield obtained are near to each other and they assert different trend corresponding to the concentration of ammonium sulfate solution.

Looking into the trend of each of the sulfonation duration, the maximum yield at the sulfonation duration was obtained at different ammonium sulfate solution concentration. When the catalyst is sulfonated for 15 minutes, 5 w/v% ammonium sulfate solution gives the highest yield of 15.175%. This 15 minutes sulfonation exhibits the decreasing trend as the concentration of ammonium sulfate solution increases. As for 30 minutes sulfonation time, the maximum yield of 23.718% was achieved at 10 w/v% ammonium sulfate solution. 60 and 90 minutes of sulfontion times has the maximum yield of 14.913% by using 20 w/v% and 16.539% by using 20 w/v% ammonium sulfate solution respectively. As a result, catalyst that has undergo 10 minutes ultrasonication, sulfonated in 30 ml of 10 w/v% ammonium sulfate solution for 30 minutes at 235 °C poses the highest yield when it was used in the esterification reaction.

Table 4.8: FAME Yield Obtained from Using Different Catalyst

Catalyst	**Methyl Esters Concentration (g/L sample solution)**					**Yield (%)**
	Methyl Palmitate	**Methyl Stearate**	**Methyl Oleate**	**Methyl Linoate**	**Total**	
Cat-A1	2.231	0.316	2.916	2.364	7.685	15.175
Cat-A2	6.034	0.303	2.571	1.789	6.800	12.496
Cat-A3	2.425	0.257	1.299	2.784	6.160	12.160
Cat-A4	0.000	0.271	2.470	1.730	6.378	12.759
Cat-A5	0.000	0.247	2.103	1.417	5.541	10.299
Cat-A6	2.440	0.170	0.076	2.389	5.075	9.945
Cat-A7	3.868	0.564	4.940	3.071	12.442	23.718
Cat-A8	2.231	0.382	4.703	3.042	10.358	20.206
Cat-A9	3.590	0.533	4.632	2.907	11.662	20.039
Cat-A10	1.773	0.491	4.855	3.046	11.434	19.665
Cat-A11	1.238	1.141	0.9715	1.277	4.727	8.855
Cat-A12	1.337	0.264	2.369	1.508	6.121	11.224
Cat-A13	2.228	0.370	3.187	2.096	8.304	16.539
Cat-A14	1.808	0.592	5.1452	0.516	10.320	16.062
Cat-A15	2.811	0.369	3.1132	2.079	8.217	14.929
Cat-A16	3.590	0.147	1.510	0.910	3.805	7.572
Cat-A17	1.337	0.307	2.805	0.971	6.312	12.020
Cat-A18	3.868	0.050	2.442	2.505	7.808	14.913
Cat-A19	3.049	0.261	2.659	1.713	6.441	12.429

Esterification Conditions: 100 °C oil bath, 4 hours, 5 wt% catalyst loading, molar ratio of methanol to PFAD 20:1

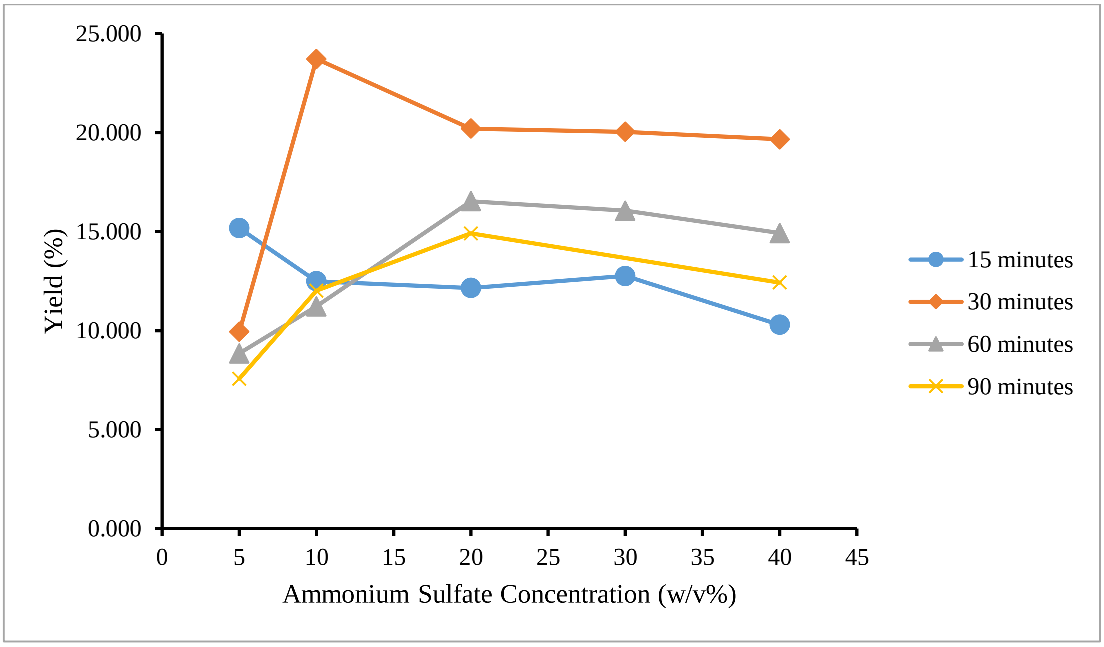


Figure 4.14: Effect of Sulfonation Duration and Ammonium Sulfate Concentration on the FAME Yield (Esterification Conditions: 100 °C Oil Bath, 4 hours, 5 wt% Catalyst Loading, Molar Ratio of Methanol to PFAD 20:1)

From Figure 4.14, it was observed that the FAME yield with increase of the ammonium sulfate solution concentration. Shuit, Ng and Tan (2015) reported that at high concentration, the solution has a higher viscosity and this will affect the dispersion of activated carbon in the solution. When the activated carbon are constraint by the high concentration solution, the activated carbon will still remained in lump and not all of the carbon are being exposed to the solution. This will result in only the outer perimeter of the carbon lump are exposed to the ammonium sulfate solution to attach SO_3H group.

In addition, the sulfonic group attached on the carbon reached the optimum density at 30 minutes and decreases when the sulfonation duration was longer than 30 minutes. As explained in Section 4.2.1, due to the high sulfonation temperature, the volatile material on the carbon will escape from the carbon leaving lesser surface for functional group attachment. Thus, the overall yield of FAME when catalysts sulfonated for 90 minutes is lower than 30 and 60 minutes.

Comparing the biodiesel yield obtained with the characterisation of catalyst, the FT-IR analysis showed that catalysts sulfonated for 30 minutes exhibit the highest SO_3H group intensity compared to other catalysts sulfonated at 15, 60 and 90 minutes. Besides that, EDX analysis also showed that Cat-A7 has the highest S content attached on the catalyst and explained that Cat-A7 produced the highest FAME yield among all other catalysts.

The FAME yield from catalysts sulfonated from different conditions show a similar trend to the acid density discussed in Section 4.2.3. Lokman, Rashid and Taufiq-Yap (2015) stated that the catalyst with high total acid density will give higher activity. Thus, Cat-A7 that has the highest total acid density at 3.32 mmol/g produced the highest FAME yield at 23.718% among all other catalysts sulfonated by different duration and concentration of ammonium sulfate.

Shuit and Tan (2014) has reported the yield of 88.0 % was obtained by using carbon nanotubes as the catalyst precursor and sulfonated through thermal decomposition of ammonium sulfate. The sulfonation conditions was the same, which were by heating carbon material with 30 ml 10 w/v% ammonium sulfate for 30 minutes at 235 °C. However, the result obtained by using seaweed derived activated carbon was much lower compared to by using carbon nanotubes. Carbon nanotubes is a type of conventional carbon material with very high surface area and this had made an advantage over the carbonised carbon from biomass. The high surface area allows the grafting of more SO_3H group onto the catalyst and this had increased the active site available for reaction. Thus, it was reasonable that the carbonised seaweed biomass did not serve as a better precursor than the carbon nanotubes.

Besides that, there was other reasons that lead to the low FAME yield obtained by using seaweed derived catalyst. Figure 4.15 shows the SEM image of catalyst at magnification of 500x and 2000x. Large numbers of microorganism was found on the surface of the catalyst. The present of these microorganism may be due to the long term exposure of seaweed to the sea water that contains numerous microorganisms. These microorganism appears in oval shape with regular texture on the body. They were attaching on the seaweed as parasites and tends to cover up pores of the carbon.

The presence of these microorganisms had reduce the surface area available for the grafting of SO_3H group as the reaction active site.

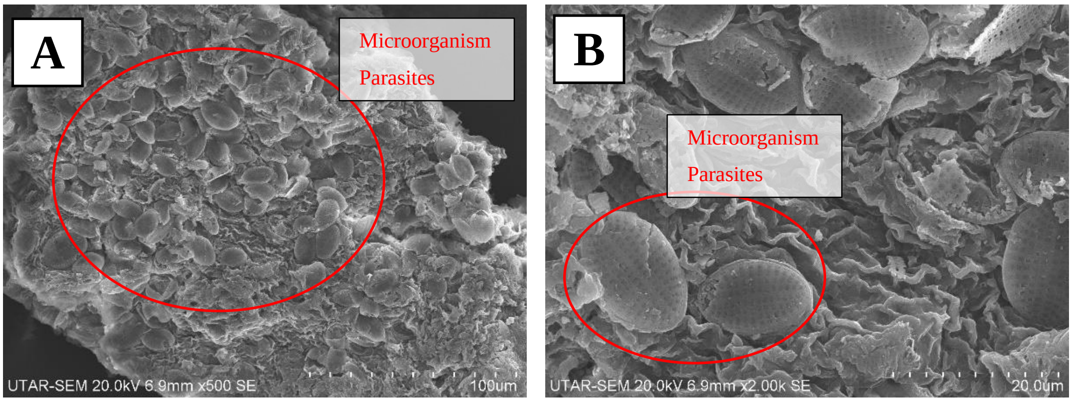


Figure 4.15: SEM Image of Catalyst with Microorganism Attached at Magnification (A) 500x and (B) 2000x

Furthermore, the reason of achieving low yield may be due to the incorrect way of doing ultrasonication. Ultrasonication was done to the mixture of carbon with ammonium solution prior to heating at high temperature during the sulfonation process. According to the actual procedure done by Shuit and Tan (2014), ultrasonication was done by using the probe-type ultrasonicator but a water bath ultrasonicator was used in this experiment. The water bath ultrasonicator is less effective than the probe-type ultrasonicator because the ultrasonic wave will hit the container first only will transfer the ultrasonic wave into the mixture for the water bath ultrasonicator but for the probe-type ultrasonicator, the ultrasonic wave will be directly emitted into the mixture.

Other than that, the type of container used in the water bath ultrasonicator was also important. During the test run of the experiment, a conical flask was used as the container to fill in the mixture. However, due to the lack of capability for conical flask to withstand high temperature for a long time at the heating process during sulfonation, a porcelain crucible was then used to replace the conical flask. The usage of crucible as the container for the mixture in the water ultrasonicator was show to be not very effective and thus, the carbon did not disperse well in the ammonium sulfate solution resulting in the les exposure of carbon surface to the solution. In this case, an extra study was conducted by using conical flask as the container for carbon and ammonium sulfate solution during ultrasonication. Table 4.9 shows the FAME yield of 63.35% was obtained when conical flask was tested to be used as the container during ultrasonication. The FAME yield of this set of experiment is much higher than the FAME yield obtained from using Cat-A7 (optimum condition catalyst) at 23.718%. This also has proven that glass container is more effective to be used in the water bath ultrasonicator compared to porcelain container.

Table 4.9: FAME Yield Obtained from the Test Run Catalyst

Catalyst	Methyl Esters Concentration (g/L sample solution)					Yield (%)
	Methyl Palmitate	Methyl Stearate	Methyl Oleate	Methyl Linoate	Total	
Cat-Test	108.111	40.406	60.253	44.627	253.398	63.35

Sulfonation Condition: 1.5 g SWAC200, 30 ml 10w/v% ammonium sulfate solution, 10 minutes ultrasonication, 235 °C for 30 minutes

Esterification Conditions: 100 °C oil bath, 4 hours, 5 wt% catalyst loading, molar ratio of methanol to PFAD 20:1

4.4.2 Optimisation Study for Esterification Conditions

Optimisation study for esterification conditions was done to determine the reaction condition that best suit the raw materials employed like the catalyst synthesised and the feedstock. The optimum condition may vary and dependant on the type of feedstock used, for this case is PFAD and also the type of catalyst used. The type of biomass used and the sulfonation method may also affect the optimum conditions for esterification reaction. The catalyst used was derived from seaweed as the biomass and undergo carbonisation to transform into carbon compound and sulfonated by thermal decomposition of ammonium sulfate. The catalyst loading in wt% and the duration of esterification was studied. In this study, Cat-A7 that was sulfonated by using 10 w/v% ammonium sulfate solution for 30 minutes at 235 °C was used for all the esterification to act as a fixed variable in the experiment.

4.4.2.1 Effect of Esterification Time on Biodiesel Yield

The effect of reaction time was studied from 2 hours to 8 hours of reaction time. Other conditions was remain constant that the esterification reaction was done at 100 °C oil bath, with methanol to PFAD molar ratio of 20:1 with catalyst loading of 5 wt% by using Cat-A7 as the fixed catalyst.

As shown in Figure 4.16, the FAME yield shows an increasing trend when the esterification time increases. At 2 hours of esterification time, the FAME yield obtained was 13.13%. The yield increased to 23.72% when the reaction time is 4 hours and the yield further increase to 27.37% when the reaction time was extended to 6 hours. At the esterification time of 8 hours, the biodiesel achieve the highest yield at 28.87% compared to the shorter esterification time. Lokman, Rashid and Taufiq-Yap (2015) reported the optimum esterification time was achieve at the reaction time of 3 hours by using PFAD as the feedstock with sulfonated starch solid acid catalyst with FAME yield of 94.6%. However, this study was only limited to 2 to 8 hours of reaction time, a longer reaction time (higher than 3 hours) may be able to achieve higher yield as the highest yield obtained in this study was still low.

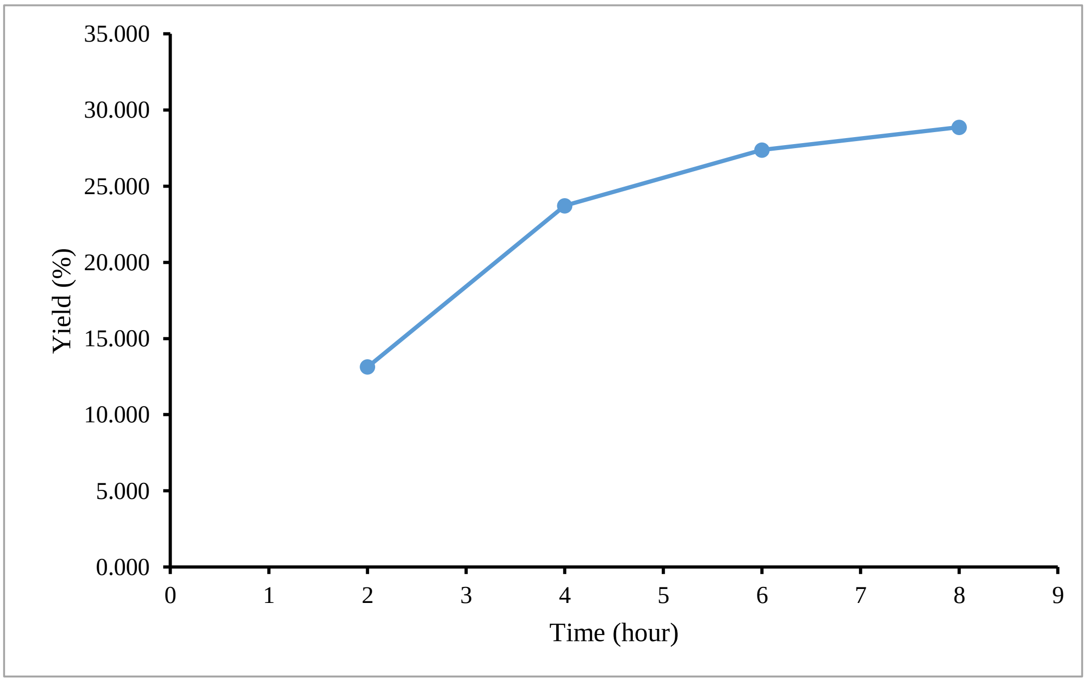


Figure 4.16: Graph of Effect of Reaction Time on FAME Yield at 100 °C Oil Bath, Methanol to PFAD Molar Ratio of 20:1 and Catalyst Cat-7 Loading of 5 wt%

4.4.2.2 Effect of Catalyst Loading on Biodiesel Yield

The catalyst loading for the esterification was chosen to study because it directly related to the catalyst synthesised. The catalyst loading will be directly affected by the efficiency of the catalyst. Catalyst loading of 2.5, 5, 10 and 15 wt% was studied for their effect towards the biodiesel yield with all other condition kept constant. For this experiment, the reaction temperature was fixed at 100 °C oil bath temperature, methanol to PFAD molar ratio of 20:1 and 8 hours reaction time by using sample Cat-A7 as the catalyst where Cat-A7 was sulfonated by using 30 ml of 10 w/v% ammonium sulfate solution heated to 235 °C for 30 minutes.

Folasegun, et al. (2014) stated that increasing the amount of catalyst would increase the production of the desired product in reaction system. The trend of yield obtained from employing different catalyst loading is shown in Figure 4.17 below. It was observed that the increase of catalyst loading asserts an increasing trend on the FAME yield. The lower catalyst loading of 2.5 wt% produced the lowest FAME yield at 19.9 %. It follows by catalyst loading of 5 wt% that poses 22.22% yield and when 10 wt% of catalyst loading was used, the FAME yield increased to 33.9 %. And lastly, 15 wt% catalyst loading gives the highest FAME yield at 47.87%. The FAME yield may be able to further increase if the catalyst loading of more than 15 wt% is employed.

Lokman, Rashid and Taufiq-Yap (2015) stated that optimum catalyst loading was achieve at 4 wt% with the FAME yield of 94.6%. The catalyst used was the sulfonated starch reacting with methanol-to-PFAD molar ratio of 10 at 75 °C for 3 hours in the esterification reaction. Konwar, et al. (2015) had also reported that the optimum catalyst loading by using catalyst derived from de-oiled waste cake is at 5 to 6.5 wt.% achieving FAME yield of 97% at condition 43:1 methanol –to-oil molar ratio at 80 °C for 8 hours. As a result, the Cat-A7 exhibits a relatively low yield compared to the other reported result and should be further improved to increase the catalyst activity in esterification reaction.

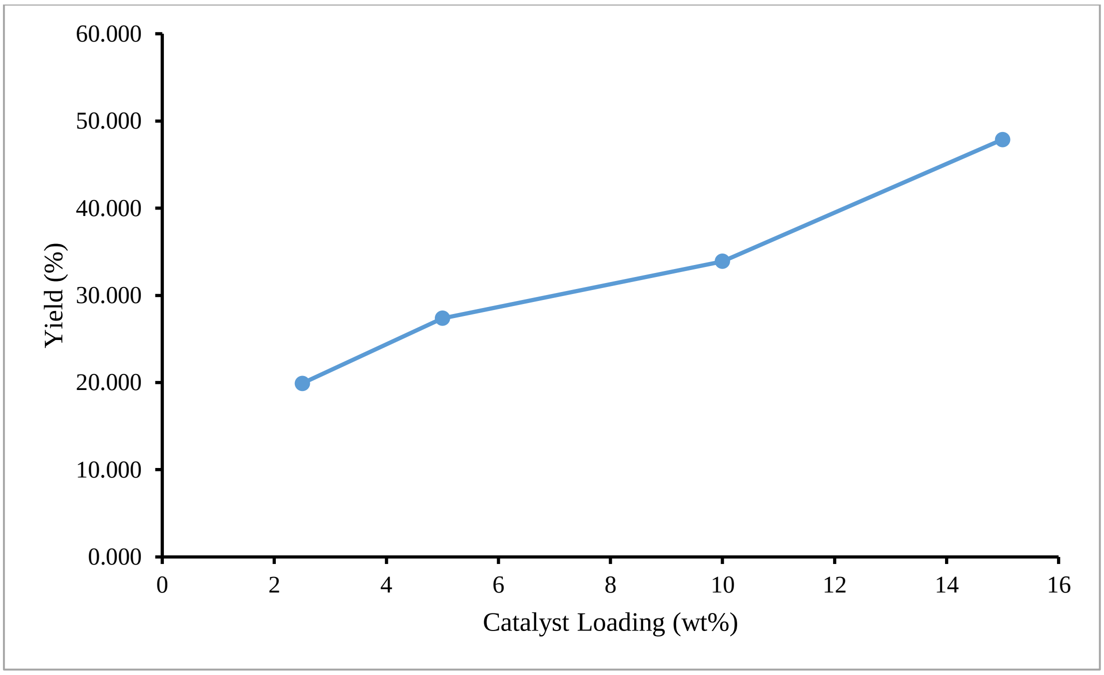


Figure 4.17: Graph of Effect of Catalyst Loading on FAME Yield at 100 °C Oil Bath, Methanol to PFAD molar ratio of 20:1 and 8 Hours Reaction Time

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Seaweed biomass was successfully carbonised at the temperature of 200, 300, 400, 500 and 600 °C. The catalyst produced by seaweed carbon produced by 200 °C exhibits the highest total acid density at 3.32 mmol/g compared to the catalyst produced by other carbonisation temperature. Thus, seaweed carbon produced by 200 °C carbonisation that is noted by SWAC200 was used as the precursor for the study of sulfonation parameters.

The synthesised catalyst was analysed with several catalyst characterisations. SEM image shows that the seaweed carbon has irregular surface with large number of pores on it. FT-IR analysis has proven the present of SO_3H group in the catalyst according to the S=O stretching and SO_3 symmetric stretching vibrations. It was also known that the catalyst contains –COOH and –OH from the present of C=C aromatic stretch and also the C=O stretch. EDX was another type of analysis to prove the present of SO_3H as the functional group in the catalyst by analysing the elemental composition of S, C and O on the catalyst. Catalyst synthesised shows the present of sulfur element, S in EDX analysis. Thermogravimetric analysis had determined the functional group decomposition temperature of the catalyst is at 537.9 °C and this shows that the catalyst has a relative high thermal stability as the catalyst will not be used at temperature higher than this.

The optimum sulfonation conditions obtained was by mixing 1.5 g of SWAC200 with 30 ml of 10 w/v% ammonium sulfate solution, 10 minutes of ultrasonication and heating time of 30 minutes at 235 °C. The catalyst sulfonated by using the above mentioned condition poses the FAME yield of 23.718%. On the other hand, the optimum esterification conditions obtained from the study was by heating the PFAD and methanol with molar ratio of 20:1 at 100 °C oil bath temperature for 8 hours with 15 wt% catalyst loading. The FAME yield obtained from the esterification process that employed the optimum condition was 47.87%.

However, the highest FAME yield obtained was relatively low. Several problem was raised and suspected that those may be the reasons of the low FAME yield. The presence of microorganism on the catalyst that covered up the pores prevented SO_3H from grafting onto the carbon surface. Another problem encountered was the usage of porcelain container instead of glass container has limited the dispersion of carbon into the sulfonating agent.

In conclusion, all the objectives of this final year project was fulfilled. Solid acid catalyst was successfully synthesised from seaweed derived activated carbon by thermal decomposition of ammonium sulfate. Some areas of the research conducted have to be improved to obtain better result in the future.

5.2 Recommendation

Experiment was done accordingly to the scope of study. However, due to time constrained, some abnormalities occurred in the experiment was ignored. The deviation of results can be due to the human error as well as the limitation on the equipment provided. In order to improve the accuracy and consistency of the experimental result, some improvement should be made in all areas when more time is given as well as in the future studies. Some recommendations on the study are listed at the following:

i. The sample that required in large amount to be used for the further studies should be mass produced. Sample should be produce in one big batch instead of producing it separately as the properties of the catalyst may be vary from one batch to another batch. Thus, the samples that are produced in the same batch has the same properties and can be used for further parameters study by remaining the samples as a constant variable.

ii. The equipment used should be consistent. Equipment used like hot plate, oil bath, glass container and so on should be the same for every set of experiment to ensure the consistency of the experiment environment.

iii. The number of parameters study should be increased. For example, besides the carbonisation time, the carbonisation durations and the temperature ramping time can also be studied on it effect to the biodiesel production. Besides that, for the sulfonation reaction, other than ammonium sulfate concentration and heating time, parameters like the ultrasound duration and ammonium sulfate volume can also be studied.

iv. The number of set of experiment for each parameter could be increased. The more set of experiment done, the more accurate optimum conditions. For ideal case, a bell share curve should be obtained to indicate the position of the optimum condition.

v. Analysis of catalyst samples and biodiesel samples should be conducted as soon as they are produced to avoid any degradation occurs.

vi. If seaweed is used as the biomass to be ca carbonised in to the activated carbon, pre-treatment is necessary to remove the microorganism attaching on the surface of the seaweed. The seaweed should be wash thoroughly either with water or with special chemical that could detach microorganism from the seaweed.

vii. When ultrasound is required in the catalyst synthesis process, a glass container should be used to maximise the ultrasound effect on the mixture in the container.

viii. Biomass with low density could be selected as low density biomass is known to be more porous and has higher surface area. Thus, the surface available for the sulfonation is high poses a high efficiency catalyst.

REFERENCES

Adam, F.L., James, A.B., Jinesh C.M. and Karen, W., 2014. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. *Royal Society of Chemistry*. 43(22), pp. 7887-7916.

Antonio, D. P., Manoela, S. S., Omar, I. B. S. and Denis, B., 2014. *Liquid Biofuels.* London: Springe-Verlag.

Ayhan, D., 2009. Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50 (1), pp. 14-34.

Bell Performance, 2014. *The Major Differences between Ethanol and Gasoline.* [online] Available at: <http://www.bellperformance.com/blog/the-major-differences-between-ethanol-and-gasoline> [Accessed 4 July 2015]

Biopact, 2007. *A quick look at fourth generation biofuels*. [online]. Available at: <http://global.mongabay.com/news/bioenergy/2007/10/quick-look-at-fourth-generation.html> [Accessed 4 July 2015]

Bozbas, K., 2008. Biodiesel as an alternative motor fuel: Production and policies in the European Union. *Renewable and Sustainable Energy Reviews*, 12 (2), pp. 542-552.

British Petroleum, 2015. *BP Statistical Review of World Energy*. [pdf] London, UK: BP. Available at <http://www.bp.com/content/dam/bp/pdf/Energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf> [Accessed 4 July 2015].

Carbon Counted, 2015. *When Will Fossil Fuels Run Out?* [online] Available at: <http://www.carboncounted.co.uk/when-will-fossil-fuels-run-out.html> [Accessed 1 August 2015].

ChemWiki, 2013. *10C: UV/Vis and IR Spectroscopy* [online] Available at: < http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Analytical_Chemistry_2.0/10_Spectroscopic_Methods/10C%3A_UV%2F%2FVis_and_IR_Spectroscopy> [Accessed 6 April 2016]

C2ES, 2013. *Biodiesel*. [online] Available at: < http://www.c2es.org/energy/source/renewables/biofuels/biodiesel#_edn14> [Accessed 4 July 2015]

Dehkhoda, A.M., West, A.H. and Ellis, N., 2010. Biochar based solid acid catalyst for biodiesel production. *Applied Catalysis A: General*, 382(2), pp. 197-204.

Dennis, Y.C., Xuan, W. and Leung, M.K.H., 2010. A review on biodiesel production using catalysed transesterification. *Applied Energy*, 87 (4), pp. 1083-1095.

Du, C.Y., Zhao, T.S., Liang, Z.X., 2007. Sulfonation of carbon-nanotube supported platinum catalyst for polymer electrolyte fuel cells. *Journal of Power Sources*, 176 (1), pp. 9-15.

Edgar, L., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D.A. and Goodwin, J.G., 2005. Synthesis of Biodiesel via Acid Catalysis. *Industrial and Engineering Chemistry Research*, 44(14), pp. 5353-5363.

Ezebor, F., Khairuddean, M., Abdullah, A.Z. and Boey, P.L., 2014. Oil palm trunk and sugarcane bagasse derived heterogeneous acid catalyst for production of fatty acid methyl esters. *Energy*, 70(2014), pp. 493-503.

Folasegun, A.D., Olubunmi, A., Jiayu, X., Suojiang, Z. and Dongxia, Y., 2013. Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst. *Applied Energy*, 114, pp. 819-826.

Gaber, A., Abdel-Rahim, M.A., Abdel-Latief, A.Y., Abdel-Salam and Mahmoud, N., 2014. Influence of Calcination Temperature on the Structure and Porosity of Nanocrystalline SnO2 Synthesized by a Conventional Precipitation method. *International Journal of Electrochemical Science*, 9(1), pp. 81-95.

Jaichandar, S. and Annamalai, K., 2011. The Status of Biodiesel as an Alternative Fuel or Diesel Engines – An Overview. *Journal of Sustainable Energy and Environment*, [online] Available at: <http://www.jseejournal.com/JSEE%202011/JSEE%20Vol%202%20Issue%202/11.%20The%20status%20of%20biodiesel%20pp.%2071-75.pdf> [Accessed 20 August 2015].

Janaun, J., Abang, S., and Anwar, A.M., 2013. Synthesis and characterization of carbon-based catalyst derived from seaweed. In: *2013 IEEE Conference on Clean Energy and Technology*. Langkawi, 18-20 November, 2013. Malaysia: IEEE.

Kastner, J.R., Miller, J., Geller, D.P., Locklin, J., Keith, L.H. and Johnson, T., 2012. Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catalysis Today*, 190 (1), pp. 122-132.

Konwar, L.J., Maki-Arvela, P., Salminen, E., Kumar, N., Thakur, A.J., Mikkola, J. and Deka, D., 2015. Towards carbon efficient biorefining: Multifunctional mesoporous solid acids obtained from biodiesel production wastes for biomass conversion. *Applied Catalyst B: Environmental*, 176(2015), pp. 20-35.

Lambert, J. B., 1987. *Introduction to Organic Spectroscopy*. New York: Macmillan.

Lee, D., 2013. Preparation of a Sulfonated Carbonaceous Material from Lignosulfonate and Its Usefulness as an Esterification Catalyst. *Molecules*, 18 (7), pp. 8168-8180.

Lee, H.V., Yunus, R., Juan, J.C. and Taufiq-Yap, Y.H., (2011). Process optimization design for jatropha-based biodiesel production using response surface methodology. *Fuel Processing Technology*, 92 (12), pp. 2420-2428.

Lee, K.T., Lam, M.K. and Mohammed, A.R., 2010. Homogeneous, heterogeneous an enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances*, 28 (4), pp. 500-518.

Liu, T., Li, Z., Li, W., Shi, C. and Wang, Y., 2013. Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol. *Bioresource Technology*, 133 (2013), pp. 618-621.

Lokman, L.M., Rashid,U. and Taufiq-Yap, Y.H., 2016. Meso- and macroporous sulfonated starch solid acid catalyst for esterification of palm fatty acid distillate. *Arabian Journal of Chemistry*, 9(2), pp. 179-189.

Maity, J.P., Bundschuh,J., Chen, C and Bhattacharya, P., 2014. Microalgae for third generation biofuel production, mitigation of greenhouse gas emissions and wastewater treatment: Present and future perspectives – A mini review. *Energy*, 78(2014), pp 355-360.

Malins, K., Kampars, V., Brinks, J., Neibolt, I. and Murnieks, R., 2015. Synthesis of activated carbon based heterogeneous acid catalyst for biodiesel production. *Applied Catalysis B: Environmental*, 176(2015), pp. 553-558.

Mar, W.W. and Somsook, E., 2012. Biomass-Based Sulfonic-Functionalized Carbon Solid Acid for Esterification of Acetic Acid. *Advanced Materials Research*, 506(2012), pp. 70-73.

Naik, S.N., Goud, V.V., Rout, P.K. and Dalai, A.K., 2010. Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 14(2), pp. 578-597.

Okamura, M., Takagaki, A., Toda, M., Konda, J.N., Domen, K., Tatsumi, T., Hara, Michikazu and Hayashi, S., 2006. Acid-Catalyzed Reactions on Flexible Polycyclic Aromatic Carbon in Amorphous Carbon, *Chemistry of Materials*, 18 (13), pp. 3039-3045.

REN21, 2015. *Renewables 2015 Global Status Report*. [pdf] Available at < http://www.ren21.net/wp-content/uploads/2015/06/REN12-GSR2015_Onlinebook_low1.pdf> [Accessed 4 July 2015].

Robles, A., Gonzalez, P.A., Esteban, L and Molina, E., 2009. Biocatalysis: Towards ever greener biodiesel production. *Biotechnology Advances*, 27 (4), pp. 398-408.

Shuit, S.H., Ng, E.P. and Tan, S.H., 2015. A facile and acid-free approach towards the preparation of sulphonated multiwalled-carbon nanotubes as a strong protonic acid catalyst for biodiesel production. Journal of Taiwan Institute of Chemical Engineers, 52(2015), pp. 100-108.

Shuit, S.H. and Tan, S.H., 2014. Feasibility study of various sulphonation methods for transforming carbon nanotubes into catalyst for the esterification of palm fatty acid distillate. *Energy Conversion and Management*, 88(2014), pp. 1283-1289.

Shu, Q., Zhang, Q., Xu, G., Nawaz, Z., Wang, D. and Wang, J., 2010. Synthesis of biodiesel from cottonseed oil and methanol using a carbon-based solid acid catalyst. *Fuel Processing Technology*, 90(7), pp. 1002-1008.

Shu, Q., Gao, J., Nawaz, Z., Liao, Y., Wang, D. and Wang, J., 2010. Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Applied Energy*, 87 (8), pp. 2589-2596.

Sims, R.E.H., Mabee, W. Saddler, J.N. and Taylor, M., 2010. An overview of second generation biofuel technology. *Bioresource Technology*, 101(6), pp. 1570-1580.

Stoytcheva, M. and Montero, G., 2011. *Biodiesel – Feedstock and Processing Technologies.* Croatia: InTech.

Sun, Z.P., Zhang, X.G., Liang, Y.Y. and Li, H.L., 2009. A facile approach towards sulfonate functionalization of multi-walled carbon nanotubes as Pd catalyst support for ethylene glycol electro-oxidation. *Journal of Power Sources*, 191 (2), pp. 366-370.

Sun, Z.X., Zheng, T.T., Bo, Q.B., Du, M. and Fosling, W., 2008. Effect of calcination temperature on the pore size and wall crystalline structure of mesoporous alumina. *Journal of Colloid and Interface Science*, 319(1), pp. 247-251.

U.S. Energy Information Administration, 2015. *August 2015, Monthly Energy Review*. [pdf] Washington, DC: EIA. Available at <http://www.eia.gov/totalenergy/data/monthly/pdf/mer.pdf> [Accessed 31 August 2015].

U.S. Energy Protection Agency, 2013. *Nuclear Energy, Electricity from Nuclear Energy*. [online] Available at: <http://www.epa.gov/cleanenergy/energy-and-you/affect/nuclear.html> [Accessed 4 July 2015].

World Energy Council, 2013. *World Energy Resources 2013 Survey*. [pdf] London, England. Available at <https://www.worldenergy.org/wp-content/uploads/2013/09/Complete_WER_2013_Survey.pdf> [Accessed 5 July 2015]

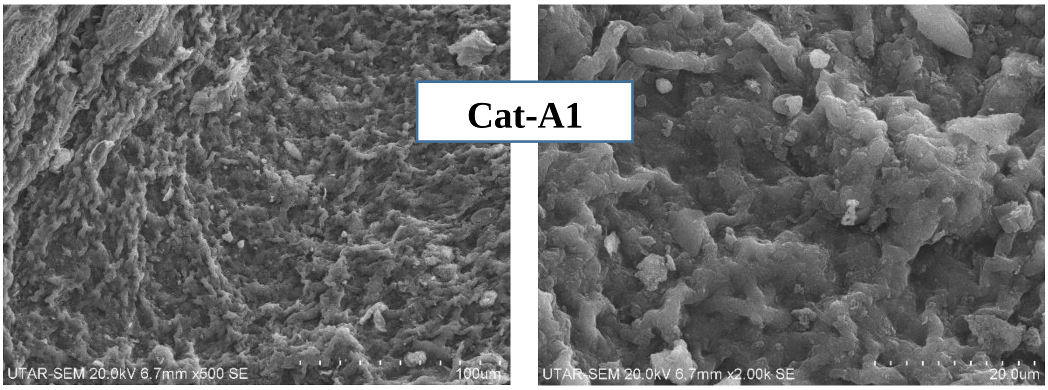
Yu, J. T., Dehkhoda, A. M. and Ellis, N., 2010. Development of Biochar-based Catalyst for Transesterification of Canola Oil. *Energy & Fuels*, 25 (1), pp. 337-344.

Zhang, B., Ren, J., Liu, X., Yun, G., Guo Y., Lu, G. and Wang, Y., 2010. Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst. *Catalysis Communications*, 11 (7), pp. 629-632.

Zhang, J., Liu, J. and Liu, R., 2015. Effect of pyrolysis temperature and heating time on biochar obtained from the pyrolysis of straw and lignosulfonate. *Bioresource Technology*, 176 (2015), pp.288-291.

APPENDICES

APPENDIX A: SEM Images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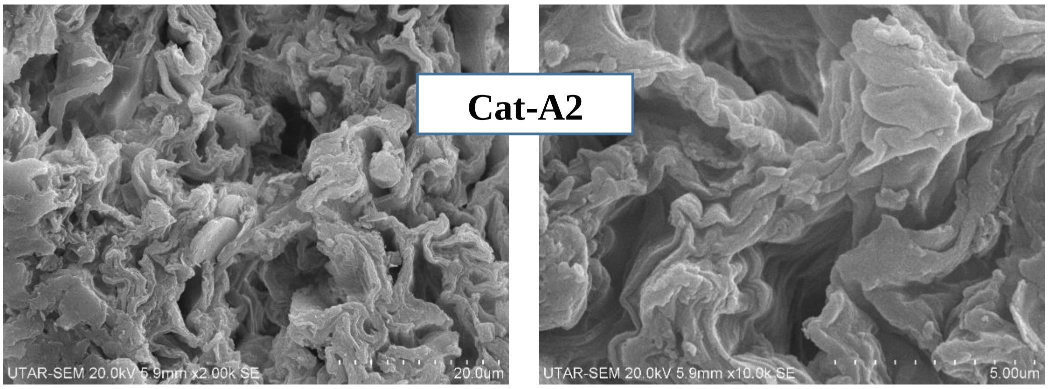
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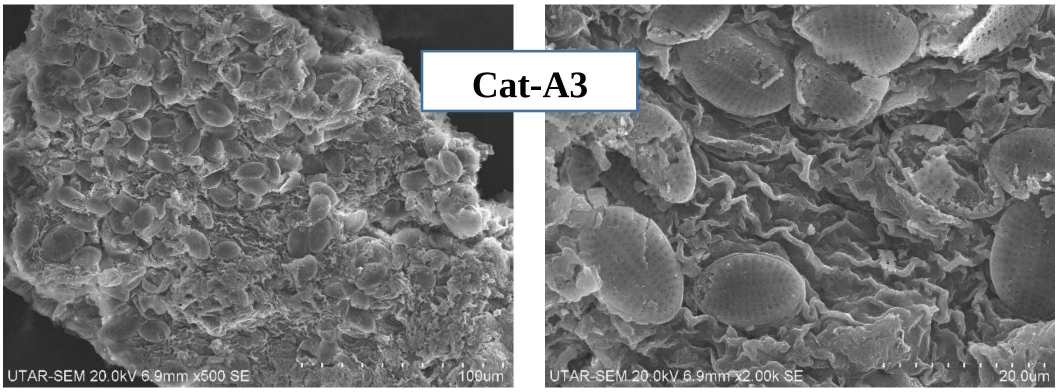
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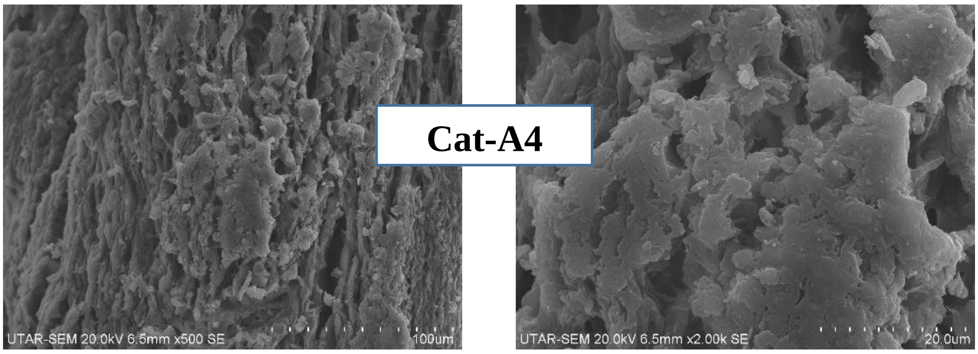

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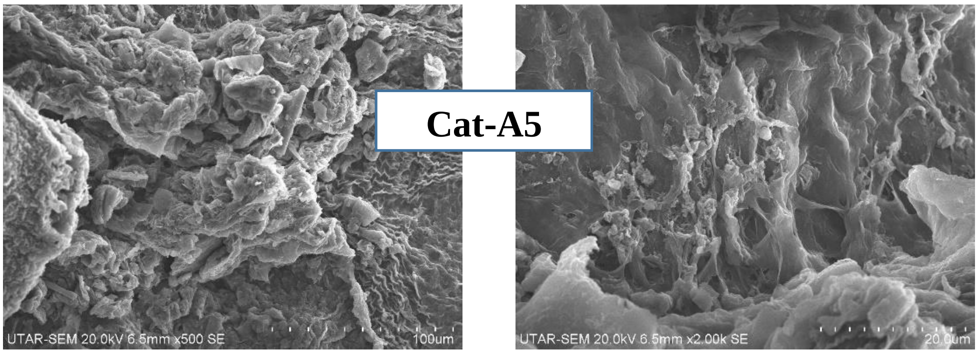

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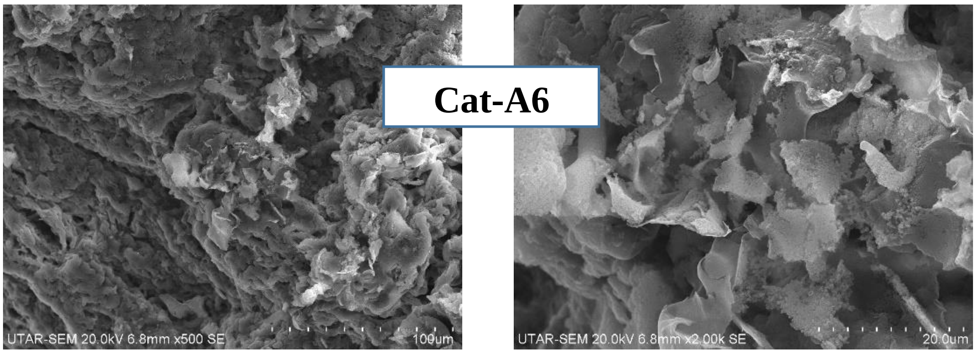

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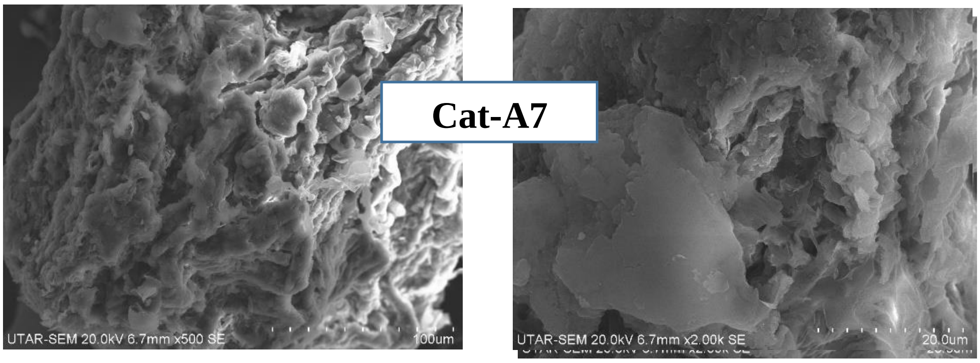

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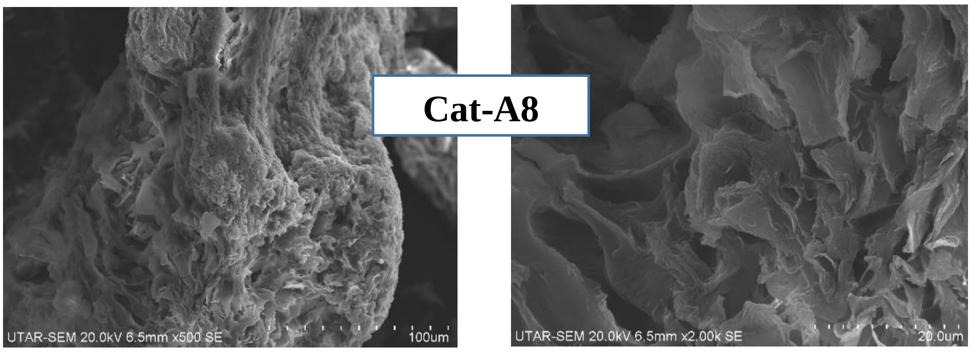

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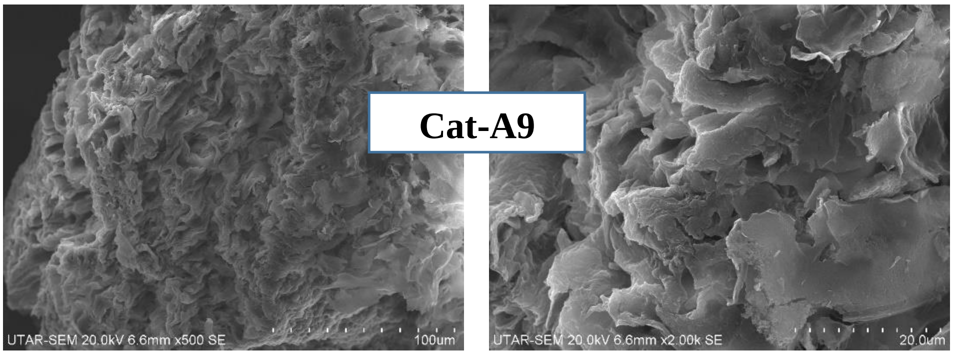
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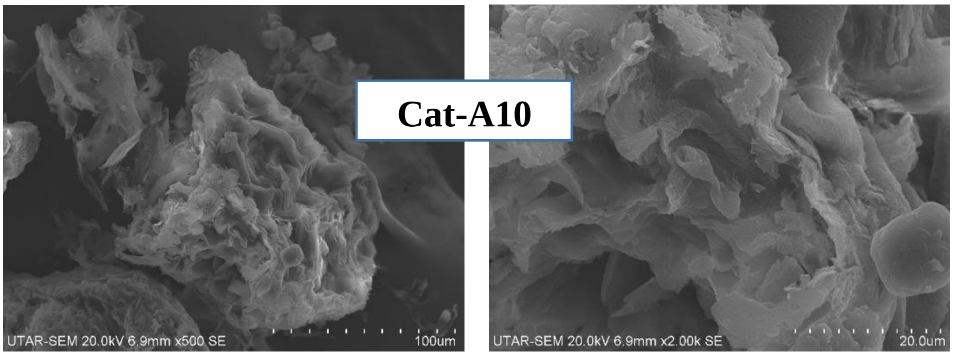
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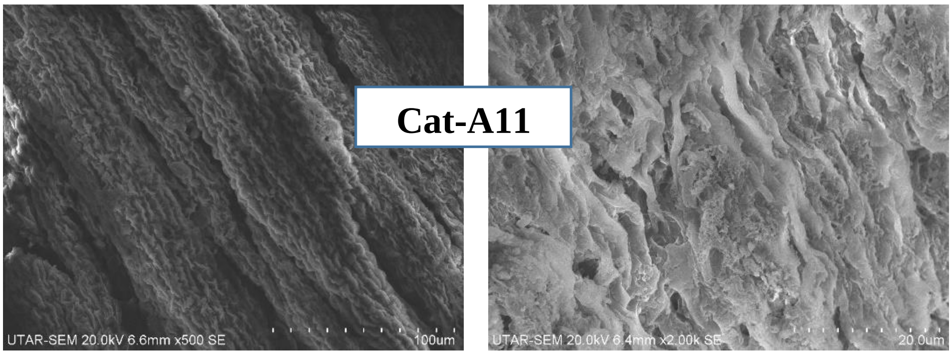
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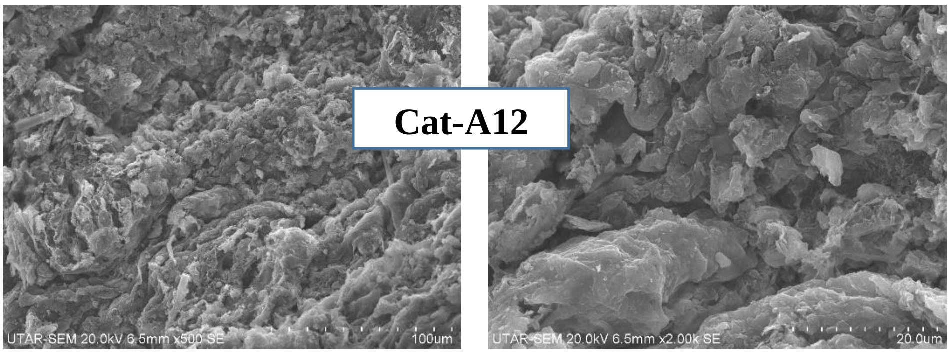
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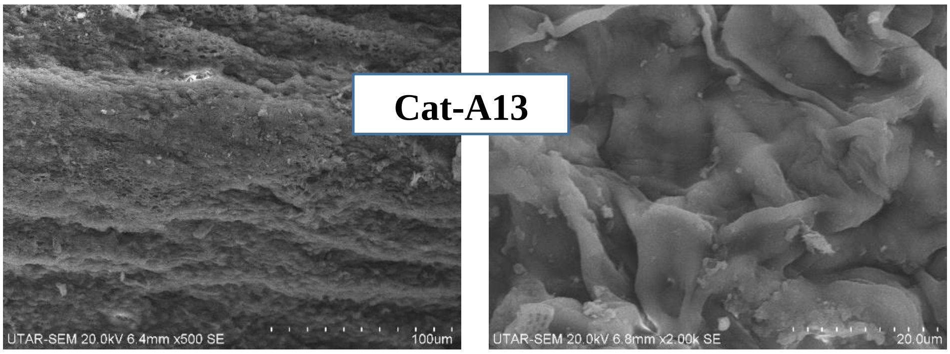
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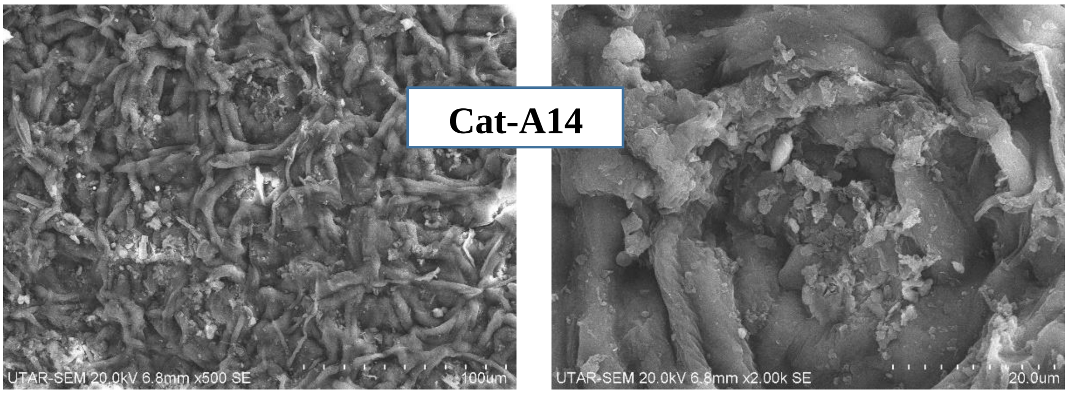

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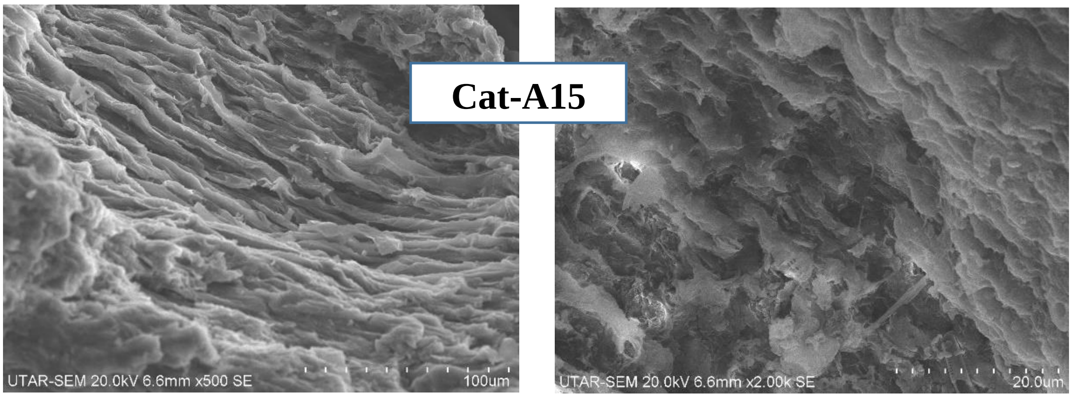

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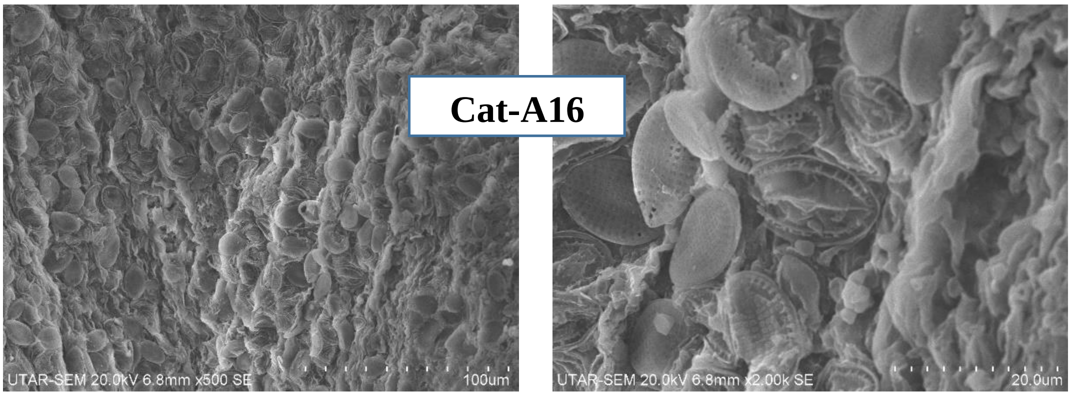

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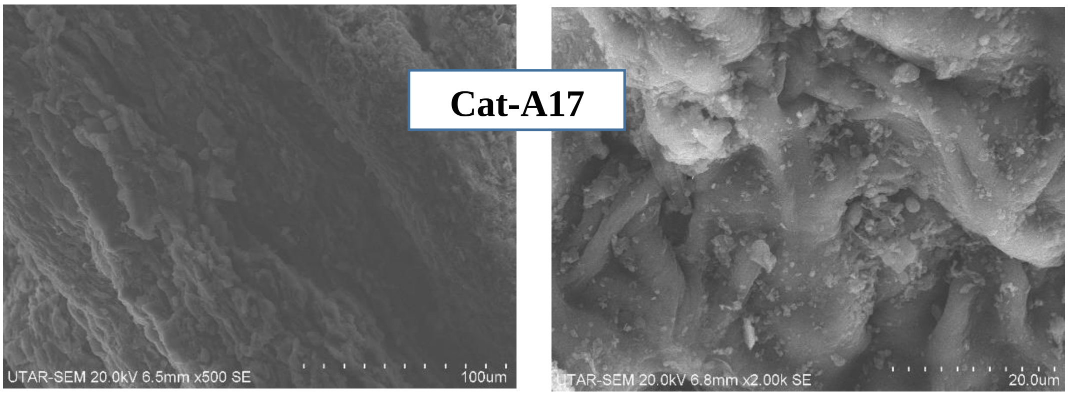

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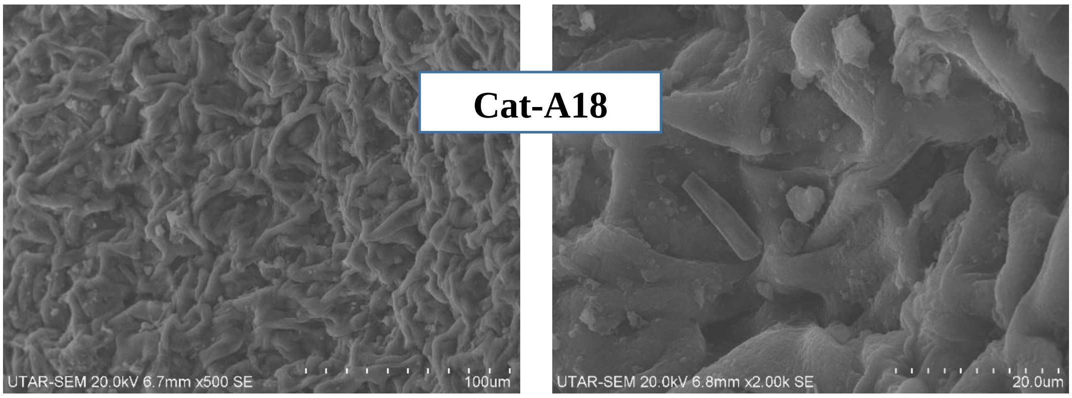

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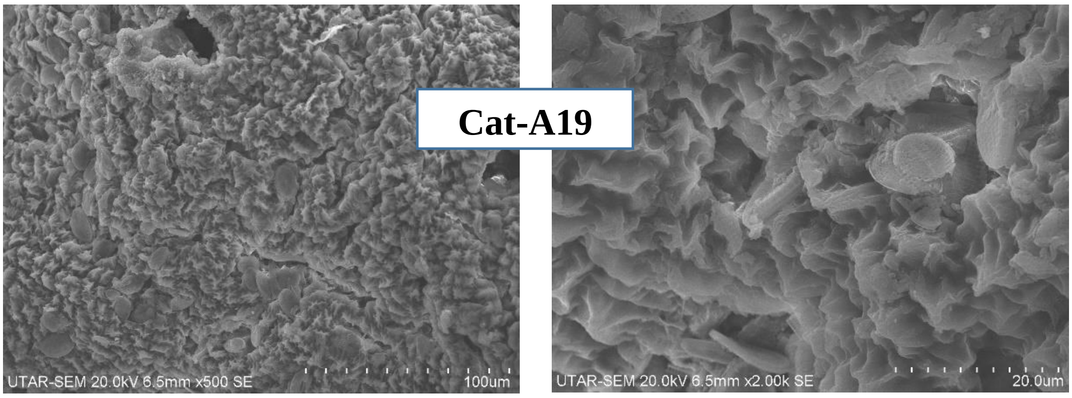

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APPENDIX B: EDX Report

APPENDIX C: Gas Chromatography Report

APPENDIX D: Gantt Chart

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Carbonisation of Raw Material	■	■												
Sulfonation of Carbon	■	■												
Characterisation of Catalyst		■	■											
Production of Biodiesel		■	■	■										
Product Analysis		■	■	■										
Results Analysis					■	■								
Chapter 4 – Results and Discussion							■	■	■					
Revision of Chapter 4									■	■				
Full Report											■	■		
Presentation Slides												■	■	
Oral Presentation														■

APPENDIX E: Material Safety Data Sheet (MSDS)