SYNTHESIS OF SOLID CATALYST FROM PALM EMPTY FRUIT BUNCH BY USING 4-BENZENEDIAZONIUM SULFONATE METHOD FOR PRODUCTION OF BIODIESEL

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

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Universiti Tunku Abdul Rahman

May 2016

DECLARATION

I hereby declare that this project report is based on my original work except for the 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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I certify that this project report entitled **SYNTHESIS OF SOLID CATALYST FROM PALM EMPTY FRUIT BUNCH BY USING 4-BENZENEDIAZONIUM SULFONATE METHOD FOR PRODUCTION OF BIODIESEL** was prepared by **YAP CHIN YI** 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.

Approved by,

Signature : ______________________________

Supervisor : ______________________________

Date : ______________________________

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ABSTRACT

Application of solid acid catalyst in biodiesel production gains much attention from researchers as it is suitable for most of the non-edible and low value oils which will significantly cut down the total production cost and reduce corrosion issue. In this research, biomass from palm empty fruit bunch is used as the carbon precursor to synthesis activated carbon (AC) and resulting AC was sulfonated by 4-benzenediazonium sulfonate (4-BDS) to produce solid acid catalyst. The synthesised catalysts were characterised and the performance were tested in esterification of palm fatty acid distillate (PFAD) to produce biodiesel. SEM showed that a clear porous and rough surface was developed after calcination at relative low temperature (200 ° C) which favours the attachment of the acid active site. This research also found that that the total acid sites of the catalyst increased when sulfanilic acid loading increased during sulfonation. TGA result showed that the catalyst support undergo two stages of mass loss due to loss of moisture and carbon decomposition respectively. It was reported that the carbons structure was thermally stable up to temperature of 549.9 ° C. FTIR analysis proved that S=O and SO_3H observed at wavelength 1020-1090 cm^{-1} and 1150-1270 cm^{-1} respectively indicated the successful attachment of sulfonic group. In catalytic activity test, the result showed that catalyst calcined at 200 ° C and catalyst sulfonated with 15:1 sulfanilic acid to AC ratio was the optimum catalyst as they gave the highest biodiesel. The esterification parameters were also studied and the result showed that reaction time of 7 h – 24 h was the optimum operating duration and 20 wt% of CAT15:1 was reported as optimum catalyst loading as it gave the highest biodiesel yield which is 98.1%.

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4-BDS	4-benzenediazonium sulfonate
AC	Activated Carbon
BET	Brunauer, Emmett and Teller
DOSM	Department of Statistics Malaysia
EDX	Energy Dispersive X-ray
EFB	Empty Fruit Bunch
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectrometer
GC	Gas Chromatography
GDP	Gross Domestic Product
GHG	Greenhouse Gases
HTC	Hydrothermal Carbonisation
MBA	Malaysian Biodiesel Association
MPOB	Malaysian Palm Oil Board
NBP	National Biofuel Policy
PFAD	Palm Fatty Acid Distillate
RBD	Refined, Bleached and Deodorised
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TPD	Thermal Desorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffractometer

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CHAPTER 1

INTRODUCTION

1.1 Current Energy Scenario

Searching for new source of energy and sustainable development is always the main challenge for all engineers in the world. Population rocketing and rapid industrial growth is the primary contributors to high demand of energy; the situation is even aggravated by global climate change and depletion of fossil fuel along with the fluctuated oil prices.

According to the Department of Statistics Malaysia (DOSM), the population in Malaysia was around 29 million in 2011(DOSM, 2014) and it is expected to reach 38.6 million by 2040 (Manan, Baharuddion & Lee, 2015). Due to increase in population and development, Malaysia consumed around 75,907.34 kt of oil equivalent energy in 2011 compare to 21,548.08 kt of oil equivalent energy in 1990 when Malaysia started to undergo a rapid industrialization (World Bank, 2015). Figure 1.1 shows the increasing trend in energy consumption among the South East Asia countries. Although Malaysia's energy usage ranks after Indonesia and Thailand, it has consistently highest transportation energy intensity amongst 11 Asian countries which is shown in Figure 1.2. This indicates that a high price or cost of converting energy into gross domestic product (GDP) in words transportation energy is not being used efficiently. The situation has worsen over the years while other countries showing signs of improvement which means the gaps with these other countries have been widening especially in the last 10 years (Timilsina & Shrestha, 2009). Besides, a report from Ong, Mahlia & Masjuki, (2012) mentioned that car ownership in Malaysia had increased from 4.5 million vehicles in 1990 to 18 million vehicles by 2008. This proves that transportation sector in Malaysia is one of the largest consumer of energy which is 40.3% while industries account for 38.6% (Yusoff *et al*., 2013). The transportation sector at the same time contributes to more than 40% of the country's total greenhouse gases (GHG) emission (Manan, Baharuddin & Lee, 2014).

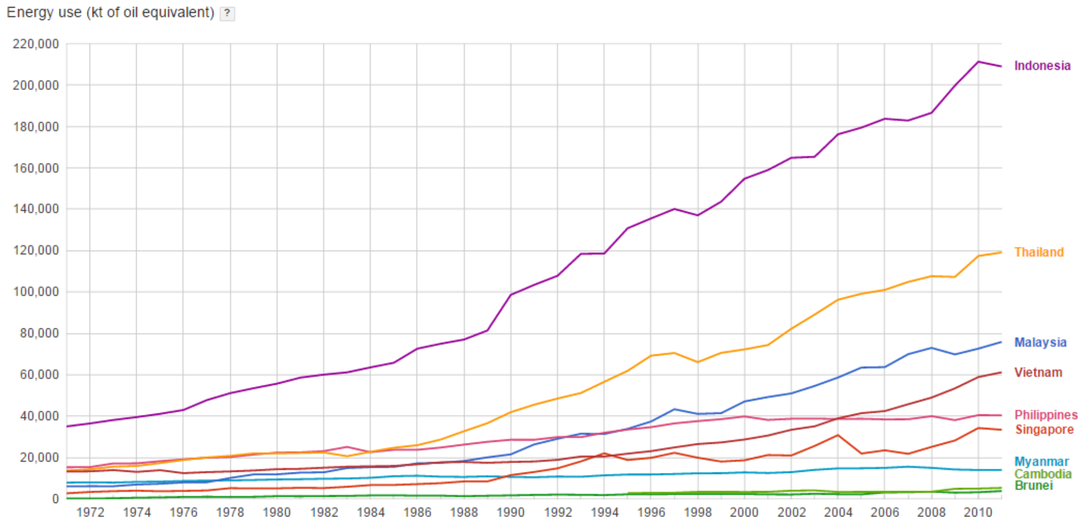

Figure 1.1: Energy Usage (kt of oil equivalent) among the South East Asia Countries. (World Bank, 2015)

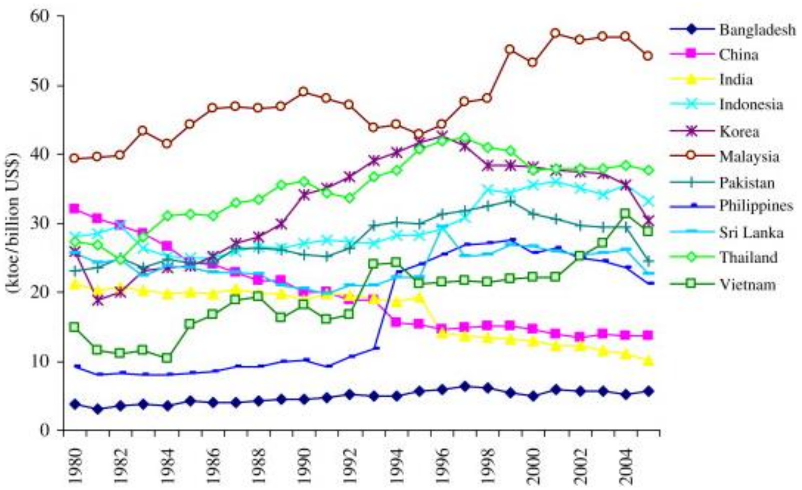

Figure 1.2: Transportation Energy Intensity in Several Asian Countries. (Timilsina & Shrestha, 2009)

1.2 Biodiesel in Malaysia

Biodiesel is defined as non-petroleum based diesel fuel which consists of the mono alkyl esters of long chain fatty acids derived from renewable lipid sources typically produced through the reaction of vegetable oil or animal fat with methanol in the presence of a catalyst. Due to depletion of fossil fuel, crude oil price volatility and security of energy supply, many countries have started to develop biodiesel as substitution to vehicle fuel.

It has reported that biodiesel has similar properties and composition with petroleum diesel. Therefore, they can be blended and burned without any modification to compression-ignition engine. Besides, sulfur compound also does not exist in vegetable, therefore does not contributes to acid rain. The energy source of biodiesel is indirectly originated from solar energy whereby through photosynthesis process, the plants store the energy chemically and release through combustion. Therefore, due to the large oxygen content inside the plants, the combustion efficiency in biodiesel theoretically will be higher than petroleum (Hosseini, 2012). Some researchers also reported that there was a declination of carbon dioxide, carbon monoxide and nitrogen oxides. However, some researchers oppose to the statement, until today the emission of biodiesel is still being debated.

As mention in section 1.1, Malaysia has the highest transportation energy intensity among the Asian countries. Therefore, it is vital for Malaysia to develop biodiesel to reduce the dependency of fossil fuel in transportation sector. Due to the difference in geographical locations and agricultural activities, the feedstock for biodiesel can be different for each country. For example, U.S. commonly uses soybean oil as feedstock while Europe uses rapeseed oil as feedstock. Generally, the feedstock of biodiesel is classified into 4 categories as shown in Table 1.1.

Table 1.1: Biodiesel Classifications.

Biodiesel Feedstock	Descriptions
Edible vegetable oil	Vegetable oil that is capable of being consumed as food or food accessory. (eg. Rapeseed, soybean, palm oil)
Non-edible vegetable oil	Vegetable oil that is not consumed as food or food accessory. (eg. Jatropha, algae)
Animal fats	eg. Tallow, yellow grease, chicken fat.
Waste or recycle oil	eg. Waste cooking oil.

Malaysia is a country blessed with tropical weather and humid climate, thus it provides excellent conditions for oil palm tree to grow. Figure 1.3 shows the palm oil expansion in Malaysia bringing the country into the biggest oil palm production of the world. In another word, palm oil is one the most promising local feedstock for biodiesel production in Malaysia. Since 1980s, Malaysia government started to develop palm diesel program in order to overcome the fossil fuel shortage problem. A series of researches and developments on palm oil based biodiesel is also continuously conducted by Malaysian Palm Oil Board (MPOB) with cooperation of PETRONAS (Hosseini, 2012). In late 2009, National Biofuel Policy (NBP) introduced biodiesel fuel blend B5 (5% methyl ester & 95% petroleum diesel) production and this implementation encountered twists and turns due to logistics, infrastructure cost and blending facilities constraints. In 2011 blend fuel finally introduced to public, nevertheless it only involved several central regions in Klang Valley. According to a report from The Star, 2004, the Malaysian Biodiesel Association (MBA) is considering to introduce higher palm methyl ester blend in B7, B10 and B20 biodiesel programs with the experts’ consultation, revision of Malaysian Standard and engine warranty issue.

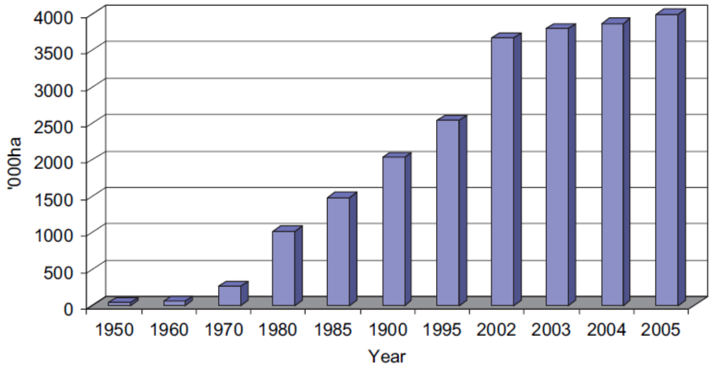

Figure 1.3: Oil Palm Expansion in Malaysia. (Sumathi *et al*., 2008)

One of the advantages of biodiesel is that the feedstock for production is wide. Palm oil, jathropha, waste oil and animal fat are the common feedstock for the production or researches on biodiesel in Malaysia. Palm oil as edible oil, the primary feedstock for biodiesel industry in Malaysia has triggered a debate on the food versus fuel; in fact it is able to compete with the other feedstock in terms of oil crop yield, land use efficiency and less labour work in harvesting. According to Figure 1.4, oil palm is the highest yielding oil crop in the world about 10 times higher yield than soybean and 5 times higher yield than rapeseed. Oil palm also has the most efficient land use compare to other crops which only occupies 4.74% of the total cultivated land compares to soybean 42.50% and rapeseed 12.25% (Umar *et al*., 2013). These two factors provide Malaysia a great opportunity to become biodiesel production and export country with palm oil as easily available feedstock.

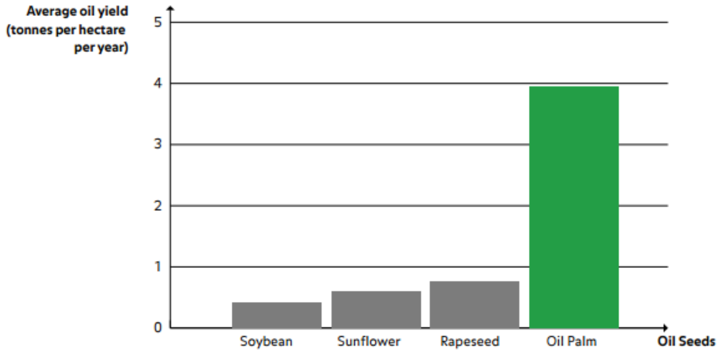

Figure 1.4: Oil Crop Efficiency of Major Oil Crops in the World. (Oil World, 2013)

Similar to other renewable energy, the initial capital cost to start up a biodiesel plant is expensive thus industrial players are usually cautious and insecure when moving into biodiesel field. In addition, the old prolonged fuel subsidies policy also created a market distortion which sent the message to public that “petrol is cheap” and hence biodiesel become unattractive and weak to compete. Fortunately, in 2014 the government ended this decade’s fuel subsidy whereby the price of gasoline and diesel will be based on managed float system (Bloomberg, 2014). It gives opportunity to promote biodiesel production among the stakeholders and raises the public awareness. On the contrary, subsidies and incentives can be useful to promote biodiesel production in catalyse technological development, deployment and adoption, hopefully will solve the current obstacles in commercializing biodiesel and environmental issues.

1.3 Biodiesel Production

Biodiesel production for usage in diesel engines started as early as 100 years ago. The key factors that affect the biodiesel production are the cloud point, pour point, free fatty acid (FFA) content, moisture content, calorific content and other impurities (Cheng, 2010). A brief explanation for these key factors is shown as below.

i. Cloud point/pour point: A measure of cold weather characteristics of the fuel. Cloud point is the temperature of the fuel at which small, solid crystals can be observed when the fuel cools. Pour point is the lowest temperature at which there is movement of the fuel when container is tipped. The temperature range between cloud point and cloud point is normally used to bracket the temperature where fuel start to fail (*Biodiesel Cloud Point and Cold Weather Issues*, 2012).

ii. FFA: A standard specification use by industry, it is defined as the amount of fatty acids which is not attached to triglyceride molecules in the oil. FFA reacts with alkalis to form soap and water which will inhibits the separation and purification of biodiesel. High FFA content reduces the biodiesel yield thus increase the production cost (Cheng, 2010).

iii. Moisture content and impurities: A standard specification use by industry, it is defined as the water amount and filterable solids. The content must be removed from the feedstock before production and during biodiesel purification (Cheng, 2010).

iv. Calorific content: It is defined as the energy content of the material. The higher the energy contents in feedstock the higher the energy content in biodiesel (Cheng, 2010).

Currently, there are four primary biodiesel production pathways which are direct usage of vegetable oil and blending, pyrolysis or thermal cracking, esterification and transesterification.

1.3.1 Direct Usage of Vegetable Oil and Blending

Before the scientists study on processing vegetable oil into biodiesel, they considered direct usage of oil as fuel. However many severe problems rose such as oil deterioration and incomplete combustion due to the oil properties which were high viscosity, low volatility and reactivity of unsaturated hydrocarbon chains. The polyunsaturated fatty acid tends to polymerize and high temperature and pressure oxidation during combustion will cause formation of gum. The incomplete combusted gum cause carbon deposition in the engine, reduce the engine durability and contaminate the lubricant oil. It was reported that microelmulsification of oil with solvents like methanol, ethanol and 1-butanol can reduce high viscosity problem in vegetable oil (Cheng, 2010).

1.3.2 Pyrolysis or Thermal Cracking

Pyrolysis is the mechanism involving thermal degradation of vegetable oils or fat without presence of oxygen while cracking is defined as breaking down of high molecular chain compound into lower molecular weight compound. In pyrolysis method, there are various reaction paths and intermediates resulting in different types of hydrocarbons such as charcoal, bio-oil and gaseous products (Zhenyi *et al.*, 2004). Normally, lower molecular weight products are formed by two simultaneous steps which are cracking and condensation while the high molecular weight products are formed by primary and secondary deoxygenation. Figure 1.5 shows that various reaction paths occur in thermal decomposition of triglycerides. This process however yields a highly unstable low grade fuel oil that can be acid corrosive, tarry and discoloured with foul odour. It also yields undesired GHG like carbon dioxide and carbon monoxide hence it does not widely implemented as biodiesel in transportation sector.

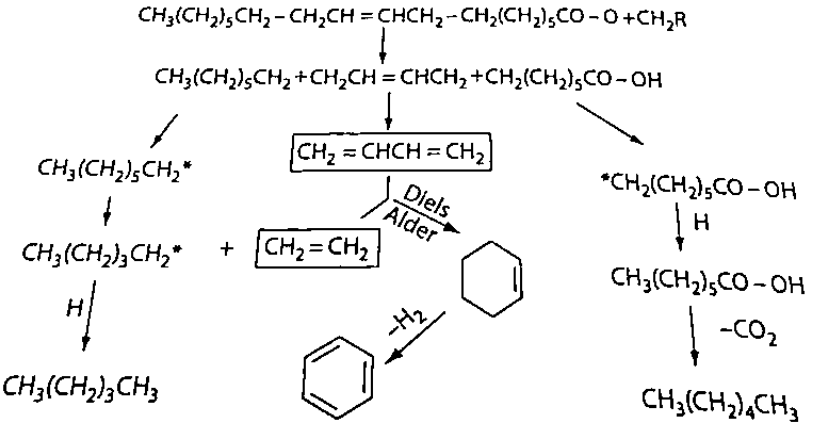

Figure 1.5: The Mechanism of Thermal Decomposition of Triglycerides. (Cheng, 2010)

1.3.3 Esterification

A high FFA content feedstock can cause several problems in single stage base catalysed transesterification (mentioned in section 1.3.4) which are:

i. More catalyst is required which result an increase in production cost.
ii. Soap formed inhibits the purification of biodiesel.
iii. Water formation reduces the performance of transesterification.
iv. Reducing the biodiesel yield (Cheng, 2010).

Therefore, feedstock with high content FFA normally will be treated before feed into transesterification unit. There are several methods of the treatment shown as following:

i. Mix the high-FFA feedstock with low FFA feedstock.

ii. Soap making by adding catalyst and water to convert FFA to soap and remove the soap.

iii. Glycerolysis by adding glycerol to high-FFA feedstock to form mono and diglyceride.

iv. Esterification by adding acid and alcohol to convert FFA into ester (Cheng, 2010).

Mixing the high-FFA and low-FFA feed into transesterification process appears to be the easiest method. However this method only works for limited high-FFA batch. Soap making method is also considered simple but this method will cause lower yield of biodiesel if soap and water are not removed properly. Next, glycerolysis is able to produce a low-FFA feed to transesterification however, the process requires high temperature (200˚C) and the reaction is relatively slow (Adami *et al.*, 2008)

Compare to first three methods, esterification is more widely used in industry as it can convert high FFA feedstock effectively. The process is normally catalysed by sulfuric acid H_2SO_4. Figure 1.6 shows that the process is initiated by protonation of acid to give an oxonium ion to fatty acid and it reacts with alcohol to give an intermediate and finally it loses a proton to give an ester.

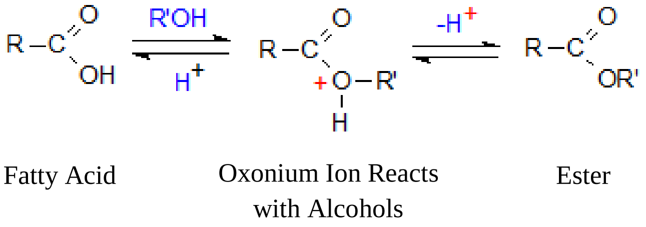

Figure 1.6: Acid Catalysed Esterification of Fatty Acid. (AOCS Lipid Library, 2014)

Each step of the process is reversible and therefore it requires excess of alcohol in so that it favours the forward reaction equilibrium. High alcohol to FFA ratio results in higher energy consumption to recover excess wet acidic methanol. Besides, this reaction also produces water as a by-product and the water will inhibit the esterification before it reaches completion which means the reaction mixture will still consist of unreacted FFA. If esterification is followed by transesterification, the water will also inhibit the transesterification process and reducing the yield. To solve these problems, allow esterification to proceed until the reaction is stopped by water, subsequently the alcohol and water is removed by either evaporation or phase separation and washing before the mixture undergo another esterification process to convert the remaining FFA.

1.3.4 Transesterification

Transesterification is defined as taking a triglyceride molecule or a complex fatty acid, neutralizing the FFA, removing the glycerol and creating an alkyl ester. When the original alkyl ester is reacted with an alcohol, the process is called alcoholysis (Cheng, 2010). Methanol and ethanol are the most common alcohol use in transesterification because methanol is relatively low cost compare to other alcohols while ethanol is more environmental friendly as it is derived from agricultural product. According to stoichiometry equation in Figure 1.7, one mole of triglyceride is reacted with 3 moles of alcohol to form the products. However, the reaction is reversible; excess of alcohol is required in the process in order to forward the reaction equilibrium and produce alkyl ester as much as possible. Transesterification usually can be catalysed by either acid, based or lipase and these catalysts can be either homogeneous or heterogeneous.

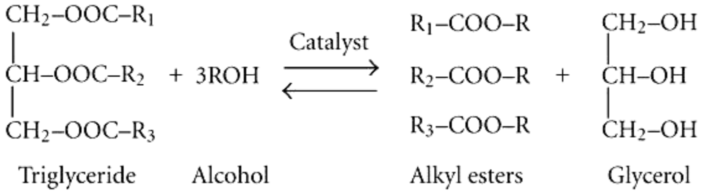

Figure 1.7: Overall Transesterification Chemical Equation.

1.3.4.1 Alkali Catalysed Transesterification

The common alkaline catalysts applied in the process are alkaline metal hydroxides (KOH and NaOH) or alkaline metal alkoxide (CH_3ONa). Base catalyst is more commonly used in industry as the reaction rate is fast (~30 minutes), operating at low temperature and less corrosive compare to acid catalyst. Alkaline metal alkoxide is reported to give a very high yield of biodiesel which is more than 98% in shorter reaction time even if they are applied in low molar concentration. Alkaline metal hydroxides are relatively cheaper but they are less reactive. Another drawback of using alkaline metal hydroxide is that they will react with alcohol and form water. Noted that the moisture content of the raw materials as well as in overall process should be as low as possible to prevent the water hydrolyse the ester and form FFA. When FFA reacts with alkaline, soap is formed and subsequently it inhibits the separation of alkyl ester from glycerol (Thanh *et al*., 2012).

1.3.4.2 Acid Catalysed Transesterification

The common acid catalysts use in the process includes sulfuric acid, hydrochloric acid and phosphoric acid. These catalysts are able to give a very high yield in alkyl ester. However, the rate of reaction is relatively slow (>3 hours) and it operates at higher temperature (>100 ̊ C) compare to alkali catalysed transesterification. Acid catalysed transesterification is more efficient to process the feedstock with high-FFA content. It also allows both esterification and transesterification processes to carry out simultaneously. Acid catalyst avoids soap formation because it is a one step process and it does not require extra steps to convert FFA, hence it is more economical according to Zhang *et al.* (2003). Similar to alkali catalysed transesterification the process theoretically have to carry out in water-free condition. This is because the formation of carboxylic acids by reaction of intermediates with water is competitive thus it reduces the yields of alkyl ester (Ulf *et al*., 1998).

1.3.4.3 Lipase Catalysed Transesterification

Lipase is enzyme that can be found in animals, plants and microorganisms. Compare to chemical catalysed transesterification mentioned in section 1.3.4.1 and 1.3.4.2 which is energy intensive, difficult in glycerol recovery, removal of chemical catalysts and FFA and water interference, lipase catalysed transesterification is able to operate under mild temperature (30 ° C – 50 ° C), easy product separation, high specificity, enzyme can be reused and enzymes or whole cells can be immobilized, therefore it is considered as a “green” reaction (Cheng, 2010). Lipase catalyse the reversible hydrolysis of glycerol ester bond hence this reaction also synthesis esters. This method also allows acceptable levels of water and able to esterify FFA. However, high cost in synthesising lipase catalysts and degradation of lipase activity become the major drawback of this reaction.

1.3.5 Homogeneous and Heterogeneous Catalysts

Generally, homogeneous catalysts such as sodium methylate and sulfuric acid are widely used in industry as they are easily available, little issues with supply and the price is economic. According to a report from Mosali & Bobbili (2011), since the catalyst is working out in same phase as the reactants, handling becomes much easier whereby handling all materials in liquid state is more convenient than handling one liquid and one solid. Besides, homogeneous base catalyst is also able to achieve high conversion rate within a short period and mild conditions. However, the issues such as sensitive to high-FFA feedstock, yield losses, higher cost of cleaning processes, glycerol quality problem always occur in homogeneous catalysed reaction. The following are the disadvantages of using homogeneous catalyst in biodiesel production (Mosali & Bobbili, 2011) & (Knothe, 2005):

i. Corrosive: The homogeneous acid and base catalyst are corrosive, this raises the corrosion issues in equipment parts and it should be handled carefully.

ii. Dilution of catalyst: As mention in section 1.3.3, acid esterification of FFA will produce water which will hinder the reaction. This is due to the dilution of acid catalyst by water. Therefore, in order to react FFA completely, water should be removed via drying hence consuming more energy and increases cost.
iii. Hygroscopic nature: The base catalyst such as sodium methylate tends to absorb moisture from the atmosphere, therefore the catalyst requires to store under nitrogen blanket.
iv. Reusability: Although reusing homogeneous catalyst theoretically is feasible, it is rarely applied due to high cost issue.
v. Separation of catalyst from reaction mixture: It is always difficult, high energy consumption and high cost to separate a liquid from another liquid.

Compare to homogeneous catalysts, heterogeneous catalyst greatly simplified the product separation process since solid catalyst can be easily removed by simple settling and filtration. This eliminates the washing step of product hence reduce the waste water generation and lower product contamination. Heterogeneous process also offers no neutralization step in glycerol thus no salt is formed. Higher purity of glycerol is more valuable in other downstream applications without additional treatment. Besides, solid catalysts are easy to be recycled and regenerated compare to liquid catalysts therefore, greatly reduce the cost of purchasing fresh catalysts. Heterogeneous catalyst is also able to reduce the corrosion problem even in the presence of strong acid species like H_2SO_4. However, heterogeneous process also has several drawbacks as following (Chouhan, 2011):

i. Slow reaction rate compare to homogeneous catalysed process.
ii. Possible undesirable side reactions occur.
iii. Poisoning of solid catalysts will occur when they are exposed to ambient air.
iv. Leaching of catalyst active site will result in contamination of product.

Table 1.2 summaries the pros and cons of common catalysts used in biodiesel industry.

Table 1.2: Summary of Catalyst Types Used in Tranesterification. (Leung *et al*., 2010)

Type	Example	Advantages	Disadvantages
Alkali Homogeneous	NaOH, KOH	• Economical operation • Favourable kinetics • High catalytic activity • Moderate operation conditions	• Anhydrous conditions sensitive • Low FFA requirement • Saponification, emulsion formation • Wastewater from purification
Alkali Heterogeneous	CaO, $CaTiO_3$, KOH/Al_2O_3, ETS-10 zeolite, alumina/silica supported K_2CO_3	• Catalyst can be reused • Ease of separation • Environmentally • Fewer wastewater disposal problems • High selectivity • longer catalyst lifetimes • Noncorrosive	• Anhydrous conditions sensitive • Diffusion limitations • High operation cost • High molar ratio of alcohol to oil requirement • High reaction temperature and pressure • Low FFA requirement, • Wastewater from purification

Continue

Type	Example	Advantages	Disadvantages
Acid Homogeneous	Concentrated H_2SO_4	• Avoid soap formation • Catalyse esterification and transesterification simultaneously	• Difficult to recycle • Equipment corrosion • Higher reaction temperature, long reaction time • Waste chemical from neutralization • Weak catalytic activity
Acid Heterogeneous	Carbohydrate-derived or carbon-based solid acid catalyst, Amberlyst-15, NafionNR50, sulfated zirconia,	• Catalyse esterification and transesterification simultaneously • Catalyst is recyclable • Eco-friendly	• Diffusion limitations • High cost • Low acid site concentrations • Low micro porosity
Lipase Catalysed	Candida Antarctica fraction B lipase, Rhizomucor mieher lipase	• Avoid soap formation • Ease of purification • Eco-friendly	• Denaturation • Expensive

1.4 Problem Statements

According to the review from section 1.3, apparently homogeneous alkali catalysed transesterification is currently the most popular process technology to produce biodiesel due to its high reaction rate and mild operating conditions. However, due to the process is FFA and moisture sensitive, the feedstock for this process are normally refined, bleached and deodorised (RBD) oil which leads to high cost in raw material. Biodiesel is produced to reduce the fossil fuel dependency, which means large amount of biodiesel is required in order to fulfil the current demand. Therefore, using high cost raw material is considered less economic as it gives lower profit margins and hence less competitiveness compare to fossil fuel. Cheaper feedstock must be used in order to overcome this primary problem in biodiesel industry. Yet, economic feedstock usually contains high FFA and moisture content which cannot be processed by the current common practice.

In order to achieve low cost biodiesel production, heterogeneous acid catalysts is proposed as it is able to promote both esterification and transesterification processes simultaneously in the presence of FFA. It also offers a lower cost purification of product and by-product, low waste generation and solid catalysts are not easily diluted by water during heterogeneous process. However, the current research on solid acid catalyst has not been widely explored due to the slower rate of reaction, possible side reactions, poisoning and leaching issues. Another concern in heterogeneous solid catalyst is the cost of synthesizing solid catalyst; therefore, the researchers are currently working on the utilization of biomass activated carbon to synthesis the solid catalyst aiming to reduce the overall production cost while concurrently also reduce the overall biomass waste disposal from agricultural sector.

1.5 Scope of Study

This project report will focus on the synthesis of solid acid catalyst from the oil palm biomass through sulfonation using 4-benzenediazonium sulfonate radicals (4-BDS) method. During preparation of catalyst, calcination temperature of catalysts and sulfanilic acid loading during sulfonation are varied in order to observe the characteristic changes in catalyst and their performance in biodiesel production. After preparation and treatment of solid catalyst, the characteristics of catalyst such as structure of catalyst, patterns of sulfonated carbon, density and distribution of sulfonic acid, porosity of solid catalyst will be studied. Subsequently, the efficiency of sulfonated solid acid catalysts will be tested in esterification of palm fatty acid distillate and optimum operating condition of the process will be determined.

1.6 Research Objectives

The following research objectives summarises the overall purpose of study on the synthesis of solid acid catalysts from oil palm biomass using 4-BDS sulfonation method.

i. To synthesis solid acid catalysts from palm biomass using 4-BDS sulfonation method.
ii. To analyse the relationship between biomass calcination temperature, acid to carbon ratio and the characteristic of the solid catalyst as prediction to the performance of the catalysts in esterification.
iii. To identify the optimum operating conditions of the catalytic reaction which gives the highest yield of biodiesel by using palm fatty acid distillate.

CHAPTER 2

LITERATURE REVIEW

2.1 Conventional Solid Acid Catalysts in Biodiesel Production

This chapter will focus on the recent technology development of acid heterogeneous catalyst. Commercial biodiesel production using homogeneous catalysts poses a few drawbacks such as difficulty of catalyst removal from product, corrosion of the equipment and moisture sensitive. Hence, heterogeneous catalysts have arisen as strong potential catalyst for biodiesel production as it is able to overcome the drawbacks of the former and catalyse both esterification and transesterification simultaneously. Most importantly, application of acid solid catalyst is preferable for most of the non-edible and low value oils which consist of high FFA content that cannot be catalysed by alkaline transesterification. Moreover, its application for low value oil also significantly reduces the cost of biodiesel production thus much attention has been paid by researchers. Table 2.1 shows some conventional solid acid catalysts that has been using in the industry.

Table 2.1: Conventional Solid Acid Catalyst in Biodiesel Production.

Catalyst	**Feedstock**	**Characterization**	**Calcination Temperature (˚ C); time (hr)**	**Esterification and Transesterification Operating Conditions**			**Conversion (%)**	**Ref.**
				Alcohol to Oil Molar Ratio	**Reaction Time (hr); Temperature (˚ C)**	**Catalyst Loading (wt%)**		
Zeolite, Ion Exchange Resin, Metal Oxides (Sulfated Zirconia)	Dodecanoic Acid	Sulfated zirconia catalyst: Surface are = 118 m^{2}g^{-1} Specific pore volume = 0.099 cm^{3}g^{-1} Average pore size = 3.0 nm	650.3	3:1	1; 140-180	3.0	96	Kiss *et al.* (2006)
Amberlyst 15, 16; Relite CFS	Soybean Waste Fatty Aicds (Oleins), 20% Acidity	N/A	N/A	8:1	0.5; 120	5 gram	95	Tesser *et al.* (2010)
Anion/Cat-ion Exchanged Resin	Triolein (63% purity)	N/A	N/A	10:1	4; 50	40	98.8	Kitakawa *et al.* (2007)

Catalyst	Feedstock	Characterization	Calcination Temperature (˚ C); time (hr)	Esterification and Transesterification Operating Conditions			Conversion (%)	Ref.
				Alcohol to Oil Molar Ratio	Reaction Time (hr); Temperature (˚ C)	Catalyst Loading (wt%)		
Cation Exchange Resin (NKC-9, 001×7, and D61)	Waste fried oil, 13.7 mg KOH/g	Surface Area = 77 m^2/g Average pore diameter = 56 nm	N/A	6:1	4; 64	20	90%	Feng *et al.* (2010)
SO_4/ZrO_2	Purified palm oil Palm fatty acid	Total acid sites (at 1.8% sulfur loading) = 495 µmol/g	500	25:1 6:1	10 minutes; 250 1 minute; 250	0.5	90 75	Petchmala *et al*. (2010)
SO_4^{2-}/SnO_2-SiO_2	Waste cooking oil	BET surface area = 13.9 m^2/g Average pore width = 13.7 nm Pore volume = 0.04 cm^3/g	300; 2	15:1	3; 150	3	Yield = 92.3%	Lam *et al.* (2009) .

Catalyst	Feedstock	Characterization	Calcination Temperature (° C); time (hr)	Esterification and Transesterification Operating Conditions			Conversion (%)	Ref.
				Alcohol to Oil Molar Ratio	**Reaction Time (hr); Temperature (° C)**	**Catalyst Loading (wt%)**		
Sulfated Zirconia and Other Mixed metal oxides	Dodecanoic Acid	ZrO_2/SO_4^{2-} Suface area = 118 m^2/g Pore volume = 0.098 cm^3/g Sulfur content = 2.3%	650; 4	3:1	1; 130-150	3.0	90%	Kiss *et al*. (2006)
H^+ ion exchanged ZSM-5 (HMFI)	Soybean oil added with oleic acid	Particle size = 0.2 - 2.0 µm	550; 6	N/A	1; 60	>0.06 mmol/g	80%	Chung & Park (2009)

According to Kiss *et al*. (2006) sulfated zirconia is the best conventional solid acid catalyst for esterification of dodecanoic acid. It was found that the catalyst has high stability of thermal decomposition which means the catalyst will not easily decompose under high temperature. Besides, Kiss also claimed that even in organic phase with a small amount of water, the catalyst did not easily get deactivated. The activity of the catalyst dropped to 90% and remained constant afterward.

Next, anion and cation exchange resins heterogeneous catalyst were used in batch and continuous transesterification of triolein by Kitakawa *et al* (2007). It was found that anion exchange resin was a better solid catalyst compare to cation exchange. This was because of the high adsorption affinity of alcohol in anion exchange. It also had less crosslinking and smaller particles size which contributed to enhancement of the rate of reaction hence result in high reaction and conversion rate. Under optimised conditions, conversion as high as 98.8% can be achieved. However, the catalytic activity decreased in the subsequent reaction most probably was caused by leaking of hydroxyl ions from resin.

Feng *et al*. (2010) also found that cation exchange resins were effective in esterification of high acid value oil. The catalyst had high water adsorbing ability which promoted the effectiveness of esterification. High average pore diameter of the catalyst (56 nm) also enabled the reactants to transport into the active sites of the resin giving conversion more than 90%. Besides, the research also showed that after repeated reaction cycles the catalytic activity did not decrease. This was because of mechanical agitation during the reaction could breakdown the resin particles which gave more resin surface area to be contacted by reactants. The loss of catalytic activity was observed after 10 cycles of reaction.

Research from Petchmala *et al*. (2010) using SO_4/ZrO_2 as solid catalyst in transesterification of pure palm oil and palm fatty acid showed conversion of 90% and 75% respectively. However, leaching of sulfate is the main drawback which will cause the biodiesel to off spec.

Another research from Lam *et al*. (2009) showed that the calcination temperature is related to catalytic activity. At low calcination temperature (200 ° C), the catalyst SO_4^{2-}/SnO_2-SiO_2 remained in amorphous form whereas at high calcination temperature (500 ° C), the structure of the catalyst collapsed due to removal of sulfate group.

A research from Chung and Park (2009) used zeolite catalyst and achieved 80% conversion of oleic acid. It was reported that catalytic activity increased with increase of acidity of feedstock.

Based on Table 2.1, it shows that conventional solid acid catalyst is able to give high catalytic activities. However, most of them have low acid densities, suffering from leaching, high mass transfer resistant due to small pore size and thermal instability. Current conventional solid catalysts also suffer from unfavourable side reaction, high cost of catalyst synthesis and presence of certain metals in catalyst raised the toxicity issues.

2.2 Carbon Based Solid Catalyst

In current development of catalyst technology, carbon based catalysts become attractive as they are chemically inert and have a good mechanical and thermal stability. Activated Carbon (AC) is the most well-known form of carbon catalyst. Generally, AC is produced from materials with high carbon content such as coconut shells, wood and coal. The materials are processed to high porosity hence AC has a very large surface area available for adsorption and reaction of chemicals. Moreover, it is also stable in both acidic and basic conditions make it suitable to be the catalyst for biodiesel production.

Generally, AC is obtained from carbon based materials by thermal decomposition in a furnace using a controlled atmosphere and undergoes physical or chemical activation. A typical process to obtain AC involves the following steps (Konwar *et al.*, 2014).

i. Dehydration. Removal of all water and moisture in carbon base materials.

ii. Carbonisation. Removing the non-carbon portion of the materials by conversion of the organic matter to elemental carbon.

iii. Activation. Tars are burned off and pores are enlarged.

2.2.1 Methods of Synthesising Porous Carbon

There are a few methods of synthesising porous carbon from biomass namely, hydrothermal carbonisation (HTC), template direct synthesis and direct synthesis method. There are two types of hydrothermal carbonisation method which are high temperature HTC and low temperature HTC. High temperature HTC involves high temperature and pressures during the carbonisation step which synthesise carbon nanotubes, graphite and AC. High temperature HTC is able to produce high surface area and porosity structure from different carbonaceous materials. The carbonisation process is performed under either supercritical water or superheated steam. It was reported that HTC under supercritical water had a higher gasification rate therefore increased the penetration power into the pore structure compared to steam activation (Sudipta *et al.*, 2015). For low temperature HTC, it was operated up to 250˚C and involved number of chemical transformations. Low temperature HTC has a low toxicology impact of materials, more energy economy and consider as 'greener' process compare to high temperature HTC. However, it is rather complex in thermochemical process involving the formation of different soluble products, such as organic acids, aldehydes, furfural-like compounds and phenol from dehydration and fragmentation of carbon materials.

Next, template direct synthesis is the synthesis of well-ordered porous carbon materials with narrow pore size distribution. According to Sudipta *et al*. (2015), this method used a template directs the formation of pores during carbonisation hence improved the structural order level and desired physical and chemical properties. Generally, template synthesis involves the following steps which are (1) Preparation of inorganic templates with controlled porosity. (2) Introduction of carbon materials into the template pores and cross linking with templates. (3) Carbonisation of the carbon materials. (4) Removal of inorganic templates. Mesoporous silica, zeolites, clay and metal organic frameworks are the examples of template apply in this method.

Direct synthesis method is simple and environmental friendly compare to previous two methods. It is able to produce highly expanded mesoporous surface from low surface area starting materials under controlled atmosphere and temperature. This method avoids the usage of templates and hydrophilic or hydrophobic nature of the catalyst can be controlled by the degree of carbonisation. Table 2.2 shows the carbonisation procedures from different literatures.

Table 2.2: Carbonisation Procedures from Different Literatures.

Carbon Source	**Carbonisation Procedure**	**Sulfonation Method**	**Ref.**
Corn Straw	2 g of corn straw was heated under N2 flow for 1 h at different temperature (523 K – 723 K)	Direct sulfonation	Liu *et al.* (2013)
D-glucose	D-glucose powder was heated under N2 flow at 400 ℃ for 12 h to produce a black solid of incomplete carbonized glucose	Direct sulfonation	Lokman *et al.* (2015)
Oil cake waste from oil seeds of *Mesua ferrea* L.	Powered oil-cake waste was impregnated in orthophoshoric acid and then carbonised at 500℃ for 1 h. Carbonised material was washed with distilled water, HCl and finally with hot distilled water until pH 6 - 7. Then, activated carbon was derived after drying at 110 ℃	Sulfonation by 4-BDS	Konwar *et al.* (2014)
Deoiled seed waste cake	DOWC was pre-soaked with 50% (v/v) phosphoric acid and were subjected to activation at 500℃. The carbonized materials were powered and sieved through an ASTM no. 60 sieve.	Sulfonation by 4-BDS	Shuit & Tan, 2014

2.2.2 Effect of Carbonisation Temperature and Time

According to the research from Liu *et al*. (2013) corn straw was carbonised for 1 hour at different temperatures (523 K - 773 K). The result showed that carbon catalyst prepared at carbonisation temperature 573 K exhibited the highest catalytic activity in esterification of oleic acid with methanol which was 92%. At temperature higher than 573 K, the activity reduced most probably due to thermal decomposition of carbon structure which reduced the sulfonic group attachment on it. Dawodu *et al*., (2013), also reported that when the carbon precursor was carbonised at higher temperature (≥425℃), hard carbon materials were formed which might be difficult for SO_3H groups to attach during sulfonation.

On the other hand, carbonisation duration is also another key factor that affects density of SO_3H attaching on the carbon structure. An experimental work that carbonised the defatted seed of C. *inophyllum* showed that when carbonisation time increased, graphitic structures was formed and resulted in rigid and hard structure of carbon (Dawodu *et al*., 2013). Incomplete carbonisation is preferable as the carbon materials will gradually dehydrate and produce an amorphous polycyclic aromatic and aliphatic carbon structure which allows ease of SO_3H attachment during sulfonation. Therefore, carbonisation duration should not be too long. Figure 2.1 and 2.2 show the relationship between acid density, ester yield, carbonisation time and carbonisation temperature.

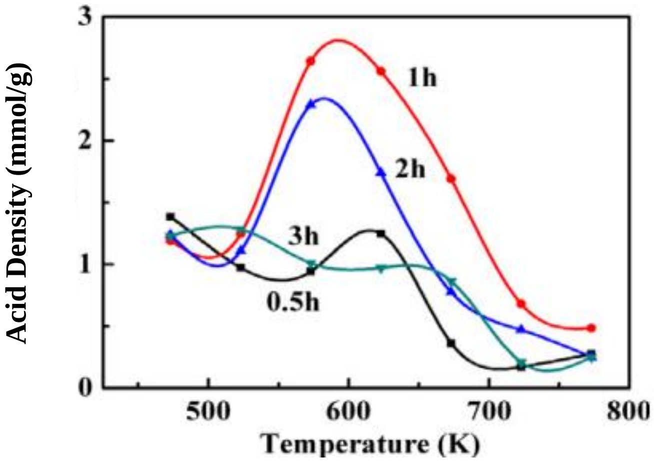

Figure 2.1: Relationship of Acid Density, Carbonisation Time and Carbonisation Temperature. (Liu *et al*., 2013)

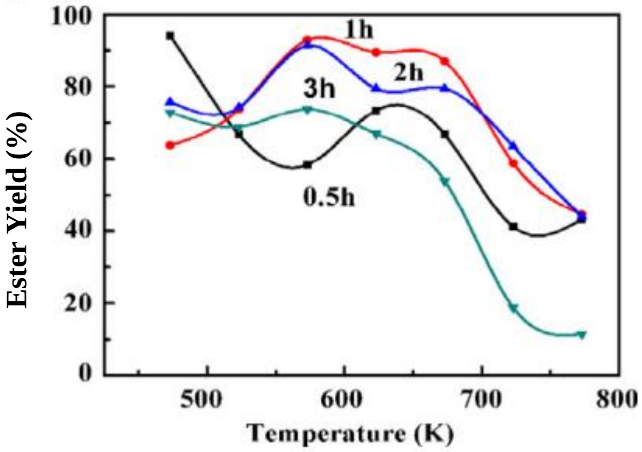

Figure 2.2: Relationship of Ester Yield, Carbonisation Time and Carbonisation Temperature. (Liu *et al*., 2013)

2.3 Sulfonation of Activated Carbon

Activated carbon obtained from biomass can be acid functionalised whereby the active part of the catalysts is attached with acid or acidic functional group. A number of literatures reported the usage of sulfonated activated carbon as an effective catalyst for biodiesel production by esterification as shown in Table 2.3.

Table 2.3: Different Sulfonation Method of Carbon Catalyst.

Sulfonation Method	Carbon Source	Characterization	Esterification			Ref.
			Operating Conditions	**Conversion (C)/ Yield (Y)**	**Catalyst Activity Loss**	
Direct Sulfonation	D-glucose	Acid density for 15 h sulfonation = 4.23 mmol/g; S content before sulfonation = 0%; S content for 15 h sulfonation 4.89%; BET surface area for 15 h sulfonation = 10.67 m^2/g	Feedstock = Palm Fatty Acid Distillate; Methanol/Oil Loading = 10:1; Reaction Time = 2 h; Catalyst Loading = 2.5 wt%	C = 95.4%; Y= 92.3%	Conversion of FFA = 81.5% and Yield = 73.4% FAME after 6 cycles of reaction	Lokman *et al.* (2015)
Direct Sulfonation	Defatted seed of C. *inophyllum*	BET before sulfonation = 1.8 m^2/g; BET after sulfonation = 3.4 m^2/g; S content before sulfonation = 0 wt%; S content = 3.6 wt%; Total acid density before sulfonation = 1.2 mmol/g; Total acid density after sulfonation = 2.8 mmol/g; SO$_3$H density before sulfonation = 0 mmol/g; SO$_3$H density after sulfonation = 1.1 mmol/g	Feedstock = C. inophyllum oil (18.9 wt% FFA); Methanol/Oil Loading = 5.5 g methanol, 5 g oil; Reaction Temperature = 150 ℃; Reaction Time = 5 h Catalyst Loading = 0.3 g	C = 84.2 wt%; Y = 36.4 wt%	Decrease in conversion after every recycling experiment	Dawodu *et al.* (2013)
Direct sulfonation	Multi-walled carbon nanotubes (MWCNT)	Acid density after sulfonation = 0.016 mmol/g	eedstock = Palm Fatty Acid Distillate; Methanol/Oil Loading = 20:1; Reaction Time = 3 h; Reaction Temperature = 170 ℃; Catalyst Loading = 2 wt%	Y = 78.1%	Yield = 69% after 5 cycles	Shuit & Tan (2014)
Direct sulfonation	*M. ferrea L.* deoiled seed waste cake	Pore volume of after sulfonation = 0.61 cm^3/g; BET of after sulfonation = 690 m^2/g; H2SO4 density after sulfonation = 0.3 mmol/g	Feedstock = Oleic Acid; Methanol/Oil Loading = 20:1; Reaction Time = 10 h; Reaction Temperature = 64 ℃; Catalyst Loading = 3 wt%	C = 42%	Conversion = 12% after 3 cycles reaction	Konwar *et al*. (2015)

Continue

Sulfonation Method	Carbon Source	Characterization	Esterification			Ref.
			Operating Conditions	Conversion (C)/ Yield (Y)	Catalyst Activity Loss	
Sulfonation by arylation of 4-BDS	Carbon coated alumina	BET after sulfonation = 570 m^2/g; Pore diameter after sulfonation = 2.52 nm; Pore volume = 0.36 cm^3/g; Strong acid density after sulfonation = 1.72 mmol/g; Total acid density after sulfonation = 2.33 mmol/g	Feedstock = Oleic Acid; Methanol/Oil Loading = 8 mL methanol, 1 g oil; Reaction Temperature = 65 ℃ ; Catalyst loading = 50 mg	Turnover frequency in = 78 h^{-1}, 5 times that Amberlyst-15 (15 h^{-1}); Highest	N/A	Geng *et al*. (2011)
		BET area after sulfonation = 39 m^2/g; Pore volume after sulfonaion = 0.04 cm^3/g; Stong acid density after sulfonation = 1.42 mmol/g; Total acid density = 2.62 mmol/g;		Turnover frequency = 109 h^{-1}, 7 times higher than Amberlyst-15	N/A	Geng *et al*. (2011)
Sulfonation by arylation of 4-BDS	Oil cake waste from oil seeds of *Mesue ferrea L*.	Total acid density of unsulfonated AC = 2.032 mmol/g; Total acid density of sulfonated AC = 2.426 mmol/g; SO_3H density of unsulfonated AC = 0 mmol/g; SO_3H density of sulfonated AC = 0.735 mmol/g; BET of unsulfonated AC = 777 m^2/g; BET of sulfonated AC = 556 m^2/g; Pore volume of unsulfonated AC = 0.28 cm^3/g; Pore volume of sulfonated AC = 0.20 cm^3/g	Feedstock = Crude Jatropha oil (8.17 wt% FFA); Methanol/Oil Loading: 43:1; Reaction Time = 6 h; Reaction Temperature = 80 ℃; Catalyst Loading = 5 wt%	C = 99%	9% activity loss at fifth cycle	Konwar *et al*. (2014)

Continue

Sulfonation Method	Carbon Source	Characterization	Esterification			Ref.
			Operating Conditions	Conversion (C)/ Yield (Y)	Catalyst Activity Loss	
Sulfonation by arylation of 4-BDS	Oil cake waste from oil seeds of *Mesue ferrea L.*	Total acid density of unsulfonated AC = 2.032 mmol/g; Total acid density of sulfonated AC = 2.215 mmol/g; SO3H density of unsulfonated AC = 0 mmol/g; SO3H density of sulfonated AC = 0.384 mmol/g; BET of unsulfonated AC = 777 m^2/g; BET of sulfonated AC = 696 m^2/g; Pore volume of unsulfonated AC = 0.28 cm^3/g; Pore volume of sulfonated AC = 0.24 cm^3/g	Feedstock = Crude Jatropha oil (8.17 wt% FFA); Methanol/Oil Loading: 43:1; Reaction Time = 6 h; Reaction Temperature = 80 ℃; Catalyst Loading = 5 wt%	C = 97%	N/A	Konwar *et al*. (2014)
Sulfonation by arylation of 4-BDS	Activated Carbon	BET before sulfonation = 751 m^2/g; BET after sulfonation= 602 m^2/g; Pore volume before sulfonation = 0.47 cm^3/g; Pore volume after sulfonation 0.38 cm^3/g; Pore diameter before sulfonation = 2.5 nm; Pore diameter after sulfonation = 2.4 nm; Total acid density before sulfonation = 0.3 mmol/g; Total acid density after sulfonation = 1.01 mmol/g; SO3H density before sulfonation = 0 mmol/g; SO3H density after sulfonation = 0.64 mmol/g	Feedstock = Acetic acid, hexanoic acid, decanoic acid; Methanol/Oil Loading = 10:1; Reaction Time = 10 h; Reaction Temperature = 70 ℃; Catalyst Loading = 0.2 g	C of acetic acid = 78 %; C of hexanoic acid =70%; C of decanoic acid = 52%	SO3H density of the catalyst dropped to 0.42 mmol/g after four cycles of reactions	Liu *et al*. (2010)

Continue

Sulfonation Method	Carbon Source	Characterization	Esterification			Ref.
			Operating Conditions	**Conversion (C)/ Yield (Y)**	**Catalyst Activity Loss**	
Sulfonation by arylation of 4-BDS	*J. curcas* deoiled seed waste cake	Pore volume after sulfonation = 0.23 cm^3/g; BET of after sulfonation = 96 m^2/g; SO3H density after sulfonation = 0.7 mmol/g	Feedstock = Oleic Acid; Methanol/Oil Loading = 20:1; Reaction Time = 10 h; Reaction Temperature = 64 ℃; Catalyst Loading = 3 wt%	C = 68%	Conversion = 50% after 3 cycles reaction	Konwar *et al*. (2015)
Sulfonation by arylation of 4-BDS	*P. pinnata* deoiled seed waste cake	Pore volume after sulfonation = 0.46 cm^3/g; BET after sulfonation = 483 m^2/g; SO3H density after sulfoantion = 0.84 mmol/g		C = 96%	Conversion = 60% after 3 cycles reaction	Konwar *et al*. (2015)
Sulfonation by arylation of 4-BDS	*M. ferrea L.* deoiled seed waste cake	Pore volume after sulfonation = 0.41 cm^3/g; BET after sulfonation = 468 m^2/g; SO3H density after sulfonation = 0.75 mmol/g		C = 95%	Conversion = 62% after 3 cycles reaction	Konwar *et al*. (2015)
Sulfuric acid fuming (50 wt% SO3)	Corn straw	XPS analysis = S 2p peak at 168eV; S content before sulfonation = 0.34%; S content after sulfonation = 7.81%; Acid density = 2.64 mmol/g NaOH	Feedstock = Oleic Acid; Methanol/Oil Loading = 7:1; Reaction Time = 4 h; Reaction Temperature = 333 K; Catalyst Loading = 7 wt%	Y = 98%	N/A	Liu *et al*. (2013)
Sulfonation by p-toluenesulfonic acid	Defatted seed of *C. inophyllum*	BET before sulfonation = 1.8 m^2/g; BET after sulfonation = 2.4 m^2/g; S content before sulfonation = 0 wt%; S content before sulfonation = 0 wt%; S content after sulfonation = 2.4 wt%; Total acid density before sulfonation = 1.2 mmol/g; Total acid density after sulfonation = 0.6 mmol/g; SO3H density before sulfonation = 0 mmol/g; SO3H density after sulfonation = 0.7 mmol/g	Feedstock = C. inophyllum oil (18.9 wt% FFA); Methanol/Oil Loading = 5.5 g methanol, 5 g oil; Reaction Temperature = 150 ℃; Catalyst Loading = 0.3 g	C = 76.7 wt%; Y = 14.2 wt%	Decrease in conversion after every recycling experiment	Dawodu *et al.* (2013)

Continue

Sulfonation Method	Carbon Source	Characterization	Esterification			Ref.
			Operating Conditions	**Conversion (C)/ Yield (Y)**	**Catalyst Activity Loss**	
Sulfonation by in situ polymerisation of poly(sodium4-styrenesulfonate) (PSS)	Multi-walled carbon nanotubes (MWCNT)	Acid density after sulfonation = 0.061 mmol/g	Feedstock = Palm Fatty Acid Distillate; Methanol/Oil Loading = 20:1; Reaction Time = 3 h; Reaction Temperature = 170 ℃; Catalyst Loading = 2 wt%	Y = 93.4%	Yield = 77% after 5 cycles of reaction	Shuit & Tan (2014)
Sulfonation by in situ polymerisation of acetic anhydride and sulfuric acid		Acid density after sulfonation = 0.03 mmol/g		Y = 85.8%	Yield = 71% after 5 cycles of reaction	Shuit & Tan (2014)
Sulfonation by thermal decomposition of ammonium sulfate		Acid density after sulfonation = 0.029 mmol/g		Y = 88%	Yield = 77% after 5 cycles of reaction	Shuit & Tan (2014)
Hydrothermal sulfonation	*M. ferrea L.* deoiled seed waste cake	Pore volume after sulfonation = 0.03 cm^3/g; BET after sulfonation = <1 m^2/g; H_2SO_4 density after sulfonation = 1.3 mmol/g	Feedstock = Oleic Acid; Methanol/Oil Loading = 20:1; Reaction Time = 10 h; Reaction Temperature = 64 ℃; Catalyst Loading = 3 wt%	C = 65%	Conversion = 38% after 3 cycles reaction	Konwar *et al.* (2015)

A research from Lokman *et al*. (2015) which synthesised catalyst by direct sulfonation (Table 2.3 entry 1) showed that the size of the catalyst particles decreased due to the acid treatment during sulfonation process. The XRD result indicates that the catalysts consist of amorphous carbon in random orientation of aromatic carbon sheet. This structure can be important in catalysts' activity during esterification process as SO_3H groups are easier to attach on the amorphous carbon structure compare to rigid, ordered carbon framework. Thermal stability of the catalysts also had been tested by TGA. Both of the unsulfonated catalyst and sulfonated catalyst had weight loss at around 100℃ due to physical absorption of water on the catalysts. From 500 to 700℃, a steady loss was observed in unsulfonated catalyst most probably due to the decomposition of the carbon structure. For sulfonated catalyst, weight loss was observed at around 201℃ from 100 to 300℃ which was contributed by the decomposition of sulfonic group. Further decomposition of the carbon structure was observed at 586℃. Therefore, the catalyst was stable up to 300℃. before the sulfonic group started to decompose.

Lokman *et al*. (2015) also found that longer sulfonation time would increase total acid site density, BET surface area and Sulfur (S) content of the catalyst. Hence, this would directly improve the catalytic activity of the catalyst. Besides, it was important to feed methanol in excess during esterification to drive the reaction equilibrium forward. The result of the research proved that the conversion of FFA will increase when the methanol to oil ratio increased. However, when the ratio exceeded 10:1, there was no significant increment of conversion. This was most probably due to large amount of water produced and reacted with fatty acid methyl ester (FAME) redirecting the backward reaction. Besides, catalyst loading amount also is one of the key factors that determined the conversion of the fatty acid. The result showed that as the catalyst loading increased from 0.5 to 2.5 wt%, the FFA conversion increased. However, further addition of catalyst did not show any significant increment in conversion. This can be explained by the mass transfer rate among the catalyst, methanol and feedstock had reached optimum condition.

Another research from Dawodu *et al*. (2013) (Table 2.3 entry 2) which was also direct synthesised acid catalyst showed that the carbon catalyst obtaining from defatted seed of *C. inophyllum* had a loose irregular network and amorphous structure which was similar to the result from Lokman. This structure enabled the ease of sulfonic group introduction on to the aliphatic carbon structure. After sulfonation, it was reported the pores of catalyst became larger and less spongy. The amorphous structure remained the same after sulfonation. Besides, the catalysts consisted of significant amount of SO_3H, COOH and OH groups however only SO_3H density directly affected the difference in catalytic activity. The pore network structure and swelling ability also determine how much SO_3H group will attach on the surface. Next, the thermal stability of the catalyst also observed a significant reduction in weight until 300℃ which was same as reported by Lokman.

In esterification activity of the catalyst, Dawodu *et al*. (2013) found that when catalyst loading increased, higher conversion of FFA can be obtained. This can be explained by larger number of active sites available to the reactants. Besides, it also reported that when reaction temperature of esterification increased, the conversion of FFA increased. However, it showed a slight decrease in the conversion of FFA when temperature exceeded 75℃ at atmospheric pressure which was beyond the boiling temperature of methanol. This was because the methanol vaporised hence the solvent was not available for the reaction. For catalyst stability experiment, due to the soft structure of catalyst as mentioned previously, sulfonic groups are tended to leach from the solid at high temperature or presence of fatty acid thus the experiment result showed that the catalytic activity gradually decrease after repeating cycles of reaction.

Another report from Konwar *et al*. (2015) using carbon precursors of J. *curcas*, P. *pinnata* and M. *ferra* L. with direct sulfonation, sulfonation by using 4-BDS and hydrothermal sulfonation were shown in (Table 2.3 entry 4, 9, 10, 11, 17). It was reported that the SO_3H density was the highest for hydrothermal sulfonating method followed by sulfonation by 4-BDS and direct sulfonation. The high SO_3H density in hydrothermal was due to ease of sulfonation of the partially carbonised structures under hydrothermal condition whereby the SO_3H groups was easy to attach on the non-graphitic carbon structure. In sulfonation by 4-BDS, it was found that increase in C content of the AC would increase SO_3H density. This was most probably due to the functionalization of 4-BDS radicals resulting from availability of more aromatic carbon sheet. In the case of direct sulfonation, the low SO_3H density was resulted from the difficulty in H_2SO_4 to react with the rigid, aromatized and ordered frameworks of AC even at higher temperature. Konwar *et al.* concluded that sulfonation by 4-BDS was a more effective sulfonating method for carbon materials with aromatised or graphitic structure while direct sulfonation was more efficient for sulfonating non-graphitic structure.

Next, Konwar *et al.* (2015) also found that the acid conversion in esterification was closely related to porosity of the catalyst. The highest acid conversion was obtained with the most porous catalyst with relatively high SO_3H density prepared from 4-BDS method. Although catalyst obtained by hydrothermal method had highest SO_3H density, it had a lower conversion in esterification and this was most probably due to its non-porous structure limiting the large molecule of oleic acid to access into the active sides. An even lower conversion was observed in the catalyst prepared from direct sulfonation due to its very low SO_3H density. Besides, catalyst obtained from sulfonation by 4-BDS also outperformed in terms of catalytic stability where by the other two methods were accounted with the ease of SO_3H leaching compared to the former.

Another report from Liu *et al.* (2010) (Table 2.3 entry 8) which also applied 4-BDS sulfonation method showed that there was no much difference in the XRD patterns between the sulfonated and unsulfonated carbon which indicated that the arylation reduction by 4-BDS does not affect the microstructure of the carbon materials. However, it was observed that there was a reduction of pore volume after sulfonation, claiming part of the pore space has been filled by sulfonic group. It was also reported that the increase in S content was closely related to the total acid density in sulfonation. The chemical state of sulfur was verified by XPS analysis and the result (Figure 2.3) showed a strong S 2p peak appears at about 168 eV which indicated the presence of SO_3H group.

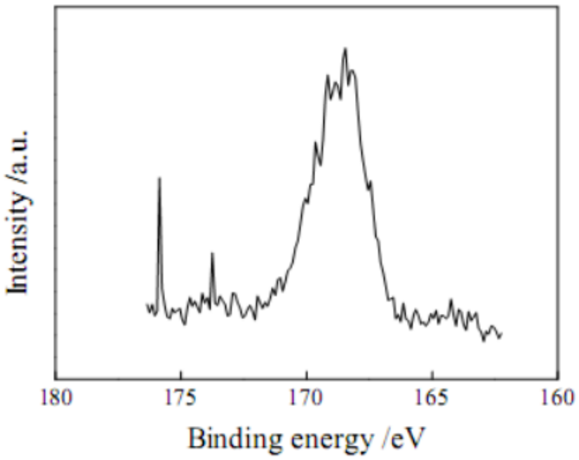

Figure 2.3: S 2p XPS Spectrum of Sulfonated Catalyst. (Liu et al., 2010)

On the other hand the thermal stability test by TGA showed that the catalyst had an insignificant weight loss below 150℃ most probably was due to the small quantity loss of water. At higher temperature, more significant weight loss was detected mainly due to the gradual desorption and thermal decomposition of $PhSO_3H$ groups.

Liu *et al.* (2010) also used the sulfonated catalyst in the esterification of three different carbon chain length of aliphatic acids (acetic acid, hexanoic acid and decanoic acid. The result showed that catalytic activity of the sulfonated AC was comparable with Amberlyst-15 in esterification of acetic and hexanoic acid and it had an even higher conversion in the esterification of decanoic acid. The result suggested that the esterification of long chain acid molecules was not solely dependent on the acid density but also the BET and pore diameters. Since the sulfonated catalyst had a large surface were and high density of mesoporous which is shown in (Table 2.3 entry 8), it was easier for larger aliphatic acid molecules to adsorb on the catalyst surface and approach to the active sites. Therefore, it was concluded that catalyst prepared from 4-BDS method had a higher potential applications in acid catalysed reaction of large organic molecules. Similar to previous reports, the leaching of SO_3H was also observed after four reaction cycles.

Fuming sulfuric acid was used in the sulfonation of corn straw derived carbon based on a report from Liu *et al.* (2013) (Table 2.3 entry 12). It was reported that the sulfonic group started to detach from the carbon structures at 523K based on the thermal stability test. The result also showed that the total acid density was around 2.64 mmol/g by NaOH titration. The result indicated the high acid density was closely related with the weak acid group mainly phenolic and carboxylic groups thus giving polarity to the carbon microspheres. However, only SO_3H which was a strong acid group served as the active sites in esterification process.

Another sulfonating method of catalyst by p-toluenesulfonic acid also performed by Dawodu *et al*. (2013) (Table 2.3 entry 13). The NH_3-TPD analysis showed a strong desorption peak at 470 to 510℃ which indicated the strong interaction of sulfonic groups with the graphite layer of the materials. In esterification of FFA, catalyst prepared by fuming sulfuric acid exhibited a lower activity compared to catalyst prepared by direct sulfonation (Table 2.3 entry 2) due to lower SO_3H acid densities (Dawodu *et al*., 2013).

A report from Shuit & Tan (2014) compared the sulfonation methods between *in situ* polymerisation of poly(sodium-4-styrene sulfonate), *in situ* polymerisation of acetic anhydride and sulfonic acid, thermal decomposition of ammonium sulfate and direct sulfonation (Table 2.3, entry 3, 14, 15, 16). The result showed that catalysts prepared by in situ polymerisation of 4-styrenesulfonate produced the highest yield of methyl ester (93.4%) followed by thermal decomposition of ammonium sulfate (88%), in situ polymerisation of acetic anhydride and sulfuric acid (85.8%). The lowest yield of methyl ester (78.1%) was obtained by using catalyst produced from direct sulfonation. This can be explained with the SO_3H density in the catalyst whereby the catalyst sulfonated by *in situ* polymerisation of poly(sodium-4-stryrenesulfonate) the highest acid site density of 0.061 mmol/g followed by 0.03 mmol/g through *in situ* polymerisation of acetic anhydride and sulfuric acid, 0.029 mmol/g by thermal decomposition of ammonium sulfate and lastly 0.016 mmol/g in direct sulfonation. In thermal stability test of the catalysts, desorption peaks at 200℃ were observed in all catalysts sulfonated by different methods, which indicated the ability of different sulfonation methods to graft strong acid densities on the carbon structures. TPD results also showed that the sulfonated catalysts were stable at the reaction temperature of 170℃ because of the high stability of active sites on the catalyst. Thus, the SO_3H leaching problem can be reduced when reaction temperature was below 170℃.

Another reason for high reaction activity by catalyst produced from polymerisation of poly(sodium4-styrenesulfonate) is that poly(sodium4-styrenesulfonate) can produce sulfonated catalyst with benzenesulfonic acid group which can contribute more active sites for esterification. However, this sulfonation method required longer synthesis duration (4 days) and involved more chemicals and processing steps. Besides, Shuit & Tan (2014) also claimed that in situ polymerisation of acetic anhydride and sulfuric acid and direct sulfonation were not eco-friendly as large amount of wastewater was generated from repeated washing process. In catalyst reusability test, it was also reported that all of the catalysts prepared from different sulfonation methods able to maintain the methyl ester yield above 70% after five cycles. Based on the literature reviews, factors that affect the conversion and yield of the esterification process is summarised in Table 2.4.

Table 2.4: Factors Affect the Conversion of FFA in Esterification.

Factors	Descriptions	Ref.
SO_3H Density	Conversion of FFA increases as SO_3H density increases. Weak acid group such as phenolic and carboxylic groups does not have significant effect in conversion of FFA.	Konwar, *et al.* (2015)
Porosity of Catalyst	Conversion of FFA increases as porosity of catalyst increases.	Konwar, *et al.* (2015)
Reaction Time	Conversion of FFA increases as reaction time increases.	Lokman *et al.* (2015)
Methanol/Oil Ratio	Conversion of FFA increases as methanol/oil ratio increases. However, when the ratio more than certain limit, conversion of FFA decreases due to large amount of water is produced redirecting the reaction backward.	Lokman *et al.* (2015)

Factors	**Descriptions**	**Ref.**
Catalyst Loading	Conversion of FFA increases as catalyst loading increases. However, when the catalyst loading increases to a certain limit, there is no significant increase in conversion due to optimum condition of mass transfer rate and contact rate among the catalyst, and reactants.	Lokman *et al.* (2015) Dawodu *et al.* (2013)
Reaction Temperature	Conversion of FFA increases as reaction temperature increases. However, when temperature increases to a certain limit, conversion decreases due to vaporisation of methanol which the methanol solvent is not available for reaction. Extreme high temperature also decomposes the carbon structure of catalyst.	Lokman *et al.* (2015) Dawodu *et al.* (2013)

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The overall research plan is shown in Figure 3.1 which summarises the methodology that will be conducted and studied throughout the research.

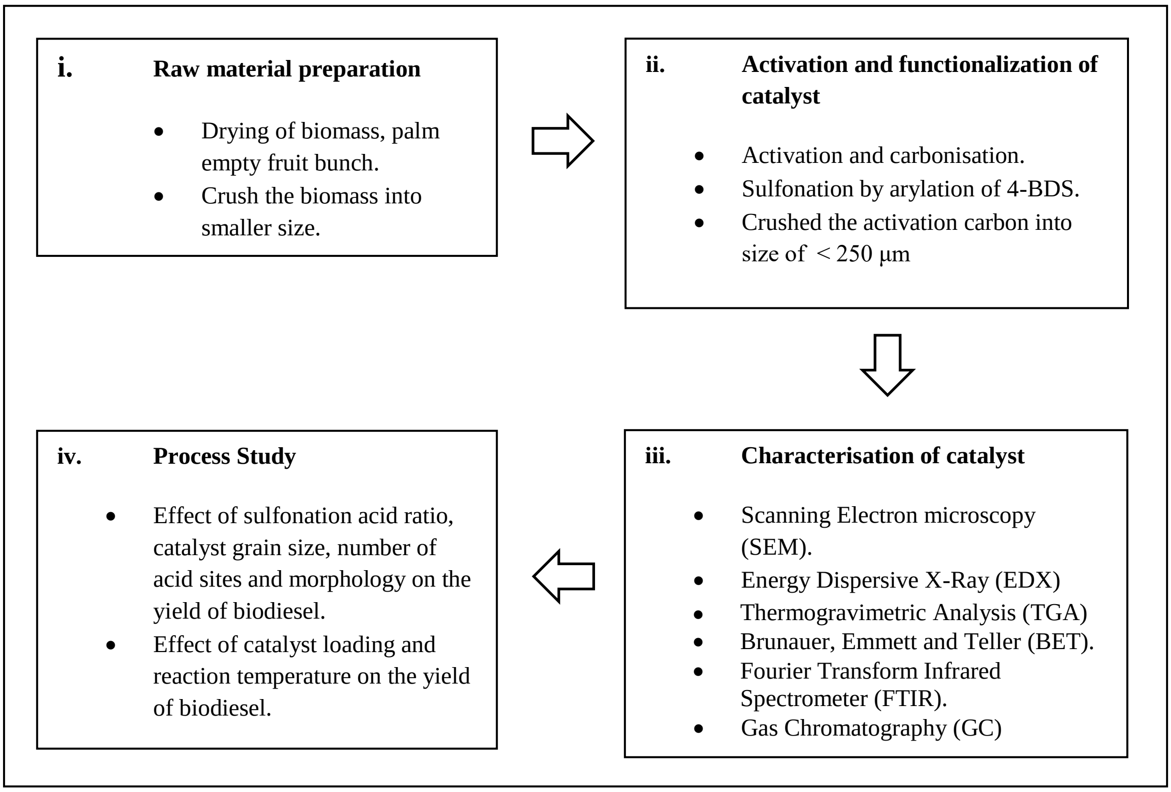

Figure 3.1: Schematic Flow of Research Methodology.

3.2 Materials and Apparatus

3.2.1 Raw Materials and Chemicals

In this study, the raw material palm empty fruit bunch (EFB) is selected as the biomass carbon precursor to synthesis the solid acid catalyst for biodiesel production. Source of EFB will be obtained from smallholder of oil palm plantation based in Melaka. Other than EFB, the complete list of chemicals and raw materials that are required in carbonisation of biomass, sulfonation of carbonised material and esterification are stated in Table 3.1.

Table 3.1: List of Chemicals and Materials Required.

Chemicals/ Materials	Source	Estimated Quantity	Usage
Palm Empty Fruit Bunch	Oil Palm Estate	1 kg	Carbon precursor to synthesis porous carbon.
Hydrochloric Acid (35%)	UTAR	3 L	To wash the carbonised biomass and to synthesise the sulfonating agent 4-BDS
Sulfanilic Acid (99%)	Synertec Enterprise	300 g	To synthesise the sulfonating agent 4-BDS.
Sodium Nitrite (98%)	UTAR	2 L	To synthesise the sulfonating agent 4-BDS.
Ethanol (99.9%)	UTAR	2 L	To synthesise the sulfonating agent 4-BDS.

Chemicals/ Materials	**Source**	**Estimated Quantity**	**Usage**
Phosphoric Acid (30-32%)	UTAR	3 L	Act as activating agent of biomass and to sulfonate the solid carbon material.
Palm Fatty Acid Distillate	UTAR	500 g	Reactant in esterification to produce biodiesel.
Methanol (99.9%)	UTAR	2 L	Reactant in esterification to produce biodiesel.
Deionised Water	UTAR	Excess	To wash the solid catalyst
Distilled Water	UTAR	Excess	To wash the solid catalyst
Potassium Hydroxide (99%)	UTAR	1 L	To measure the acid value of ester by titration
Hexane	UTAR	1 L	To dissolve biodiesel
Isopropanol	UTAR	1 L	To dissolve biodiesel

3.2.2 Apparatus, Equipment and Instruments

Table 3.2 shows the apparatus and equipment required in carbonisation of biomass, sulfonation of carbonised material and esterification. Table 3.3 shows the instruments required in catalyst characterisation.

Table 3.2: List of Apparatus and Equipment.

Apparatus/ Equipment	Specification	Usage
Carbolite Furnace	RHF 15/8 Type Serial 20-703062	To Carbonised the EFB.
Oven	80˚C	To dry the carbonised material and solid acid catalyst.
Mortar and Pestle	3 oz	To crush the carbonised material.
Sieving Machine	ASTM no. 60 sieve	To sieve the carbonised material.
Ice Water Bath	2 L	To maintain the temperature during synthesis of 4-BDS and solid acid catalyst.
Filter Funnel	90 mm diameter	To filter 4-BDS precipitate and solid acid catalyst.
Oil Bath	400 mL	To maintain the reaction temperature of esterification.

Continue

Apparatus/ Equipment	Specification	Usage
Round Bottom Flask	250 mL	To carry out esterification of PFAD
Condenser Column	Coil Type	To condense vapour methanol during esterification

Table 3.3: List of Instruments for Catalyst Characterisation.

Instrument	Specification	Usage
Scanning Electron Microscopy (SEM)	Hitachi SEM Model S-3400N	To determine the topography, morphology and crystallographic structure of the catalyst.
Energy Dispersive X-ray Spectroscopy (EDX)	Hitachi SEM Model S-3400N	To identify the chemical element presence in solid catalyst.
Thermogravimetric Analysis (TGA)	NETZSCH model STA 2500 Regulus	To measure the mass change and transformation energetics of catalyst
Brunauer, Emmett and Teller (BET)	TheroFinnigan Sorptomatic 1990	To determine the surface area, pore volume and the pyhsisorption of catalyst.
Fourier Transform Infrared Spectrometer (FTIR)	Nicholet IS10 FTIR	To determine the adsorb species and chemisorption of the solid catalyst.

Instrument	Specification	Usage
Gas Chromatography (GC)	Perkin Elmer Clarus 500	To identify the compound presence in biodiesel sample
GC Biodiesel Column	ZB-FFAP (60m × 0.25 mm × 0.25 µm)	

3.3 Experiment Procedures

3.3.1 Activation and Calcination of Biomass

EFB biomass was broken down into smaller pieces for better efficiency of carbonisation. The biomass was impregnated with 30 % phosphoric acid in weight ratio of 7:1 for 24 h. Then, the pre-soaked biomass was washed and dried in a heating oven at temperature 85 ℃ for 24 h to remove moisture and trace of phosphoric acid. After that, the pre-soaked biomass was carbonised in a furnace at different temperature varying from 200˚C to 600℃ for 2.5 h. After that, the resulting carbon was powdered using a mortar and pestle.

The activated carbon calcined at 200˚C to 600℃ was named as AC200, AC300, AC400, AC500 and AC600 respectively for convenient of discussion later. Figure 3.2 shows the process flow of activation and calcination of biomass.

Palm empty fruit bunch

Dried, crushed and sieved palm empty fruit bunch

Phosphoric acid Impregnated palm empty fruit bunch

Calcination of pre-soak biomass

Activation carbon was powdered by using mortar and pestle

Figure 3.2: Activation and Calcination of Palm Empty Fruit Bunch.

3.3.2 Sulfonation by Arylation of 4-Benzenediazonium Sulfonate

15 g of sulfanilic acid was dispersed in 300 mL of 1 M HCl aqueous solution in a round bottom flask. The temperature of the flask was maintained at 3 – 5 ˚ C in ice water bath with continuous stirring. 90 mL of 1 M $NaNO_2$ aqueous solution was added dropwise. After all the $NaNO_2$ was added, a clear solution was obtained, the mixture was stirred for another 1 h at same temperature. The mixture in the flask was allowed to settle down and white precipitate of 4-BDS formed was filtered off, washed with deionised water and weighed. 4-BDS precipitate was then mixed with 200 mL deionised water and 60 mL ethanol in a 500 mL beaker. 3 g of activated carbon (AC200) was added into the beaker and maintained the temperature at 3 – 5 ˚ C. Subsequently, 100 mL of 30 – 32% H_3PO_2 was added and stirred for 30 min. Another 50 mL of H_3PO_2 was added and allowed to stir for 1 h. The resulting sulfonated AC was filtered, washed distilled water and dried in the vacuum overnight.

The procedure of sulfonation was repeated by using activated carbon with different calcination temperatures and also different sulfanilic acid to AC weight ratios. The manipulated sulfonation parameters and the samples naming is shown in Table 3.4. Figure 3.3 shows the setup of the activated carbon sulfonation.

Table 3.4: Sulfonation Parameters and Sample Naming.

Sulfonation Parameters	Before Sulfonation	After Sulfonation
Calcination Temperature		
200˚C	AC200	CAT200
300˚C	AC300	CAT300
400˚C	AC400	CAT400
500˚C	AC500	CAT500
600˚C	AC600	CAT600
Sulfanilic Acid to Activated Carbon Weight Ratio		
0.5:1	AC200	CAT0.5:1
1:1	AC200	CAT1:1
5:1	AC200	CAT5:1
10:1	AC200	CAT10:1
15:1	AC200	CAT15:1

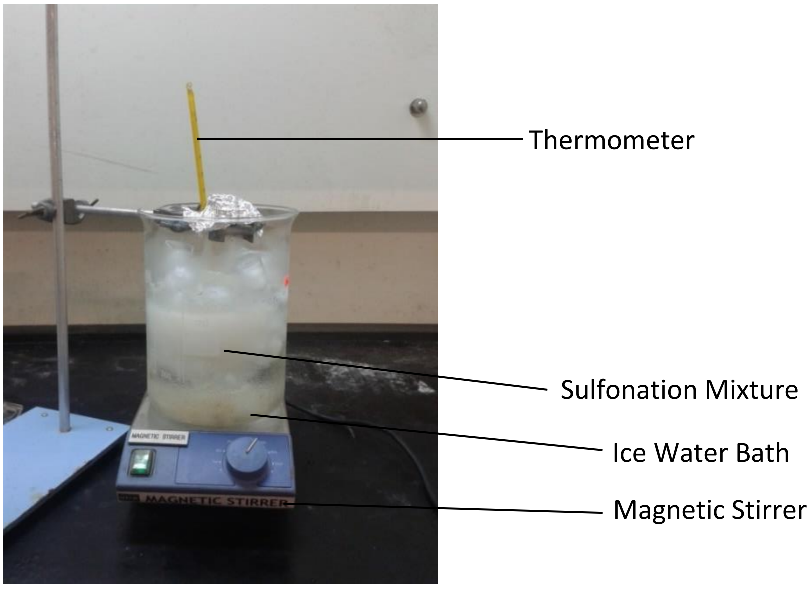

Figure 3.3: Setup for Functionalisation of Activated Carbon by 4-BDS Method.

3.3.3 Catalytic Activity Test

The solid acid catalyst synthesised in section 3.3.2 was then used to test its catalytic performance in esterification of palm fatty acid distillate to produce biodiesel. Figure 3.4 shows the experimental setup of the esterification.

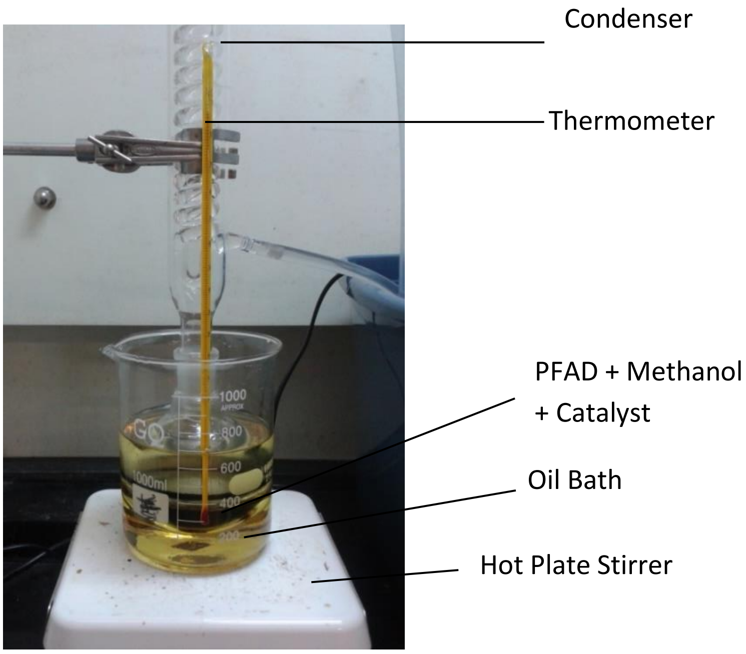

Figure 3.4: Experimental Setup of PFAD Esterification.

The reaction was performed in a 250 mL round bottom flask equipped with a magnetic stirrer and oil bath at 110 ˚ C. 5 wt% of catalyst was added to reaction mixture with 10 g PFAD and methanol with molar ratio to oil of 30. The reaction was allowed to run for 4 hours at 350 rpm stirring speed. After the reaction, the excess methanol was removed by evaporation and the weight of the product was recorded. The procedure was repeated for various parameters as shown in Table 3.5.

Table 3.5: Esterification Parameters.

Parameters	Variables
Different calcination temperature catalyst	CAT200, CAT300, CAT400, CAT500, CAT600
Different sulfanilic acid weight ratio catalyst	CAT0.5:1, CAT1:1, CAT5:1, CAT10:1, CAT15:1
Esterification Duration	2h, 4h, 7hr, 24 hr
Catalyst loading	1 wt%, 5wt%, 10wt%, 20wt%)

3.3.4 Biodiesel Characterisation

The biodiesel samples were tested with GC by injecting and vaporising the sample into the head of the chromatography column and allow the inert gas flow through the column. Vaporisation and separation of sample mixture into individual component in GC enable the components in the biodiesel sample can be quantitatively measured. Table 3.6 shows the setting of the GC that used to analyse biodiesel sample.

The GC peak areas obtained from the analysis were compared with the methyl ester standard calibration curves to calculate the biodiesel concentration and yield. The weight and yield of biodiesel can be calculated by using Eq. 3.1 and Eq. 3.2.

Table 3.6: Gas Chromatography Setting for Biodiesel Sample.

Gas Chromatography Setting	Specification
Injector Temperature (˚C)	250
Split Flow Ratio	50:1
Carrier Gas Pressure (psi)	24.7
Column Flow (mL/min)	Helium at 2 mL/min constant flow
Flame Ionization Temperature (˚C)	270

$$Actual\ Weight\ of\ Methyl\ Ester\ Produced\ (g) = \frac{concetration\ of\ methyl\ ester\ \frac{g}{L}}{Dilution\ Factor\ \frac{g}{L}} \times Weight\ of\ reaction\ product\ g \qquad \textbf{(Eq. 3.1)}$$

$$Biodiesel\ Yield\ (\%) = \frac{Actual\ Weight\ of\ Methyl\ Ester\ Produced\ g}{Theoretical\ Weight\ of\ Methyl\ Ester\ Produced\ g} \times 100\% \qquad \textbf{(Eq. 3.2)}$$

3.3.5 Catalyst Characterisation

3.3.5.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

The topography, morphology and crystallographic structure of the catalyst will be observed by using SEM under 20.0kV; X 500, 20.0kV; X 2000; 20.0kV; X 10000. The observation images were saved and the grain size and pore diameter of the catalyst can be estimated by comparing with the measurement obtained from those images. EDX is an attached instrument system to SEM that is used to obtain elemental and chemical information of the sample. Through this analysis, the weight percentage of different element presented in the catalyst was obtained and the possible chemical species that attached on the catalyst could be predicted.

3.3.5.2 Thermogravimetric Analysis (TGA)

TGA analysis was used to study the relationship between physical and chemical properties of catalysts such as mass change and mass change stages as a function of temperature and time in an atmosphere of air or nitrogen. The resulting temperature dependent mass loss and mass loss rate indicated the physical stability of the activated carbon. Table 3.7 shows the specification of TGA analyser.

Table 3.7: Measurement Parameters of TGA.

Method	Specifications
Furnace	PtRh-Furnace
Sample Carrier	Platinized slip-on plates
Crucible	Al_2O_3 crucibles with pierced lids
Temperature Program	RT – 1000 ˚C with 5 K/min 1000 ˚C – RT with 5 K /min
Atmosphere	RT – 900 ˚C under nitrogen (70 mL/min) 900 – 1000 ˚C under synthetic air (70 mL/min)

3.3.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to study the chemisorption of adsorbed species on the solid catalyst by passing through the sample with infrared spectroscopy with scanning range from 400 cm^{-1} to 2000 cm^{-1}. The resulting spectrum indicated the functional groups that attached on the solid catalyst. The size of the peaks in the spectrum also indicated the amount of the functional group present.

3.3.5.4 Total Acid Density Test

The total acid density of the functionalised catalyst can be tested by using back titration method. 0.1 g of sample catalyst first was added into 60 mL of 0.01 M sodium hydroxide (NaOH) and stirred for 30 minutes. After that the catalyst was filtered off and the filtrate with phenolphthalein was titrated with 0.02 M hydrochloric acid (HCl) until the solution turn from pink to colourless. The volume of HCl used to neutralise the filtrate was recorded and the acid density of the catalyst was calculate by using formulas below.

$$Mole\ of\ HCl\ used = Volume\ of\ HCl\ used\ mL \times 0.02\frac{mol}{L} \times \frac{1\ L}{1000\ mL} \qquad \textbf{(Eq. 3.3)}$$

According to stoichiometry equation, $NaOH + HCl \rightarrow NaCl + H_2O$

$$Mole\ of\ HCl\ used = Mole\ of\ NaOH\ neutralised\ by\ HCl \qquad \textbf{(Eq. 3.4)}$$

$$Mole\ of\ NaOH\ used\ to\ neutralise\ acid\ sites\ on\ catalyst = Original\ mole\ of\ NaOH - Mole\ of\ NaOH\ eutralised\ by\ HCl \qquad \textbf{(Eq. 3.5)}$$

$$Total\ acid\ density\ \left(\frac{mmol}{g}NaOH\right) = \frac{Mole\ of\ NaOH\ used\ to\ neutralised\ acid\ sites\ on\ catalyst}{0.1\ g} \qquad \textbf{(Eq. 3.6)}$$

3.3.5.5 Brunauer Emmett Teller (BET)

Through BET, the specific area of the activated carbon and catalyst was determined by physical adsorption of gas molecules on their surfaces and by calculating the amount of adsorbate gas corresponding to the monomolecular layer on the surface. The analysis was carried out at the temperature of liquid nitrogen and amount of gas adsorbed was measured by volumetric or continuous flow procedure.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

Based on the images shown by SEM, raw palm empty fruit bunch (EFB) naturally had a tough lignocellulosic structure as shown in Figure 4.1(a) & (b). The surface of the raw EFB was dense and consisted less cracks and crevices that were available for acid sites adsorption. It can be observed that the lignocellulosic structure was still covered with some natural plant wax and pectin which contributed a part of smooth flat surface in raw EFB that inhibited the attachment of acid sites.

As comparison with raw EFB, a phosphoric acid activated and calcined activated carbon (AC) had a clear pore structure development as shown in Figure 4.1 (c) & (d). The activating agent phosphoric acid and calcination allowed the development of mesoporous structure by attacking hemicellulose and lignin. Almost all AC calcined at different temperatures exhibited a rough texture surface. Noted that in Figure 4.2 (a) & (b), AC200 has a very well defined mesoporous structure and this gave a high surface area capacity for acid adsorption. As the calcination temperature increased as shown in Figure 4.2 and 4.3, the structure of AC became more irregular, loose, more flakes appeared and ladder shape structure formed indicated the beginning of carbon structure decomposition at high temperature which reduced the surface area and porosity for sulfonic group attachment.

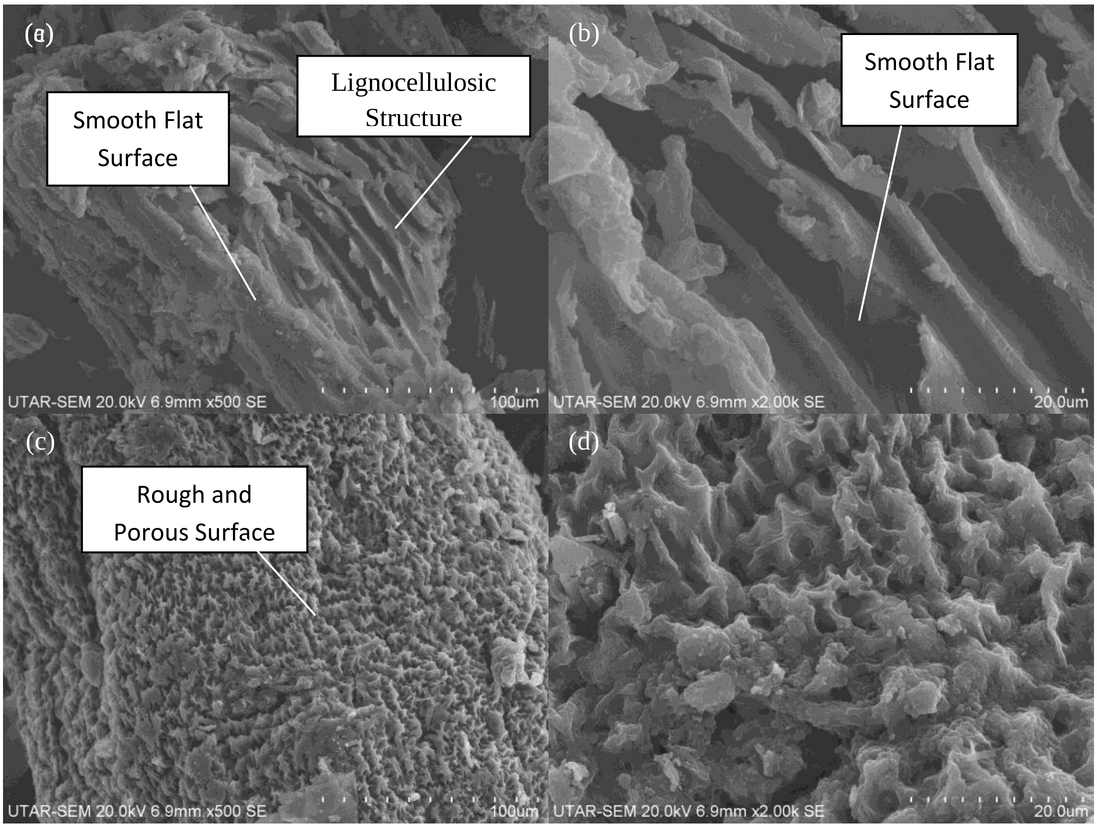

Figure 4.1: (a) Raw EFB X500; (b) Raw EFB X2000; (c) AC200 X500; (d) AC200 X2000.

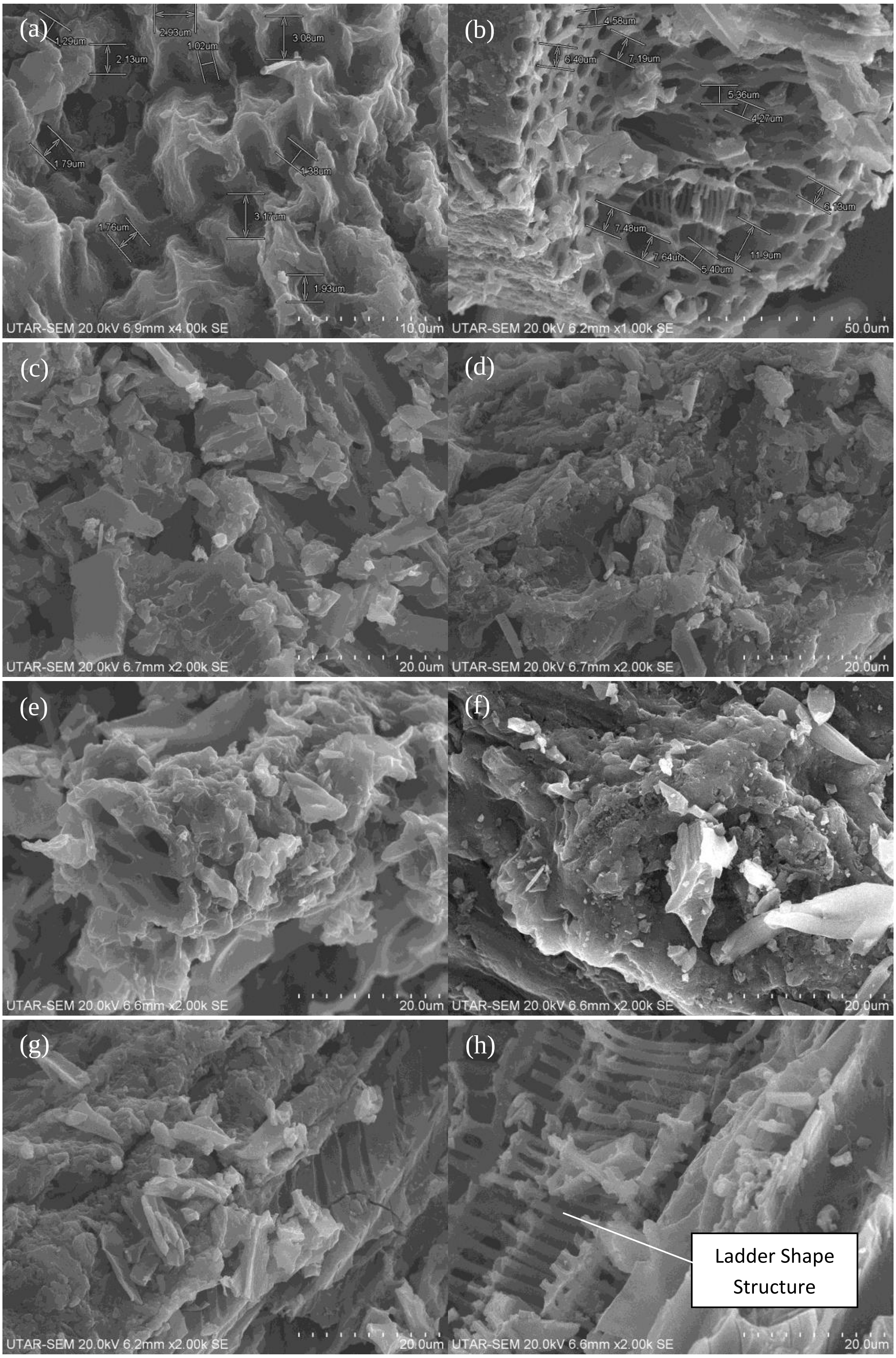

Figure 4.2: (a) AC200 (before sulfonation); (b) CAT200 (after sulfonation); (c) AC300 (before sulfonation); (d) CAT300 (after sulfonation); (e) AC400 (before sulfonation); (f) CAT400 (after sulfonation); (g) AC500 (before sulfonation); (h) CAT500 (after sulfonation).

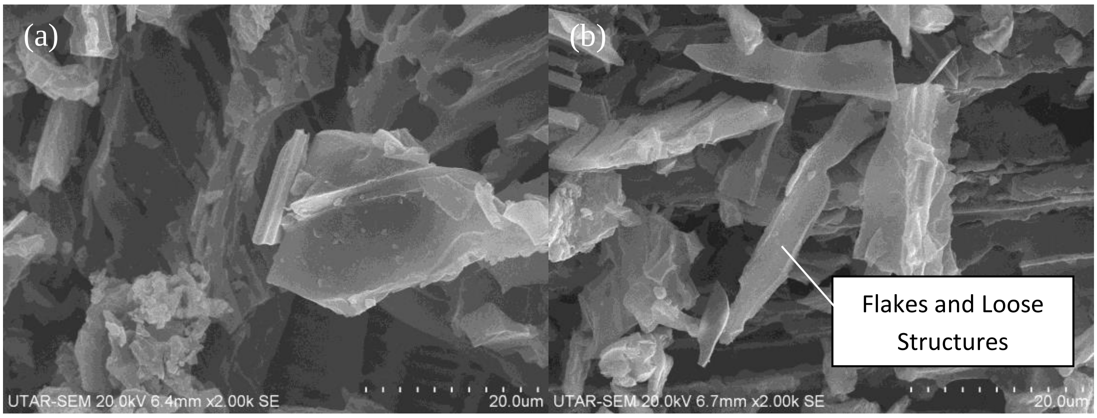

Figure 4.3: (a) AC600 (before sulfonation); (b) CAT600 (after sulfonation).

Figure 4.2 and 4.3 also show that the surface structure of AC had no significant changes after sulfonation by using sulfanilic acid to AC ratio of 5:1. However Figure 4.2(b) shows the pore diameter after sulfonation had significantly increased from average of 2.048 μm to 6.635 μm, indicating the pores of activated carbon enlarged during sulfonation. This result appeared to be different from discussion by Liu et al., (2010) that showed slight decrease in pore diameter (2.5 nm to 2.4 nm). Yet, it was possible for pore with such small diameter (Nano size) to have blockage in their case therefore resulted in this difference.

Besides, when the sulfanilic acid loading increased during sulfonation, the surface of the catalyst appeared to be coated with a layer of substances as shown in Figure 4.4 (d) & (e). This might indicated higher degree of sulfonation when sulfanilic acid loading increased. The high sulfanilic acid loading sulfonation (15:1) also shows a sharp increase in pore diameter from average of 2.048 μm to 8.784 μm as shown in Figure 4.4 (f), once again proved that the pore diameter of the activated carbon enlarged during sulfonation. The large pore diameter was convenient for large fatty acid molecules to transport and approach the active sites inside the pore. Yet, larger pore diameter also might have risk of acid sites leaching. The clearer images of pore size estimation are shown in Appendix C.

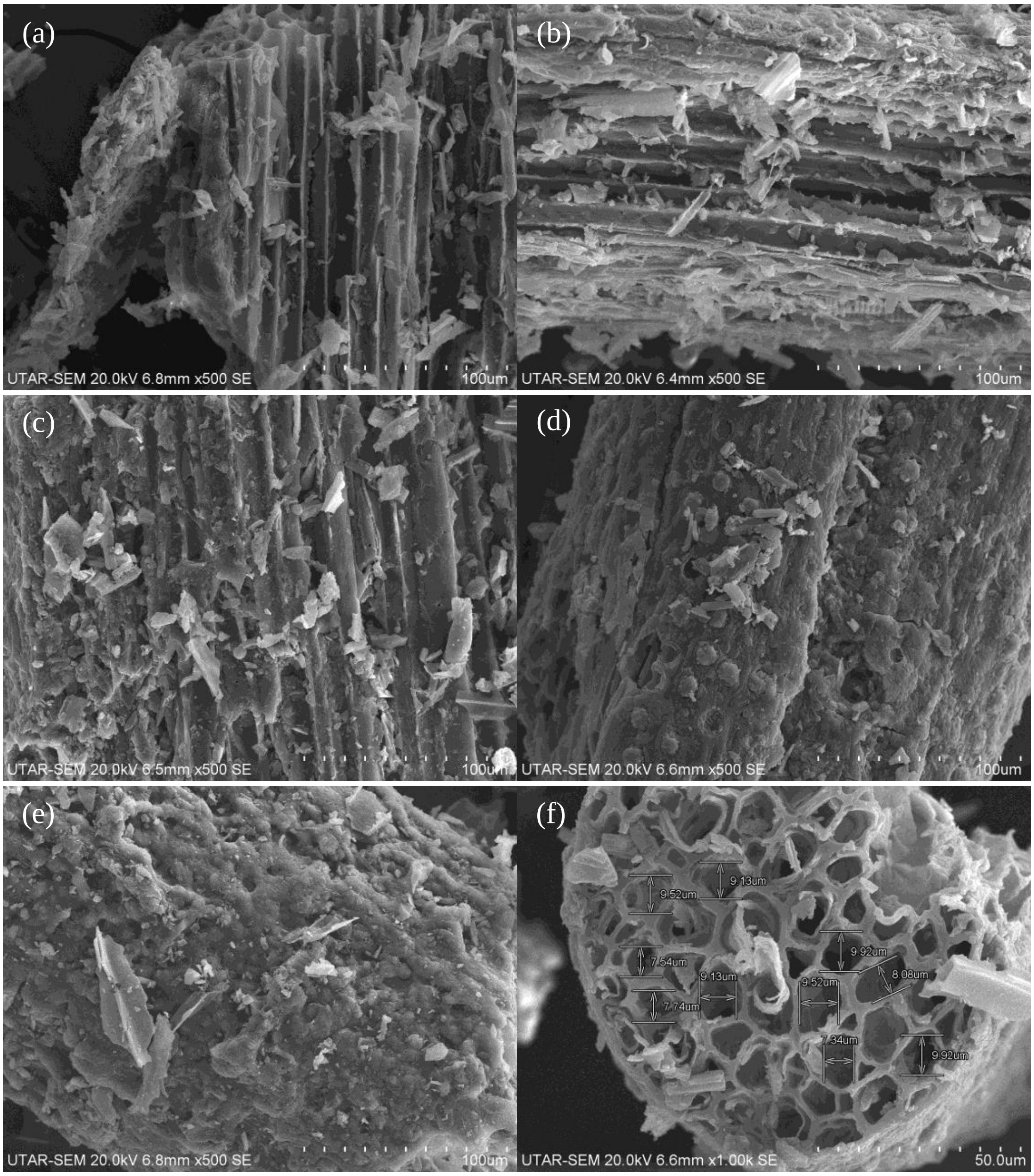

Figure 4.4: AC200 Sulfonated with different sulfanilic acid to AC Weight Ratio; (a) CAT0.5:1; (b) CAT1:1, (c) CAT5:1; (d) CAT10:1 (e) CAT15:1; (f) CAT15:1 (Cross Section).

The elements present in the raw EFB, activated carbons and sulfonated activated carbons from EDX analysis are shown in Table 4.1. Note that the raw EFB consisted of magnesium and calcium mineral which might possibly gained from their contact with soil during harvesting and transportation itself. It showed that magnesium and calcium mineral are completely removed after pre-treatment of phosphoric acid, water washing and calcination. According to the study by Abdullah and Sulaiman (2013), these mineral elements can be removed by using mild acid leaching and water washing treatment which explained the EDX result in Table 4.1 entry 1. High phosphorus content in AC and catalyst was most probably due to phosphoric acid retained inside the pores during pre-treatment and sulfonation and hardly to be washed out completely with distilled water.

Table 4.1 also shows that all catalysts had sulfur content (S) increased after sulfonation which indicated the successful attachment of sulfonic group on AC. For catalyst calcined at different temperatures, CAT200 showed that highest S content which is 3.52% followed by CAT500 2.89%, CAT300 1.90%, CAT400 1.87% and CAT600 0.99%. For catalyst sulfonated with different amount of sulfanilic acid, CAT15:1 showed the highest S content 15.98% followed by CAT10:1 7.55%, CAT5:1 3.67%, CAT1:1 0.51% and CAT0.5:1 0.31%. Therefore, when higher sulfanilic acid loading was used in sulfonation, there were higher chances for sulfonic group to attach on AC. Hence, based on the previous interpretation, CAT200 was predicted to have better sulfonic group attachment and 15:1 was the optimum sulfanilic acid to AC sulfonation ratio.

Besides, previous research from Konwar *et al.*, (2015) mentioned that there was a relation between sulfonic group density and carbon content (C). In current research, it can be observed that the C content of all catalysts increased after sulfonation compare with AC before sulfonation. The increase in C content after sulfonation was due to addition of 4-BDS radicals during functionalisation which provided more aromatic carbon sheet in the catalysts.

Table 4.1: Elements Present in Raw EFB, AC and Solid Acid Catalyst.

Sample	C%	O%	Mg%	Ca%	Si%	P%	S%
Raw EFB	14.24	54.21	12.56	18.99	0	0	0
AC200	20.87	29.40	0	0	11.80	37.93	0
AC300	19.99	28.07	0	0	3.38	45.62	0
AC400	28.10	20.82	0	0	25.64	24.00	0
AC500	18.42	21.38	0	0	5.12	52.11	0
AC600	19.86	18.65	0	0	34.74	25.32	0
CAT200	64.01	32.47	0	0	0	0	3.52
CAT300	29.79	26.60	0	0	21.20	16.59	1.90
CAT400	41.94	19.24	0	0	6.95	27.53	1.87
CAT500	46.52	16.55	0	0	8.18	22.29	2.89
CAT600	42.01	17.17	0	0	23.44	15.03	0.99
CAT0.5:1	62.68	34.19	0	0	2.40	0	0.31
CAT1:1	58.55	36.64	0	0	4.31	0	0.51
CAT5:1	60.05	34.30	0	0	0	1.98	3.67
CAT10:1	54.64	30.56	0	0	3.97	3.27	7.55
CAT15:1	46.24	25.53	0	0	4.22	8.03	15.98

4.2 Thermogravimetric Analysis (TGA)

AC300 was selected as a sample to study the thermal stability of EFB activated carbon. Temperature dependent curve Figure 4.5 shows that AC300 undergo a multi-step decomposition whereby there was two mass loss stages under nitrogen atmosphere (inert condition) and one mass loss under synthetic air atmosphere (oxidative condition).

The first mass loss stage under inert condition was most likely due to the loss of inherent moisture which is between 0 ˚ C to 150 ˚ C. The further mass loss stages mostly related to the pyrolytic decomposition of the sample. For oxidative mass loss, it was attributed to the bum-up of present carbon component of the activated carbon. Overall, the activated carbon was stable and suitable for operating temperature up to 549.9 ˚ C which was corresponded to the observation in SEM images whereby the carbon structure started to collapse at around 500 ˚ C to 600 ˚ C.

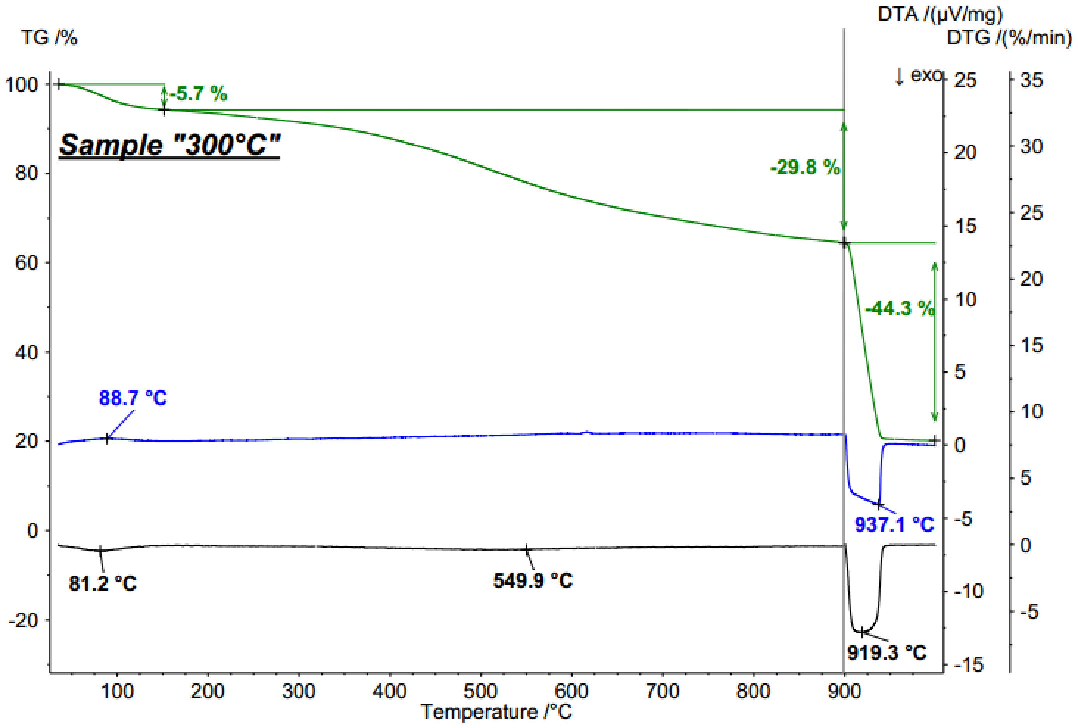

Figure 4.5: Temperature-dependent Mass Loss (TG, green); Mass Loss Rate (DTG, black); DTA-curve (blue) of AC300.

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

According to Figure 4.6, all catalysts calcined at different temperatures show an obvious stretching vibration of aromatic ring C=C at wavelength around 1580 cm^{-1} which had same observation as Konwar *et al.*, (2015). This stretching was due to the incomplete carbonisation of carbon material and form polycyclic aromatic carbon sheet with phenolic group (Mo *et al.*, 2008).

Figure 4.6 also shows S=O stretching vibration at wavelength range between 1020-1090 cm^{-1} and SO_3H stretching at 1150-1270 cm^{-1} which indicated the presence of sulfonic group on catalyst (Thomas, n.d.). The catalyst also exhibited C=O band of carbonyl group at 1700 cm^{-1} and Figure 4.7 shows the intensity of C=O does not have significant changes after sulfonation. Figure 4.8 shows that CAT15:1 had the highest intensity of SO_3H peak follow by CAT10:1, while CAT5:1 and CAT1:1 showed almost similar SO_3H intensity and CAT0.5:1 showed the lowest.

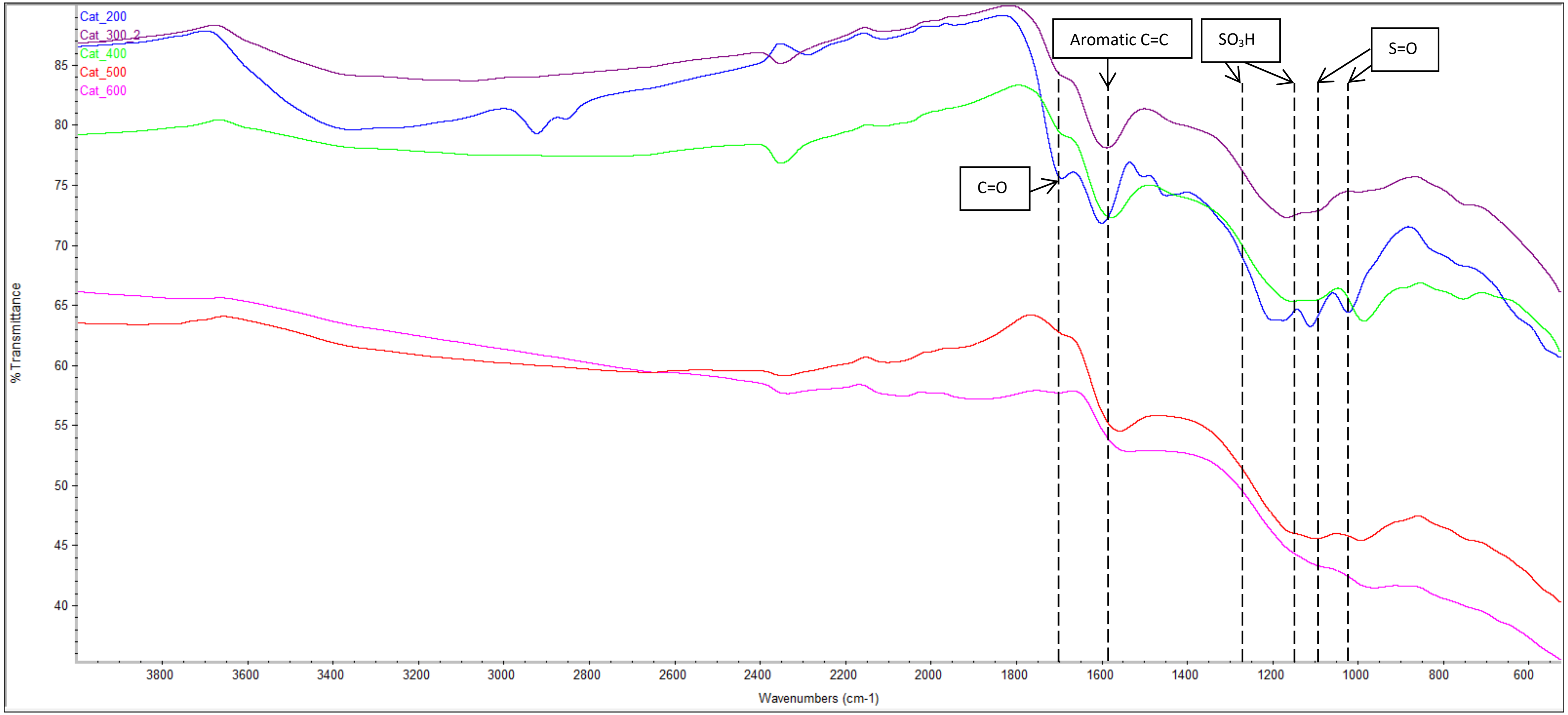

Figure 4.6: FTIR Spectra of Catalysts Calcined at Different Temperature.

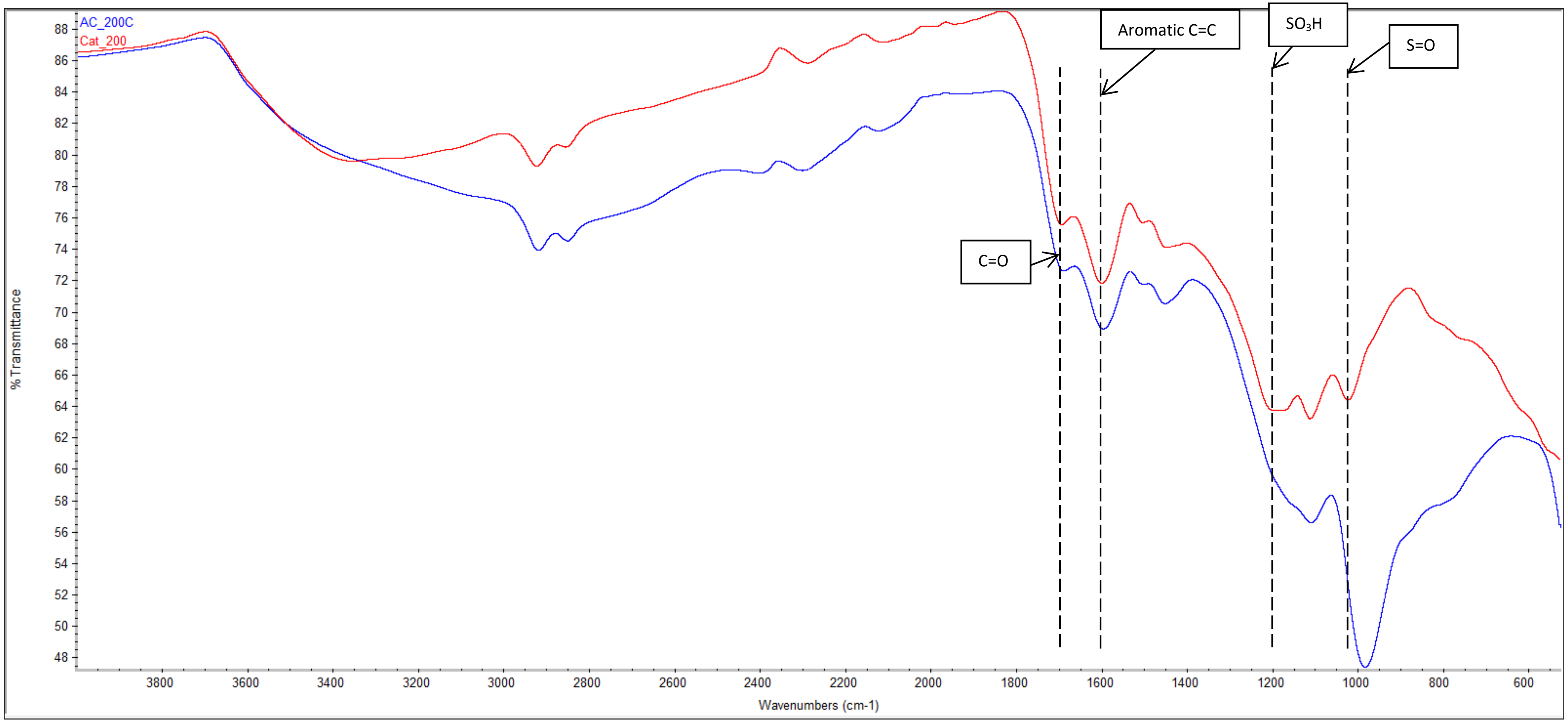

Figure 4.7: FTIR Spectra of AC200 and CAT200.

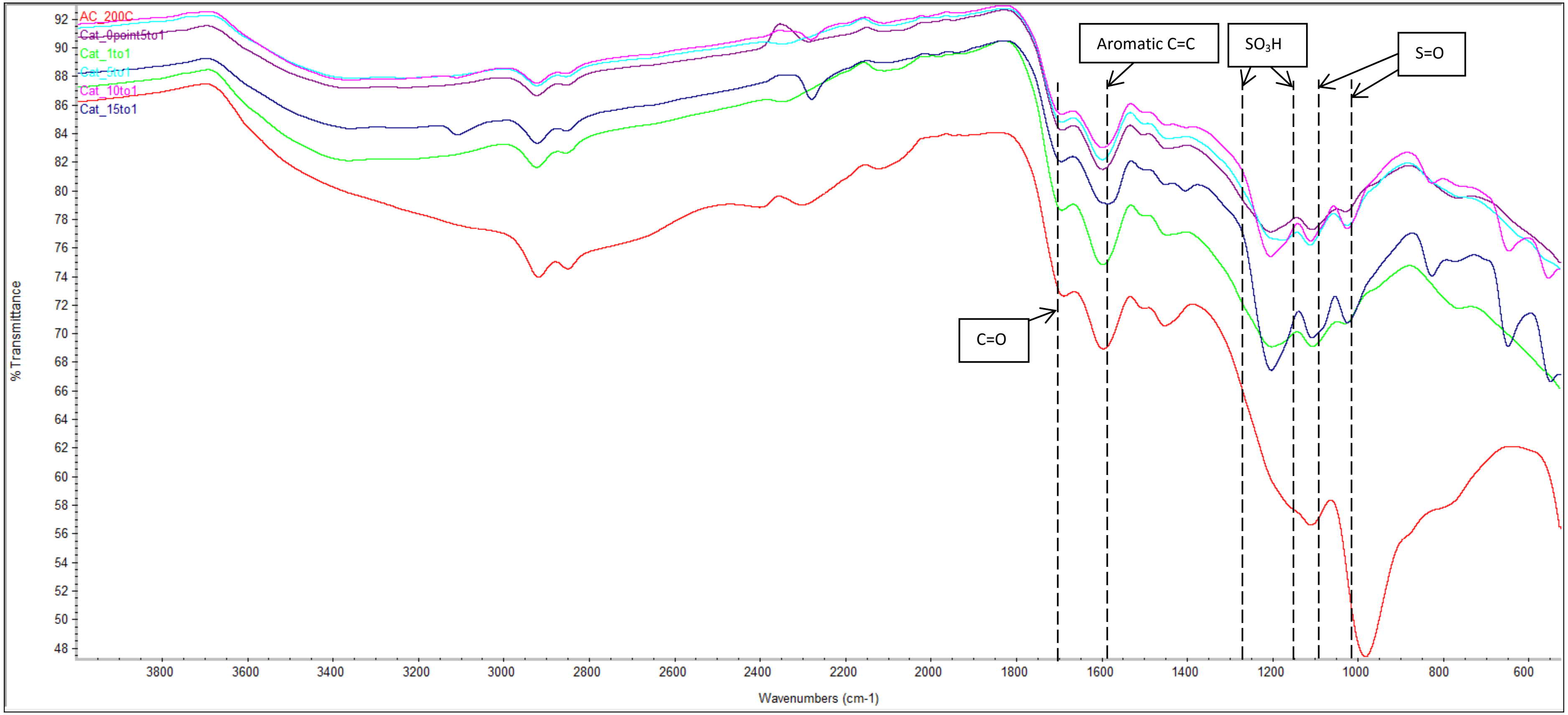

Figure 4.8: FTIR Spectra of AC200 and Catalyst Sulfonated at Different Sulfanilic Acid Ratio.

4.4 Total Acid Density Test

Figure 4.9 and Figure 4.10 show the trend line of total acid density for catalyst calcined at different temperature and catalyst sulfonated at different sulfanilic ratio. The calculation steps to obtain total acid density can be found in Appendix G.

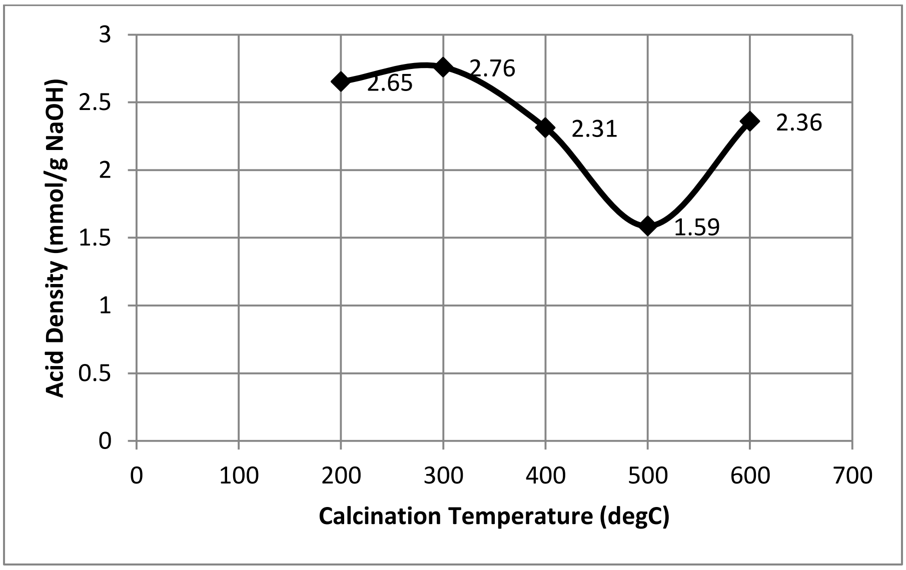

Figure 4.9: Effect of Calcination Temperature against Total Acid Density of Catalyst. ***(Sulfonation conditions: 5:1 sulfanilic acid to AC weight ratio, 1.5 h sulfonation duration; 3 – 5 ˚C sulfonation temperature)***

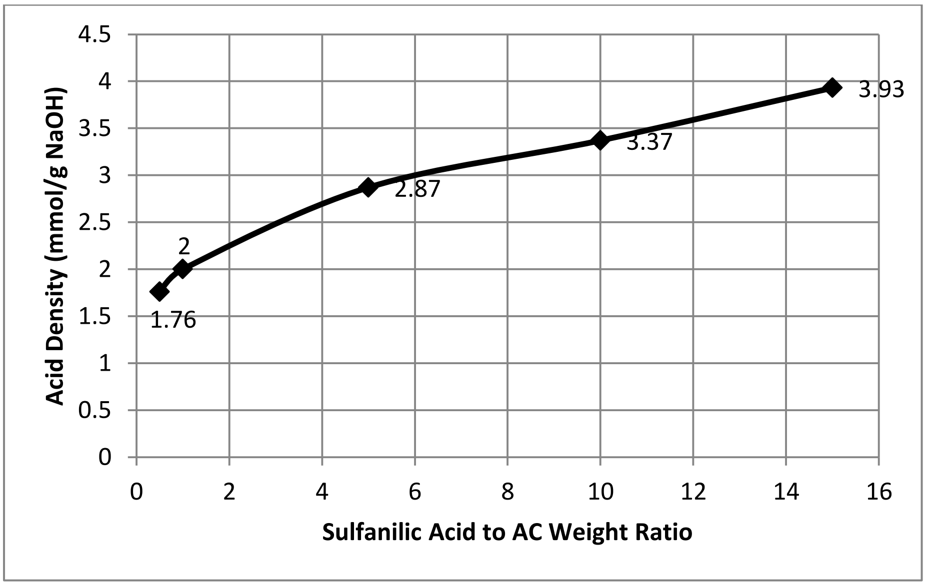

Figure 4.10: Effect of Sulfanilic Acid to AC Ratio Against Total Acid Density of Catalyst. ***(Sulfonation conditions: AC200 as catalyst support, 1.5 h sulfonation duration; 3 – 5 ˚C sulfonation temperature)***

According to Figure 4.9, the total acid density of the catalyst of CAT200 and CAT300 were similar and it decreased as the calcination temperature increased from 200 ˚ C to 500 ˚ C. However, at 600 ˚ C calcination temperature, the total acid density bounced back to 2.36 mmol/g NaOH and this mostly related to the structure of CAT600. CAT600 which was flakier compare to other catalysts caused its existing acid sites were exposed directly to the NaOH solution while the acid sites of the other catalysts might trapped within the pores hence not easy to react with NaOH. Besides another reason might due to random sampling error whereby the collected CAT600 samples coincidently had more acid sites attached on it. This error can be eliminated by shaking the catalyst batch before sampling and collect more sample data from different point.

In the case of sulfonation by using different sulfanilic acid to AC ratio, Figure 4.10 shows the total acid density of catalysts increased as the ratio increased. For CAT0.5:1 and CAT1:1 show almost similar and lowest total acid density which was 1.76 mmol/g and 2 mmol/g while CAT15:1 exhibited the highest total density among all which was 3.93 mmol/g. This result was supported by previous EDX anlaysis (Section 4.1) whereby CAT15:1 exhibited the highest S content (15.98%) followed by CAT10:1 (7.55%), CAT5:1 (3.67%), CAT1:1 (0.51%) and CAT0.5:1 (0.31%). The high S content indicated more sulfonic group on the catalyst.

Comparing the result of CAT15:1 with Konwar *et al.*, (2015) who used the similar procedure and sulfonation method, their catalyst only had 2.032 mmol/g of total acid density, this difference was most probably due to different carbon precursor was used caused the acid sites attached differently. Besides, their method also involved intensive washing of catalyst after sulfonation with acetone and distilled water while in current research only distilled water was used with several rounds of washing.

4.5 Brunauer Emmett and Teller (BET)

AC300 and CAT300 were selected as the samples to study the specific surface area of AC and catalyst. According to result attached in Appendix K, sample before sulfonation (AC300) had the specific surface area of 5.6771 m^2/g and after sulfonation (CAT300) it reduced to 2.85067 m^2/g. Comparing to Konwar et al. (2014) using oil cake waste and Liu et al. (2010) using conventional activated carbon as carbon precursor with same sulfonation method, the specific surface area of AC and catalyst in this study were much lower. Konwar et al. (2014) reported 777 m^2/g before sulfonation and 696 m^2/g after sulfonation while Liu et al. (2010) reported 751 m^2/g before sulfonation and 602 m^2/g after sulfonation. Such as big difference between current research and literatures was most probably due to the different carbon precursor were used as the pores and surface development of activated carbon also depended on the original carbon material itself. However, both of the current research and literatures showed a reduction of specific surface area after sulfonation and this might due to part of the surface area has been filled by sulfonic group.

4.6 Catalytic Activity Test

The catalytic activities of all synthesised catalysts were tested in esterification of palm fatty acid distillate (PFAD) with methanol in order to identify the optimum catalyst. Several reaction parameters were also adjusted to obtain the best conditions for optimum catalyst to perform. The calculation steps to obtain biodiesel yield can be found in Appendix J.

4.5.1 Effect of Calcination Temperature

CAT200, CAT300, CAT400, CAT500 and CAT600 were used to study the effect of catalyst calcination temperature on biodiesel yield and their relationship is shown in Figure 4.11.

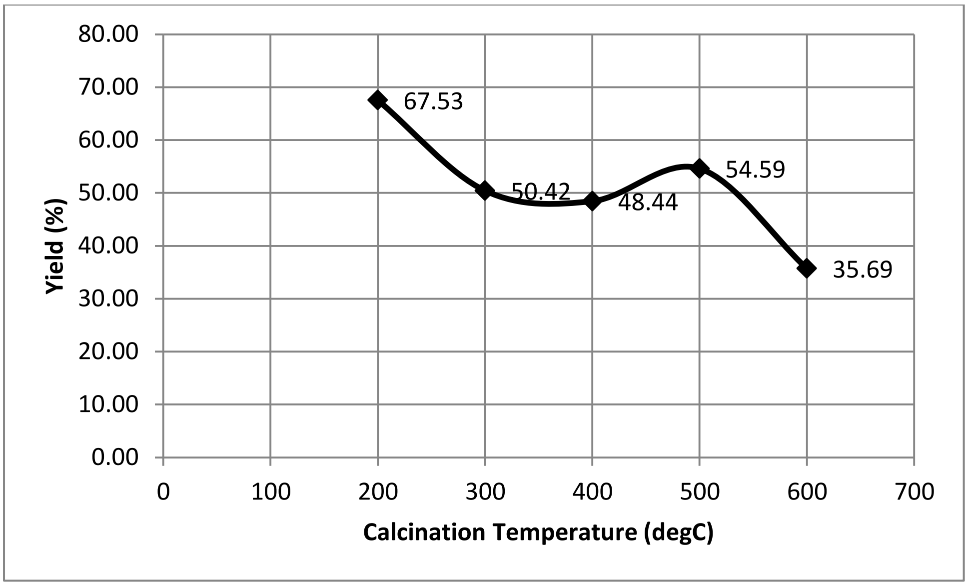

Figure 4.11: Graph of Biodiesel Yield against Catalyst Calcination Temperature. ***(Esterification conditions: 5wt% catalyst, 10 g PFAD, 30:1 methanol to oil molar ratio, 110 ˚C reaction temperature, 4 h reaction duration)***

Figure 4.11 shows that CAT200 had the highest biodiesel yield which was 67.53% followed by CAT500 54.59%, CAT300 50.42%, CAT400 48.44% and the lowest yield CAT600 35.60%. This result is tally with the trend of the previous elemental analysis in Section 4.1 whereby the higher S content indicated higher chances of sulfonic group attachment on the catalyst hence more active sites were available to catalyse the reaction.

CAT200 had the highest catalytic activity was most probably due to incomplete carbonisation at lower temperature. At 200˚ C, the biomass dehydrated and developed the amorphous mesoporous surface without complete destruction of carbon structure but sufficient to remove wax and pectin on the raw EFB. Besides, catalyst with large pore size and high specified area would be favour to convert large fatty acid molecules in PFAD. Although CAT200 showed the highest biodiesel yield compared to other catalyst calcined at higher temperature, it was still unable to convert solid PFAD into liquid biodiesel. The sample product solidified at room temperature once methanol had removed and this indicated that the sample was still far away from the pour point standard target of biodiesel which is 15˚ C in tropical countries and -21˚C to 0˚C in winter countries (MPOB, n.d.). There was still a large portion of unreacted PFAD which contributed to the solidification of sample.

As calcination temperature increased, especially at high temperature 600˚C, the carbon structure started to decomposed and became hard which inhibited the attachment of acid sites. At extreme high temperature, the pores of biomass also will became compact due to sintering effect hence reduce the sulfonic group attachment. Researches from Liu *et al*., (2013) and Dawodu *et al*., (2013) also suggested that incomplete carbonisation at lower temperature favour the attachment of sulfonic group on biomass AC.

4.6.2 Effect of Sulfanilic Acid to Activated Carbon Ratio

CAT0.5:1, CAT1:1, CAT5:1, CAT10:1 and CAT15:1 were used to study the effect of sulfanilic acid loading during sulfonation on the biodiesel yield and their relationship is shown in Figure 4.12.

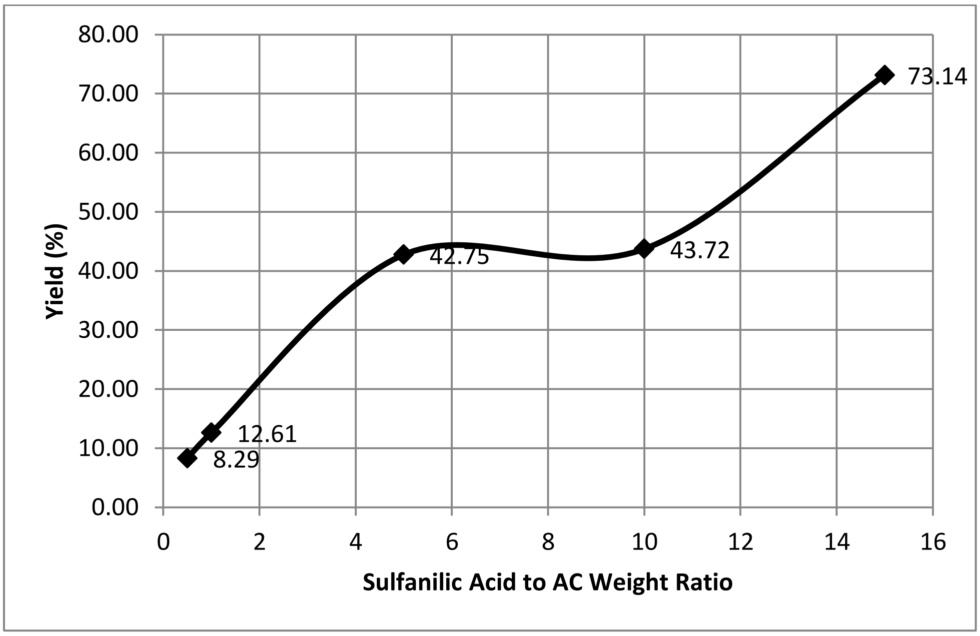

Figure 4.12: Graph of Biodiesel Yield against Catalyst Sulfonated with Different Sulfanilic Acid Ratio. ***(Esterification conditions: 5wt% catalyst, 10 g PFAD, 30:1 methanol to oil molar ratio, 110˚C reaction temperature, 4 h reaction duration)***

Figure 4.12 shows that CAT0.5:1 that sulfonated with less sulfanilic acid contributed the lowest biodiesel yield which is 8.29% followed by CAT1:1 12.62%. The low biodiesel yield by using these two catalysts can be related back to the total acid density test in Section 4.4 whereby CAT0.5:1 and CAT1:1 showed the lowest acid density value which were 1.76 mmol/g NaOH and 2 mmol/g NaOH respectively. Although the total acid density of these two catalysts were considered almost similar and comparable with results by Geng *et al.* (2011), Konwar *et al*. (2014) and Liu *et al.* (2010), but the acid density was most probably contributed by the weak acid group such as phosphate group, -COOH and -OH which had negligible catalytic effect during esterification.

CAT5:1 and CAT10:1 showed almost similar biodiesel yield 42.75% and 43.72% indicated that when sulfanilic acid ratio increase from 5 to 10 did not have significant effect on the catalyst performance. As sulfanilic acid to AC ratio increase to 15:1 during sulfonation, a sharp improvement was observed in biodiesel yield which was 73.14%. This result can be proven by previous catalyst characterisation which showed CAT15:1 was the potential high performance catalyst. Therefore, it can be concluded that higher sulfanilic acid loading during sulfonation increased the number of sulfonic group that were available to attach on the AC surface. Yet, at biodiesel yield of 73.14% the sample still remained solidified at room temperature and adjustment of reaction parameters should be carried out in order to identify the best performance conditions of the catalyst.

4.6.3 Effect of Esterification Duration

Reaction time was varied for 2 h, 4 h, 7 h and 24 h to study its effect on biodiesel yield by using CAT15:1 and their relationship are shown in Figure 4.13. It shows that the biodiesel yield was improved gradually over the reaction time from 2 h to 7 h. At 4 h reaction time, the biodiesel yield was 73.14% which was higher than the result obtained from Dawodu *et al.* (2013) who applied direct sulfonation method and obtained 36.4% in 5 h reaction. However, compared to Shuit & Tan (2014) which had 78.1% in 3 h reaction by using direct sulfonation method, the biodiesel yield in current research was much lower.

From 7 h onwards, the biodiesel yield reached 91.74% and showed only a slight increment of 0.37% per hour until 24 h. According to the graph, 7 h to 24 h is the optimum range of esterification duration, however due to laboratory regulation and time constraint, the biodiesel yield between 7 h to 24 h could not be identified. Uncertainty might occur between this duration whereby the biodiesel yield might be higher than 97.97% and dropped due to reverse reaction. Thus, the reaction setup for duration between 7 h and 24 h can be further studied in next research to narrow down the optimum range.

Next, Figure 4.14 shows that when CAT15:1 was used for reaction duration of 7 h and 24 h, large portion of PFAD was successfully converted into liquid state biodiesel at room temperature. Based on the observation on the behaviour of the biodiesel samples, it can be assumed that when biodiesel yield larger than 90%, the biodiesel sample would not solidify. Besides, a few droplets of glycerol were observed at bottom of these samples which implied that the catalyst was able to catalyse transesterification of triglyceride in PFAD.

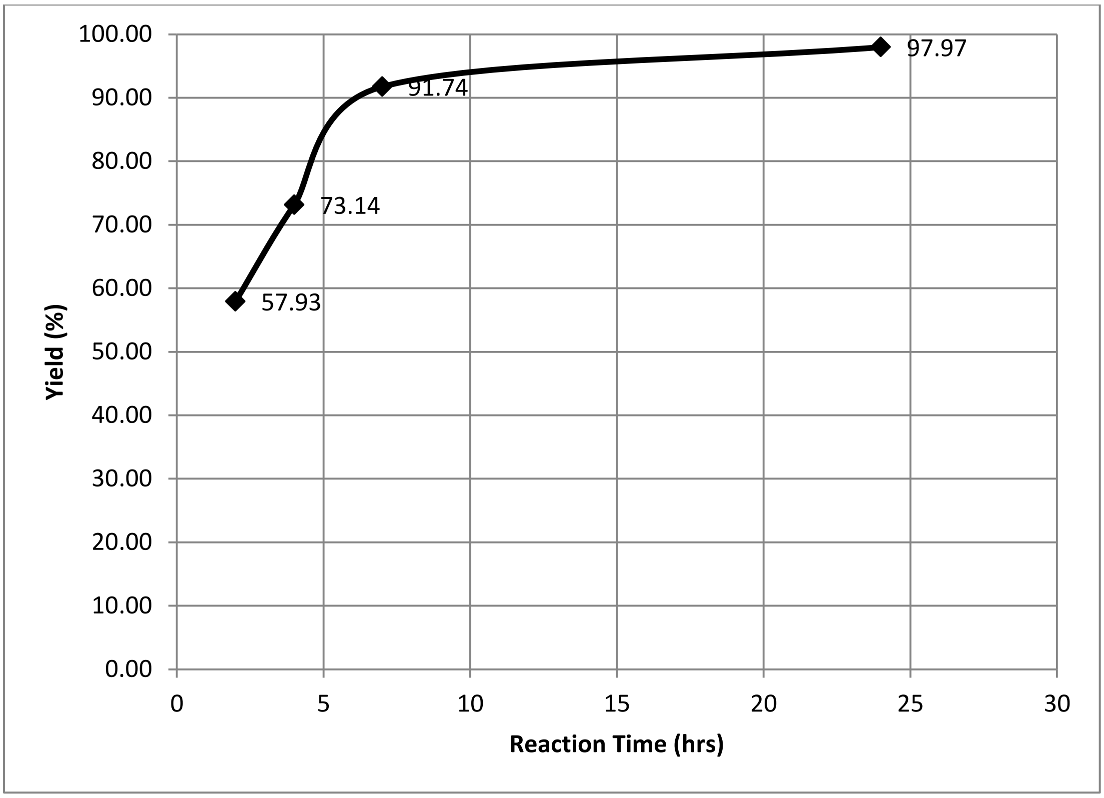

Figure 4.13: Graph of Biodiesel Yield against Esterification Duration. ***(Esterification conditions: 5wt% CAT15:1 catalyst, 10 g PFAD, 30:1 methanol to oil molar ratio, 110°C reaction temperature)***

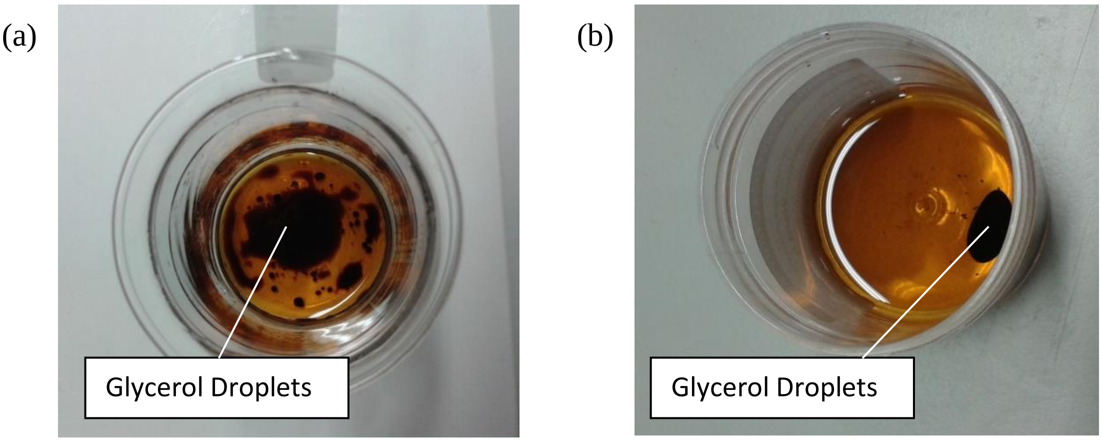

Figure 4.14: (a) Biodiesel Sample (24 h); (b) Biodiesel Sample (7 h).

4.6.4 Effect of Catalyst Loading

Catalyst loading of CAT15:1 was varied for 1wt%, 5wt%, 10wt% and 20wt% to study its effect on biodiesel yield and their relationship is shown in Figure 4.15. Reaction duration of 7 h was used as it fell in optimum temperature range as discussed in Section 4.6.3.

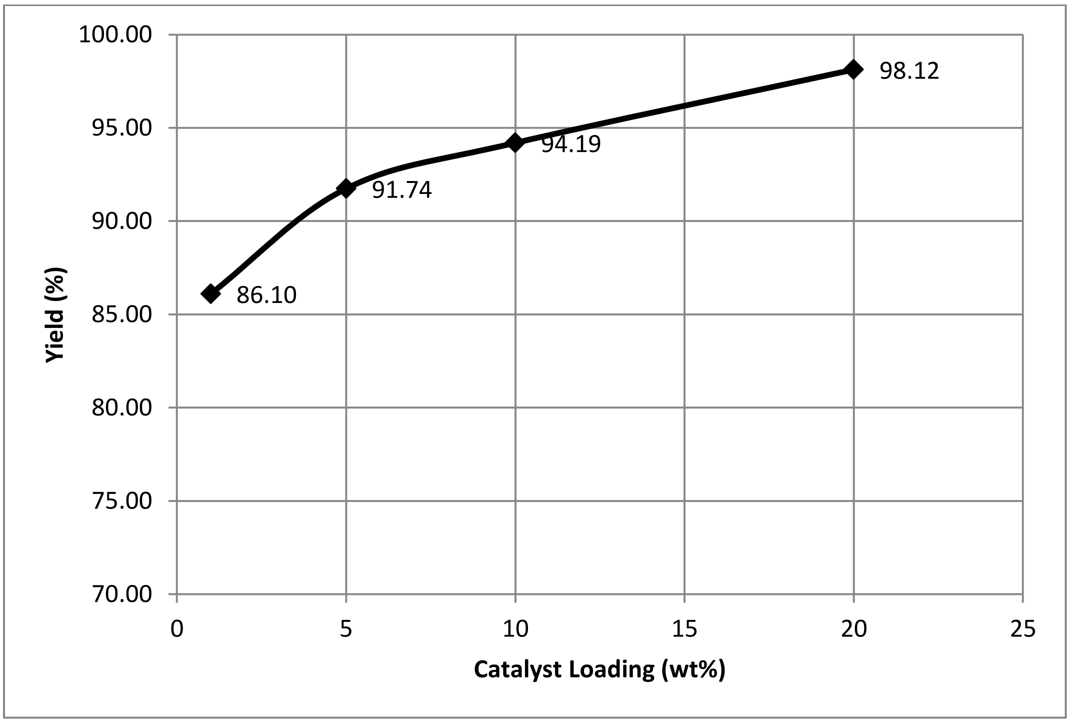

Figure 4.15: Graph of Biodiesel Yield against Catalyst Loading. ***(Esterification conditions: CAT15:1 catalyst, 10 g PFAD, 30:1 methanol to oil molar ratio, 110 ˚C reaction temperature, 7 h reaction duration)***

Figure 4.15 shows that the biodiesel yield increased gradually as the catalyst loading increased. The highest biodiesel yield was obtained at 20 wt% of CAT15:1 which was 98.12%. This implied that higher catalyst loading had more acid active sites available for fatty acid to attach thus speed up the reaction. This result was supported by the study from Fadhil *et al*. (2016) who claimed that the conversion of FFA increased as the amount of the catalyst increased as there was more hydrophilic functional groups on the catalyst surface such as –COOH, -OH and most importantly the sulfonic group act as an active sites for polar FFA and methanol to attach on it.

However, catalyst loading higher than 20 wt% was not suggested to be studied in next research because it was observed that during separation of solid catalyst from reaction mixture, higher catalyst volume tended to have more reaction mixture absorbed or stick on it and this might influence the final produced volume indirectly affecting the biodiesel yield. Higher catalyst loading will also change the stirring pattern in the reactor and the reaction mixture become viscous and hardly to be agitated which mean higher energy was required for stirring. Fadhil *et al*. (2016) also stated that higher catalyst loading than the optimum did not have significant effect on biodiesel yield as the mass transfer between the catalyst and FFA became poor.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Palm empty fruit bunch (EFB) biomass was used as carbon precursor to synthesis activated carbon and then sulfonate through 4- benzenediazonium sulfonate (4-BDS) arlyration. SEM analysis showed a clear porous and rough surface was developed after calcination. However, calcination at higher temperature caused destruction of carbon structure and the activated carbon became loose which prevented the sulfonic group attachment.

EDX result showed that CAT200 had the highest sulfur content as compare to other catalyst calcined at higher temperature. EDX also showed that CAT15:1 had the highest sulfur content among all catalyst which indicated that when sulfanilic acid loading increased during sulfonation, more sulfonic groups were available for attachment.

TGA result showed that the AC300 undergo two stages of mass loss under inert condition where first mass loss step was due to the loss of moisture that trapped within the activated carbon and the second mass loss stage was due to pyrolytic decomposition of the carbon structure. It was reported that the carbons structure was thermally stable up to temperature of 549.9 ˚C.

FTIR analysis reported that C=C stretching was detected around 1580 cm^{-1} indicated the incomplete carbonisation and form polycyclic aromatic carbon sheet.

S=O and SO_3H also observed at wavelength 1020-1090 cm^{-1} and 1150-1270 cm^{-1} respectively proved the successful attachment of sulfonic group. As for total acid density test, CAT200 and CAT15:1 showed the highest acid attachment which was tally with the result of elemental analysis. Next, BET analysis showed that the specific surface area of AC before sulfonation was 5.6771 m^2/g and it reduced to 2.85067 m^2/g after sulfonation.

Catalytic activity of catalyst calcined at different temperature and sulfonated with different sulfanilic acid loading were also tested through esterification of PFAD. The result showed that CAT200 was the optimum catalyst as it gave the highest biodiesel yield compared to other catalyst calcined at different temperatures. CAT15:1 also reported to have highest biodiesel yield which is 73.14% compare to other catalyst sulfonated with lower sulfanilic acid ratio.

The esterification parameters were also studied and the result showed that reaction time of 7 h – 24 h was the optimum operating duration for CAT15:1 and 20 wt% of CAT15:1 was reported as optimum catalyst loading as it gave the highest biodiesel yield which is 98.12%.

5.2 Limitations and Recommendations

After conducting the current research, some suggestions were made to improve accuracy and reliability of the experimental results. Due to time constraint, material and equipment limitations, some of the optimum reaction parameter, catalyst and biodiesel characterisation could not be identified. It was suggested that, these parameters can be further studied to obtain to most optimum operating condition for the catalyst. Several suggestions were made as listed below.

1. Impregnate the biomass with different activating agent such as sulfuric acid and nitric acid as different activating agent will affect the surface of the AC.

2. Calcined the biomass in absence of air. Current calcination of biomass using carbolite furnace was not conducted in absence of air. Severe oxidation of acid can cause pores blocking and reduce the porosity of AC.
3. Use digital ice bath control in sulfonation. Current sulfonation was done by soaking the round bottom flask in a beaker of ice bath which resulted difficulty in temperature control as the surrounding heat melted the ice relatively fast.
4. Use heating mental in esterification. Current esterification was done by soaking the round bottom flask in a beaker of hot oil bath which resulted difficulty in temperature control and also risk of water dripping into hot oil bath.
5. Use internal standard while conducting gas chromatography test. Current biodiesel yield was calculated based on external calibration curve which might result in inaccuracy. Internal standard was used to correct the concentration of the target compound or external standard.
6. Biodiesel and catalyst characterisation should be done as soon as the samples were produced to avoid contamination of samples.
7. Reaction parameters such as calcination duration, esterification temperature, methanol to PFAD ratio, stirring speed and catalyst reusability can be studied in next research.

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