BIODIESEL SYNTHESIS VIA SOLID ACID CATALYST BY USING PALM FATTY ACID DISTILLATE (PFAD) AS FEEDSTOCK

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By

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ABSTRACT

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Liaw Kai Jun

Sucrose was used to synthesis the catalyst for biodiesel production. SEM, XRD, FTIR and EDS were used to characterize the synthesized catalyst. PFAD was used as the feedstock for the biodiesel synthesis through esterification reaction with methanol by using the synthesized catalyst. The effect of reaction temperature, reaction time, agitation speed, molar ratio of methanol to feedstock and catalyst concentration towards the PFAD conversion was investigated. One-Variable-At-One-Time and RSM were used to optimize biodiesel synthesis. The conversion of PFAD to biodiesel reached 88.73% under the optimal condition of 140 min of reaction time, 10:1 of molar ratio of methanol to PFAD, 4 wt.% of catalyst concentration, 70°C of reaction time and 600 rpm of agitation speed. Reusability test was carried out and the conversion of PFAD was less than 26% when the catalyst was reused.

ABSTRAK

PENGGUNAAN PEMANGKIN ASID PEPEJAL UNTUK MENGHASILKAN BIODIESEL DARIPADA PALM FATTY ACID DISTILLATE (PFAD)

Liaw Kai Jun

Sukrosa telah diubah suai sebagai pemangkin untuk menghasilkan biodiesel daripada methanol dan PFAD sebagai bahan mentah. SEM, XRD, FTIR dan EDS telah digunakan untuk mengajikan ciri-ciri pemangkin disintesis. Kesan suhu reaksi, masa reaksi, kelajuan pergolakan, nisbah molar metanol kepada bahan mentah dan penumpuan pemangkin kepada penukaran PFAD telah dikaji. One-Variable-At-One-Time dan RSM telah digunakan sebagai cara untuk mengoptimumkan sintesis biodiesel. Penukaran PFAD kepada biodiesel adalah 88.73% dalam keadaan optimum dengan 140 min masa reaksi, 10:1 nisbah molar metanol kepada bahan mentah, 4 wt.% penumpuan pemangkin, 70 ° C masa reaksi dan 600 rpm kelajuan pergolakan. Penukaran PFAD adalah kurang daripada 26% apabila pemangkin telah digunakan semula.

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Lastly, I wish to thank to my family and lovely friends for their unconditional support and advice during my studies.

DECLARATION

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

Liaw Kai Jun

APPROVAL SHEET

This project report entitled "**BIODIESEL SYNTHESIS VIA SOLID ACID CATALYST BY USING PALM FATTY ACID DISTILLATE (PFAD) AS FEEDSTOCK**" was prepared by LIAW KAI JUN and submitted as partial fulfillment of the requirements for the degree of Bachelor of Science (Hons) Chemistry at Universiti Tunku Abdul Rahman.

Approved by:

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(Mr Theam Kok Leong) Date: 27 May 2013

Supervisor

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Date: 27 May 2013

PERMISSION SHEET

It is hereby certified that **LIAW KAI JUN** (ID No: **09ADB04830**) has completed this final year project entitled "**BIODIESEL SYNTHESIS VIA SOLID ACID CATALYST BY USING PALM FATTY ACID DISTILLATE (PFAD) AS FEEDSTOCK**" supervised by Mr. Theam Kok Leong (Supervisor) from Department of Chemical Science, Faculty of Science.

I hereby give permission to my supervisor to write and prepare manuscripts of theses research findings for publishing in any form, if I do not prepare it within six (6) months from this date, provided that my name is included as one of the authors for this article. The arrangement of the name depends on my supervisor.

Yours truly,

____

(LIAW KAI JUN)

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LIST OF ABBREVIATIONS

FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
PFAD	Palm Fatty Acid Distillate
$Al(HSO_4)_3$	Aluminum hydrogen sulfate
RSM	Respond Surface Methodology
CCD	Central Composite Design
ZrO_2	Zirconium dioxide
GC-FID	Gas Chromatography – Flame Ionization Detector
S400P	Partial Carbonized Sucrose Precursor
S400	Sulfonated Partial Carbonized Sucrose
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier transform infrared spectroscopy
TPD – NH_3	Temperature Programmed Desorption – Ammonia

CHAPTER 1

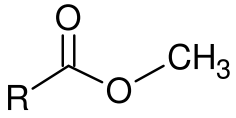
INTRODUCTION

1.1 Current Issue

Energy resources are the resources that provide energy and it can be classified into renewable and non-renewable resource. The renewable resources are those that are replenished through biogeochemical and physical cycles. By contrast, non-renewable resources do not replenish themselves. However, fossil fuels are considered as non-renewable resource because they replenish at a very slow rate (Demirbas, 2008). The depleting of petroleum reserves and the environmental issue as the consequence by the exhaust gases from petroleum-fuelled engine increases the demand for the alternating fuels for the diesel engines (Vasudevan and Briggs, 2008).

1.2 Biodiesel

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent fuel that derived from biological source (Demirbas, 2008; Demirbas, 2009). Chemically, biodiesel is defined as the mono-alkyl esters of fatty acids that derived from vegetable oil or animal fat and its chemical name is known as fatty acid methyl ester (FAME) (Gerpen, Shanks, Pruszko, Clements and Knothe, 2004). In addition to animal fat and edible vegetable oils, the raw material as source of biodiesel are included non-edible vegetable oils, used frying oil, trap grease and float grease (Demirbas, 2009; Gerpen et al., 2004; Lotero et al., 2005).



where R is the long chain fatty acid

Figure 1.1: The structure of the FAME.

1.2.1 Technical Properties of Biodiesel

Biodiesel is an ester comprise of alkyl fatty acid chain and short chain alcohols, where the chain length of fatty acid is C_{14}-C_{22} and the alcohols are primarily methanol and ethanol. Biodiesel is a clear amber yellow liquid with a viscosity range of 3.3-5.2 mm^2/s at 313K and density range from 860-894 kg/m^3 at 288K. The flash point and distillation range of biodiesel are 420-450K and 470-600K respectively. The boiling point range of biodiesel is higher than 475K and its vapor pressure is greater than 5 mmHg at 295K (Demirbas, 2008).

1.2.2 Advantages of Biodiesel

The existence of biodiesel has been concerned by scientist about the advantages and disadvantages of biodiesel. The advantages of biodiesel are included ready availability, renewability, lower sulfur and aromatic content (Ma and Hanna, 1999). This is because the raw material used to synthesis biodiesel are included edible and non-edible vegetable oils and animal fats, waste frying oil and other low-grade feedstock (Demirbas, 2009; Gerpen et al., 2004; Lotero et al., 2005). Biodiesel can be blended with diesel and run on conventional unmodified engines. Besides, biodiesel is safe to handle and transport due to its biodegrability (Knothe, 2005; Demirbas, 2007).

Biodiesel contains 11% oxygen by weight and it is also claimed by having higher combustion efficiency of biodiesel due to the oxygen-content of biodiesel improves the combustion process. Moreover, the use of biodiesel can extended the life of engines because biodiesel have better lubricant properties than petrodiesel. Biodiesel also have lower emissions with 90% reduction in total unburned hydrocarbons and reduction in polycyclic aromatic hydrocarbons (PAHs), reduction in particulates and carbon monoxide (Ma and Hanna, 1999).

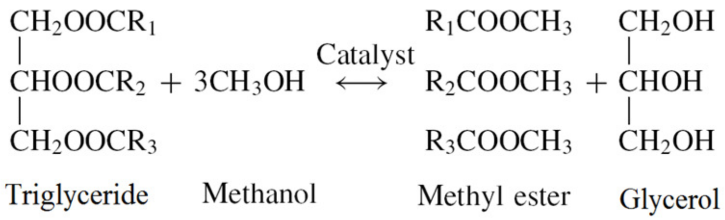
1.2.3 Disadvantages of Biodiesel

Major disadvantages of biodiesel are higher viscosity, higher cloud point and pour point, higher nitrogen oxides (NO_X) emissions, expensive, lower energy content, injector coking and engine compatibility (Demirbas, 2008). The operating disadvantages of biodiesel is also included cold start problems, higher copper strip corrosion and fuel pumping difficulty from higher viscosity (Ma and Hanna, 1999).

1.3 Methods to Synthesize Biodiesel

1.3.1 Transesterification/ Esterification

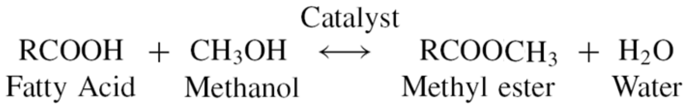
Transesterification (can be called as alcholysis) is a reversible process that converting the fat or oil triglycerides with an alcohol to form esters and glycerol. It requires catalyst to improve the reaction rate and yield and excess alcohol to shift the equilibrium to the product side (Demirbas, 2009). All the feedstock that can use to synthesize biodiesel consists primarily of triglycerides molecules and during the transesterification process, the triglyceride molecule is heated with an excess of alcohol in the presence of a catalyst to produce the fatty esters and glycerol (Gerpen et al., 2004). The reaction of transesterification was illustrated in Figure 1.2.



$$\begin{matrix} CH_2OOCR_1 & & & R_1COOCH_3 & & CH_2OH \\ | & & & & & | \\ CHOOCR_2 & + \; 3CH_3OH & \xleftrightarrow{\text{Catalyst}} & R_2COOCH_3 & + & CHOH \\ | & & & & & | \\ CH_2OOCR_3 & & & R_3COOCH_3 & & CH_2OH \\ \text{Triglyceride} & \text{Methanol} & & \text{Methyl ester} & & \text{Glycerol} \end{matrix}$$

Figure 1.2: Transesterification reaction between triglycerides and methanol

Esterification is an acid-catalyzed chemical reaction between free fatty acid (FFA) and alcohol which yields fatty acid alkyl ester and water (Zhang et al., 2003). Esterification of fatty acid is faster than transesterification of triglycerides due to esterification is one step reaction while transesterification of triglycerides consists of three stepwise reactions (Warabi, Kusdiana and Saka, 2004). The reaction of esterification was illustrated in Figure 1.3.



$$\underset{\text{Fatty Acid}}{RCOOH} + \underset{\text{Methanol}}{CH_3OH} \xleftrightarrow{\text{Catalyst}} \underset{\text{Methyl ester}}{RCOOCH_3} + \underset{\text{Water}}{H_2O}$$

Figure 1.3: Esterification reaction between fatty acid and methanol

1.4 Catalyst Used in Transesterification and Esterification

1.4.1 Basic Catalyst for Transesterification

There have two types of basic catalyst mainly homogeneous basic catalyst and heterogeneous basic catalyst. The examples of homogeneous alkali catalyst are included sodium hydroxide, potassium hydroxide and sodium methoxide

(Leung and Guo, 2006). The examples of heterogeneous alkaline catalyst are basic Mg–Al–CO_3 hydrotalcite catalyst (Barakos et al., 2007), CaO, MgO and CaO/Al_2O_3 (Umdu et al., 2009).

1.4.1.1 Advantages of Homogeneous Basic Catalysts

Homogeneous basic catalyst is mainly used in biodiesel production via transesterification due to several advantages possessed by this catalyst. High yield of biodiesel (> 96%) can achieve under these optimum condition of reaction temperature of 70°C, reaction time of 1 h, catalyst concentration 1 wt% and molar ratio of methanol to oil of 6:1 (Agarwal et al., 2011). This result also have agreement with other researchers that homogeneous basic catalyst can produce biodiesel from neat oil with high yield in low temperature and pressure, short reaction time, low catalyst concentration and low molar ratio of methanol to oil (Ejikeme et al., 2009; Leung and Guo, 2006).

1.4.1.2 Disadvantages of Homogeneous Basic Catalysts

This process required anhydrous condition (Demirbas, 2006) and low content of FFA (Leung and Guo, 2006; Donato et al., 2008; Demirbas, 2006). This is due to presence of water will decrease the yield of the alkyl ester (Demirbas, 2006) while presence of FFA will react with the base catalyst and form saponification product and tend to emulsify the biodiesel and glycerol, resulting difficulty of separating these two products (Leung and Guo, 2006; Donato et al., 2008; Melero, Iglesias and Morales, 2009), consume catalyst and reduce effectiveness of catalyst (Demirbas, 2006; Leung and Guo, 2006).

1.4.1.3 Advantages of Heterogeneous Basic Catalysts

Heterogeneous basic catalyst was developed to overcome the limitation of homogeneous basic catalyst which mainly is separation of catalyst from reaction mixture, generation of waste water during washing stages (Sharma et al., 2010) and reusability of catalyst (Shahid and Jamal, 2011). Besides, the heterogeneous catalyst also preferred due to reusability of catalyst for continuous process. The biodiesel obtained from heterogeneous catalyst were better than those biodiesel synthesized from homogeneous catalyst in term of physical properties of pour and cloud point (Agarwal, 2011).

1.4.1.4 Disadvantages of Heterogeneous Basic Catalysts

However, the heterogeneous base catalyst only can use to covert neat vegetable oil into biodiesel due to it will react with FFA and moisture to form soap and caused deactivation of catalyst respectively (Kouzu et al., 2007). Besides, the catalyst have low stability that the reusability of the catalyst drop after 3 cycles resulted low yield of biodiesel production (Agarwal et al., 2011).

In addition, longer reaction duration and higher reaction temperature were needed to improve the yield of biodiesel production (Sharma et al., 2010).

1.4.2 Acidic Catalyst for Transesterification and Esterification

Similar to basic catalyst, acidic catalyst composed of homogeneous catalyt and heterogeneous catalyst. Sulfuric acid, methanesulfonic acid, phosphoric acid and trichloroacetic acid (Melero, Iglesias and Morales, 2009; Warabi, Kusdiana and Saka, 2004) are the types of homogeneous acidic catalyst while alkyl sulfonic compounds (Melero, Iglesias and Morales, 2009; Warabi, Kusdiana and Saka, 2004), sulfated zirconia (Garcia et al., 2007), and Zirconia supported tungsten oxide (WO_3/ZrO_2) (Ramu et al., 2004).

1.4.2.1 Advantages of Homogeneous Acidic Catalysts

Warabi et al. (2004) concluded that sulfuric acid and methanesulfonic acid were the best catalyst with nearly 90% conversion from triglycerides to biodiesel among phosphoric acid and trichloroacetic acid. Besides, those homogeneous acid catalyst can convert feedstock with high FFA into biodiesel with yield that higher than 90%. This is because homogeneous acidic catalyst can catalyze esterification and transesterification simultaneously to convert the FFA and triglycerides respectively into fatty acid methyl ester without any soap formation.

1.4.2.2 Disadvantages of Homogeneous Acidic Catalysts

However, the disadvantages by using homogeneous catalyst are formation of acidic effluent, no reusable catalyst and high cost of equipment. In addition, it has low catalytic activity that it need long reaction time and high mole ratio of methanol to feedstock (Wang et al., 2006). There have research shown that the usage of sulfuric acid will lead to biodiesel with high sulfur content which cannot fulfill the specification (Melero, Iglesias and Morales, 2009).

1.4.2.3 Advantages of Heterogeneous Acidic Catalysts

Heterogeneous acid catalyst can replace homogeneous acid catalyst to eliminate the problem of equipment corrosion and the treatment of water effluent produced after the process. Besides, heterogeneous acid catalysts can remove easily from the reaction medium through filtration and the catalyst can be recycled for reuse in the new process, thus, no loss of catalyst (Melero, Iglesias and Morales, 2009; Shu et al., 2010). In addition, heterogeneous acid catalyst has higher stability that able to have high tolerance of free fatty acid without catalyst deactivation (Lotero et al., 2005).

1.4.2.4 Disadvantages of Heterogeneous Acidic Catalysts

However, heterogeneous catalyzed reaction has low catalytic activity (Lotero et al., 2005). Some other group of author also stated that heterogeneous catalyzed reaction requires extreme reaction conditions in order to increase the yield of biodiesel and to shorten the reaction time (Rattanaphra et al., 2012). In addition, high temperature and pressure is needed and higher methanol to oil ratio is needed as well (Melero, Iglesias and Morales, 2009).

1.5 Palm Fatty Acid Distillate (PFAD) as Feedstock

Palm fatty acid distillate (PFAD) is the by-product during the refining of palm oil and is mainly produced in the fatty acid stripping and deodorization stage. According to Chongkhong et al. (2007), the free fatty acid content present in PFAD is 93 wt.% which composed of 45.6 % of palmitic acid, 33.3 % oleic acid, 7.7 % of linoleic acid, 3.8 % stearic acid, 1.0% myristic acid, and other. PFAD is low-cost and non-food source of feedstock. It has been used as a fuel in power plants and industrial boilers. In Sumatra, Indonesia, biodiesel plant was set up and PFAD was used as the raw material to manufacture biodiesel (Cheah, Toh, and Koh 2010).

1.6 Objectives

The major objectives of this research study are as followings:

I. To synthesize biodiesel from PFAD through esterification reaction with methanol
II. To characterize a synthesized catalyst and determine its catalytic activity in esterification reaction
III. To optimize the synthesis condition for biodiesel production from PFAD

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel Synthesis from PFAD or Other Feedstocks with High FFA Level

In study of Peng et al. (2008), waste oil feedstock was used in esterification for biodiesel synthesis by using a solid catalyst comprising SO_4^{2-}/TiO_2-SiO_2. This catalyst has a large specific surface of 258 m^2/g and big average pore diameter of 10.8 nm. This properties of large specific surface catalyst ensured good contact between the reactant molecules and catalytic active site, and the big average pore allow the molecules of reactant and product can pass through the channel. High content of Ti and S on the surface also indicate this catalyst have high catalytic activity. The optimized reaction parameters have about 95% yield of biodiesel with the parameter of reaction temperature 200˚C, reaction time 6 h, molar ratio of methanol to oil 9:1 and catalyst concentration 3 wt. %.

Another group of researchers (Ramachandran, Sivakumar and Suganya, 2011) used $Al(HSO_4)_3$ heterogeneous acid catalyst to catalyze transesterification reaction to synthesis methyl ester from a mixed waste vegetable oil. This catalyst has a loose irregular network structure and it existed as granular and porous structure. The big average pore size of 69.22 nm allowed the incorporation of sulfonic group into the aluminum powder increased the catalytic activity of this catalyst. In the optimum condition of 16:1 molar ratio of methanol to oil, 0.5 wt.% of catalyst, 50 min reaction time at 220°C, the maximum conversion of triglyceride was achieved as 81 wt.%. The high catalytic activity and stability of this catalyst was related to its high acid site density (–OH, Brönsted acid sites), hydrophobicity that prevented the hydration of –OH group, hydrophilic functional groups (–SO_3H) that gave improved accessibility of methanol to the triglyceride.

Lou et al. (2008) reported preparation of carbohydrate-derived catalysts from various D-glucose, sucrose, cellulose and starch type carbohydrates, had the best catalytic performance. The carbohydrate-derived catalysts have high density of SO_3H group as 1.47-1.83 mmol/g, small surface areas ranged from 4.1-7.2 m^2/g and average pore size of 4.0-8.2 nm. Those properties made carbohydrate-derived catalyst have higher activities for both esterification and transesterification after compared to the two typical solid acid catalysts (sulfated zirconia and Niobic acid). The comparison of catalytic activities of those carbohydrate-derived catalysts, typical solid acid catalyst and concentrated H_2SO_4 was shown in Figure 2.1 in the reaction condition of 10mmol oleic acid or triolein as feedstock, 100 mmol methanol, 80˚C, 500 rpm and 0.14 g of catalyst.

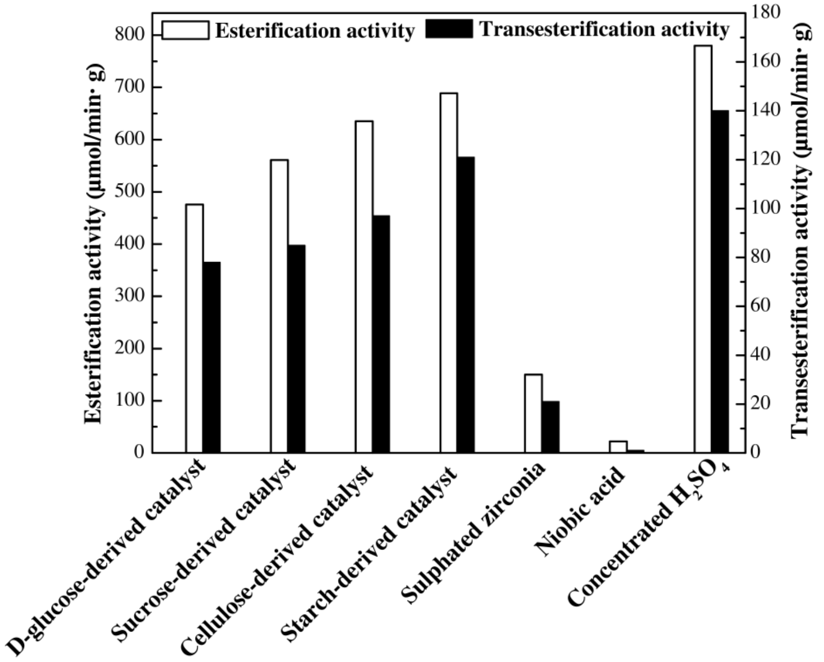


Figure 2.1: Comparison of catalytic performance of different acidic catalyst

Under the optimized reaction conditions, this starch-derived catalyst gave markedly enhanced yield of methyl esters (92%) in converting waste cooking oils containing 27.8 wt. % high free fatty acids (FFAs) to biodiesel even after 50 cycles of successive re-use (8 h per cycle) and thus displayed very excellent operational stability.

2.2 Proposed Catalyst for Biodiesel Synthesis from PFAD

Based on section 2.1 above, and the choice of feedstock used (PFAD), which contained high amount of FFA (Chongkong et al., 2007), the starch-derived catalyst would be a suitable catalyst for biodiesel production from PFAD through esterification method due to its comparable catalytic activity with concentration H_2SO_4 (Lou et al., 2008). Starch-derived catalyst can undergo incomplete carbonization to form a rigid carbon material that composed of small polycyclic aromatic carbon sheet with carbonyl group and phenolic group (Mo et al., 2008). This material can undergo sulfonation to create a stable solid with a high density of active sites by oxidizing the aliphatic CH_3/CH_2 groups to carboxylic acid and introducing SO_3H group (Mo et al., 2007; Takagaki et al., 2006; Lou et al., 2008, Toda et al., 2005). The reaction of pyrolysis, carbonization, and sulfonation is shown in Figure 2.2.

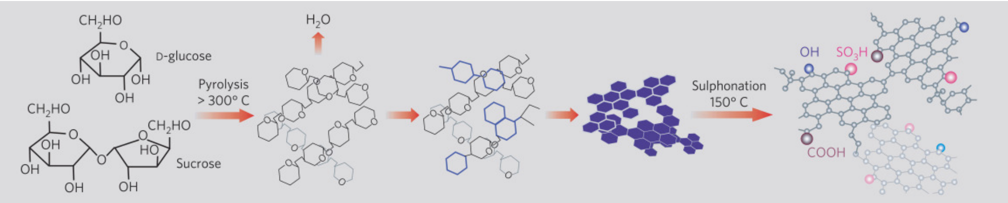


Figure 2.2: The reaction of pyrolysis, carbonization and sulfonation of D-glucose and sucrose

According to Lou et al. (2008), starch-derived catalyst was non-toxic, inexpensive and recyclable. Besides, this catalyst has higher effectiveness then typical sulfated zirconia in converting waste oil with high FFA content to biodiesel through esterification and transesterification. However, another group of author (Mo et al., 2008; Chen and Fang, 2010) stated that the catalyst activity of this sulfonated carbon catalysts will be depressed due to the leaching of sulfonic group. Nevertheless, in study of Chen and Fang (2010), the catalyst activity of solid acid catalyst prepared from glucose-starch mixture, can be reactivated by washing by 5% and 98% H_2SO_4 but the mechanism of catalyst regeneration by 98% H_2SO_4 needed verifying in the future research.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Palm Fatty Acid Distillate, PGEO Edible Oils Sdn, Bhd.

Methanol Analytical Grade, Fisher Scientific U.K. Limited

Sulfuric Acid 98%, RCI LabScan Limited

Sucrose, R&M Chemical

Ethanol vol 95%, HmbG Chemicals

Diethyl Ether Analytical Grade, Fisher Scientific U.K. Limited

Potassium Hydroxide Pellets Analytical Grade, Systerm

Phenolphthalein, HmbG Chemicals

Hexane HPLC Grade, Merck KGaA

Hexane Analytical Grade, R&M Chemical

3.2 Characterization of Feedstock

3.2.1 Preparation of Samples for Acid Value Test

The biodiesel samples were taken as close to 0.5g in a conical flask. 5 mL of the solvent was added into the flask and was shaken until all the sample had dissolved. 1 mL of Phenolphthalein was added into the flask. The sample was titrated with standardized potassium hydroxide solution until the first permanent pink colour. The acid value test was calculated using the following Formula 3.1:-

$$\text{Acid Value} = \frac{\text{N}\times\text{MW}\times\text{Volume of Titrant Used}}{\text{Mass of Biodiesel Sample}}$$

where, (Formula 3.1)

N= Normality of Potassium Hydroxide (KOH) used

MW= Molecular Weight of Potassium Hydroxide; 56.11g/mol

The percentage of conversion of the Free Fatty Acids was calculated using the Formula 3.2 below:-

$$\text{Percentage of Conversion, \%} = \frac{(\text{Acid Value of Feedstock} - \text{Acid Value of Sample})}{\text{Acid Value of Feedstock}} \times 100\%$$

(Formula 3.2)

3.3 Synthesis of Catalyst

3.3.1 Preparation of Partial Carbonized Sucrose Precursor, S400P

The calcines were pyrolysed in the flow of nitrogen gas. The resultant solid was ground then dried in desiccators.

3.3.2 Preparation of Partial Sulfonated Carbonized Sucrose, S400

The precursor was mixed with concentrated sulfuric acid. Then the mixture was heated for 15 hours in the flow of nitrogen gas. After the sulfonation, the mixture was diluted by distillated water with a 20 times of the total volume of sulfuric acid used. The diluted mixture then filtered and washed with hot water. This sulfonated carbonized sucrose was denoted as S400.

3.4 Catalyst Characterization

3.4.1 X-Ray Diffraction (XRD)

The analysis was carried out by using Shimadze Diffractometer model XRD-6000. The scanning parameters of the X-Ray Diffractometer were as followed:-

- CuK α radiation with 1.5418Å wavelength
- Scan axis of Theta-2 Theta
- Range of 5° to 80°
- Speed of 2°/mins
- 0.02° pitch
- Present time of 0.6 sec
- 40kV
- 30mA

3.4.2 Scanning Electron Microscope (SEM)

The observation was done by using JSM – 6701 F Field Emission SEM. The catalyst sample was put under Scanning Electron Microscope to observe its morphology of the sample surface under 3.0kV; X 1900, 3.0kV; X 15000; 3.0kV; X 40000. The specifications of the SEM done were listed as below:-

- 1.0nm (15kV), 2.2nm (1kV)
- Accelerating Voltage of 0.5kV to 30kV
- Magnification of ×25 to ×650,000
- Cold field emission electron gun

After the observation, the images were saved, and a rough estimation of the particle size can be done by comparing the particle size observed with the measurement obtained from the SEM image.
value of known element then the presence of an element in the sample can be identified.

3.4.3 Infrared (IR) Spectroscopy

Infrared (IR) Spectroscopy was done using Potassium Bromide (KBr) plate and Perkin Elmer FT-IR Spectrometer. A radio of 10:1 of KBR pellets to the catalyst powder was mixed and the mixture of KBr powder and catalyst powder was compressed into a thin plate by using hydraulic press. The plate was later placed on the sample holder and scanned using Infrared Spectrometer at the scan range of $4000cm^{-1}$ to $600cm^{-1}$.

3.5 Synthesis of Biodiesel

10g of preheated PFAD was poured into the 250 mL conical flask and immersed in a 70˚C oil bath under 600 rpm agitation speed. The mass of methanol with the methanol/PFAD molar ratio of 20:1 was mixed with 2 wt.% of synthesized solid catalyst and poured into the preheated PFAD then refluxed for 90 min. The biodiesel was bottled for further analysis.

3.6 Preparation of Various Solutions for Biodiesel Characteristics

3.6.1 Preparation of Various Solutions for Acid Value Test

(Discussed previously in Section 3.2)

3.6.2 Preparation of Solvent for Thin Layer Chromatography

Analytical grade of Hexane, Diethyl Ether and Acetic Acid were used with the ratio of the solvent of 75:25:1.

3.6.3 Preparation of Dye for Thin Layer Chromatography

10% by mass of Phosphomolybdic Acid was added into 95% Ethanol by volume, the solution was stirred with a stir bar until the solution is homogeneous. The solution was then poured into a screw capped bottle and the cap was screwed tight, parafilm sealed and kept in the fridge until further usage.

3.7 Preparation of Samples for Biodiesel Characterization

3.7.1 Acid Value Test

(Discussed previously in Section 3.2)

3.7.2 Thin Layer Chromatography (TLC)

3.7.2.1 Preparation of TLC Development Chamber

A container with a good cover such as a used jar can be used as a developing chamber. A piece of filter paper was placed into the jar and about 1 cm high solvent was poured into the flask. The jar was left sealed for 5 minutes for the solvent to saturate the tank.

3.7.2.2 Dilution for Sample and Feedstock

The feedstock and biodiesel samples were diluted with analytical grade hexane with a ratio of 1:4.

3.7.2.3 Preparation of the TLC Plate

The silica Thin Layer Chromatography (TLC) plates were cut into 10x4 cm in size, and 1 cm lines were drawn across the top and bottom of the plates. The samples were spotted carefully at the bottom line of the surface of the plate and labeled. The plates were put into the developing tank. When the solvent reaches the top line, the plate was taken out and was dipped in the dye prepared. After dipping, the plates were immediately left to develop at 80˚C oven for 15 minutes.

3.7.3 Viscosity Test

The sample biodiesel was poured into the viscometer (Poulten Selfe & Lee Ltd) until the maximum point of the viscometer. The viscometer was then immersed in the water bath until thermal equilibrium. Then the sample biodiesel was pumped above the top mark and when the biodiesel drops until the top mark, the timer was started and stopped when it drops to the lower mark. The viscosity can be calculated by using the Formula 3.4 below:-

$$\text{Viscosity} = Ct$$

Where, (Formula 3.4)

t = time taken for sample to drop from top mark to lower mark

C = Calibration Constant of Viscometer = 0.009794 (mm^2/s)/s (Poulten Selfe & Lee Ltd)

3.7.4 Liquid Infrared (IR) Spectroscopy

Liquid Infrared (IR) was done using Zinc Selenide Sample Holder and Perkin Elmer FT-IR Spectrometer instead of the normal infrared plates using Potassium Bromide (KBr) pellets. The sample was added drop wise onto the plate, then covered slowly to ensure there were no bubbles trapped between the plates and the sample was scanned using Infrared Spectrometer at the scan range of $4000cm^{-1}$ to $600cm^{-1}$.

3.7.5 Water Contents

5 g of biodiesel was weighed and heated on 110˚C with stirring for 1 hour. After the biodiesel was allowed to cold down to room temperature, the mass of the biodiesel was measured.

3.8 Reusability Test of Catalyst

After determined the exact optimized parameters for biodiesel synthesize, biodiesel was synthesized through the exact optimized parameters. The catalyst was removed after each synthesis and washed with methanol. The methanol was removed and new methanol was introduced to the catalyst with the optimized amount and the biodiesel synthesis was repeated again for 2 times.

3.9 Characterization of Biodiesel from Reusability Test

3.9.1 Acid Value Test

(Discussed previously in Section 3.2)

CHAPTRER 4

RESULTS AND DISCUSSIONS

4.1 Characterization of Feedstock (PFAD)

4.1.1 Acid Value Test

The solid nature of the feedstock was due to the presence of high saturation fatty acid. Therefore, the feedstock needs to be heated to liquid state before the addition of other reactants. The acid value for feedstock is 252.56 mg KOH/g. This value will be used to calculate the conversion of PFAD to biodiesel.

4.1.2 Liquid Infrared (IR) Spectroscopy

Figure 4.1 shows the IR spectrum of PFAD. The spectrum of PFAD was compared with the oleic acid in the database (No. F75093) and they have similar pattern. Hence this can be concluded that PFAD mainly containing fatty acid. The peak at 1704 cm^{-1} indicate the stretching of carbonyl group of carboxylic acid and the broad peak near 3000cm^{-1} is due to stretching of hydroxide group (-OH). Posada et al. (2007) stated that PFAD is a mixture containing free fatty acids, squalene, vitamin E, sterols, glycerides and other unknown compound. Therefore those minor compound present in PFAD contribute the peak near 2360 and 2340 cm^{-1}.

```
Peak Table:

PFAD 3011201...  3401  4000.00  600.00  1.14  107.13  4.00  %T  3  1.00

REF: 4000 103.17  2000 100.88  600
  3699.00 99.60  3007.00 45.69  2920.00  2.22  2853.00  5.71
  2673.00 62.80  2361.00 75.42  2341.00 80.33  1708.00  1.14
  1463.00 27.39  1412.00 26.02  1378.00 63.37  1283.00 24.42
  1243.00 34.18  1117.00 71.46   932.00 33.94   782.00 101.96
   721.00 41.67   684.00 84.95   668.00 90.38
END 19 Peaks found
```

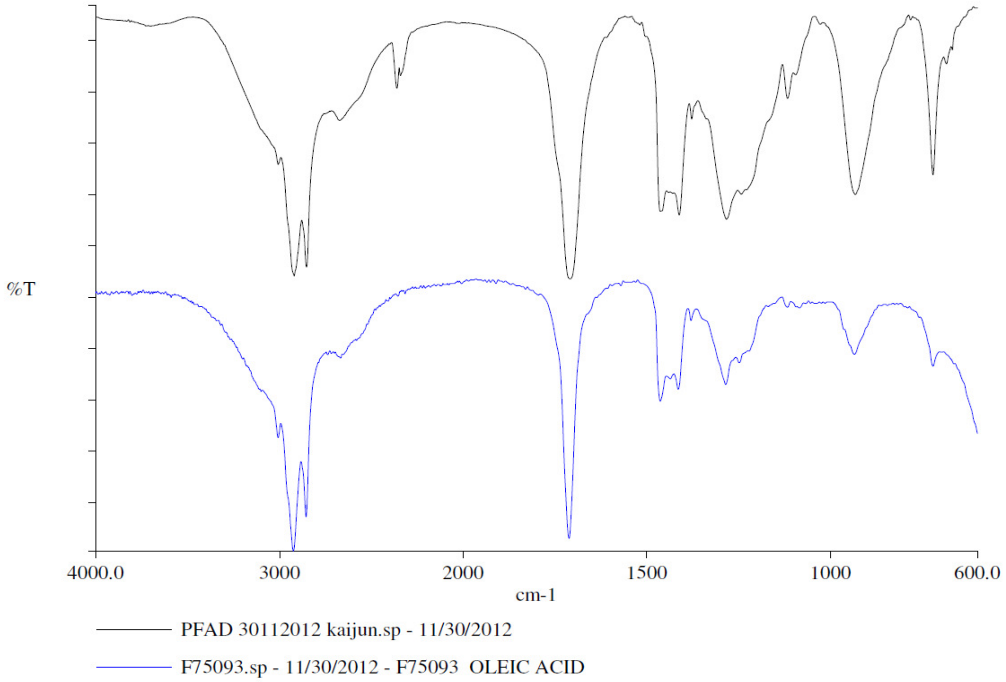


Figure 4.1: FTIR spectrum of PFAD

4.2 Characterization of catalyst

4.2.1 X-Ray Diffraction (XRD)

The XRD pattern of the precursor, S400P and sulfonated catalyst, S400 were shown Figure 4.2. According to Tsubouchi et al. (2003), the broad and weak peak at around 20° are assigned to the graphitic (0 0 2) planes.

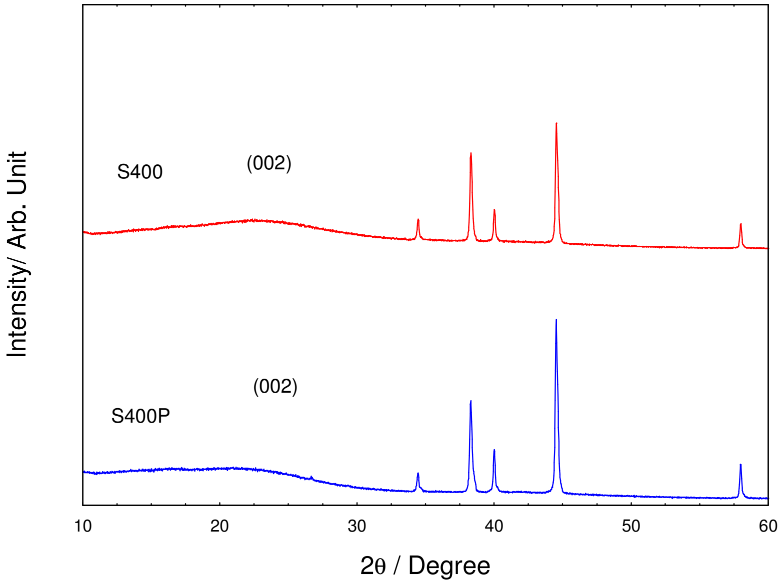


Figure 4.2: XRD pattern of S400P and S400

4.2.2 Scanning Electron Microscope (SEM)

Figure 4.3 shows the SEM images of the catalyst. The particle size of the catalyst is about 40μm and no obvious pores can be observed from the SEM images. When the particles were magnified to 4000 times, the SEM images was shown that the surface of the catalyst was not organized.

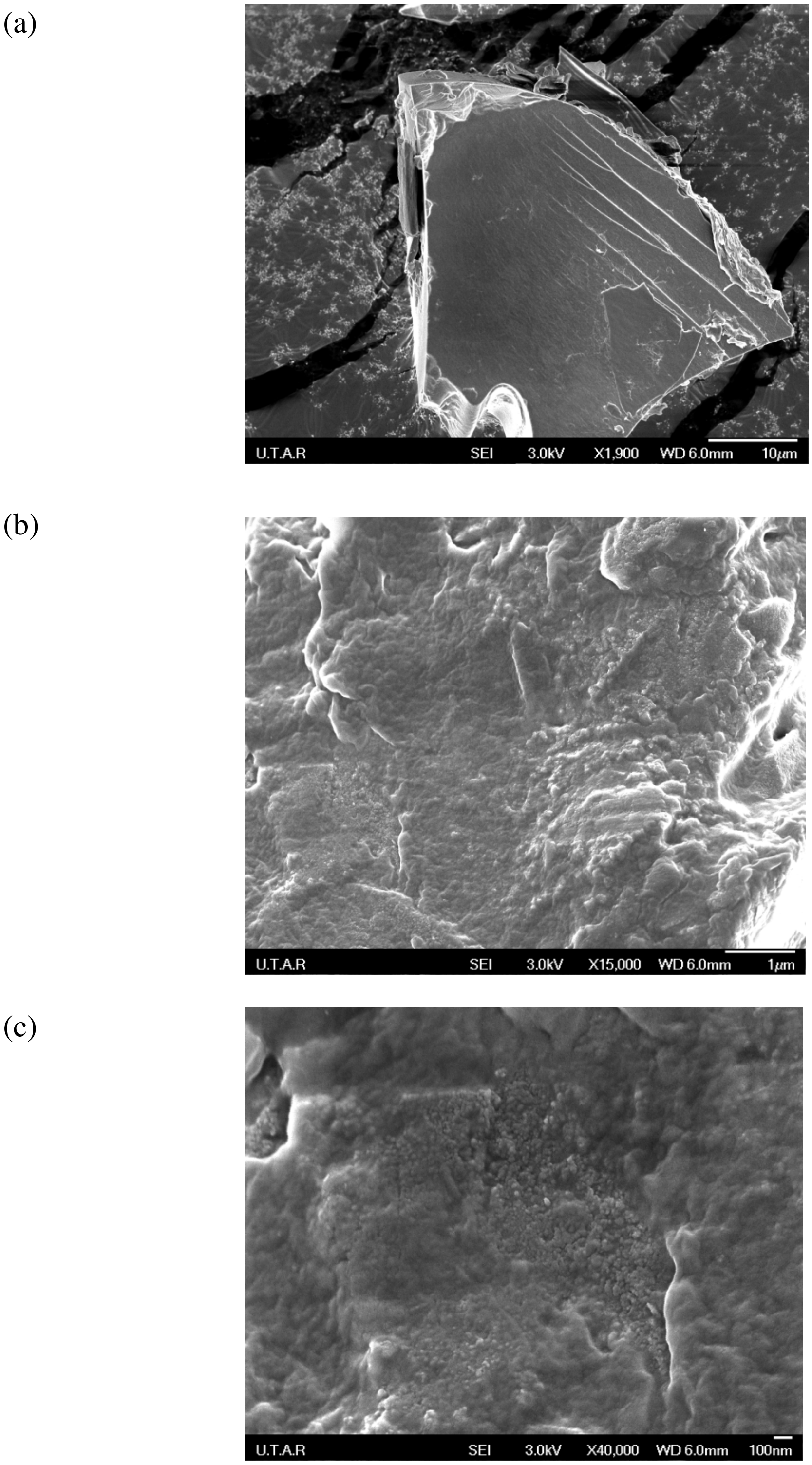


Figure 4.3: SEM images of sulfonated catalyst, S400 with magnification X1,900 (a), X15,000 (b) and X40,000 (c)

4.2.3 Infrared (IR) Spectroscopy

The IR spectrum for catalyst S400P as the precursor and S400 as the sulfonated catalyst were attached in Figure 4.4 and 4.5 respectively. The band at 3444 cm^{-1} were assigned to the –OH stretching modes of phenolic –OH groups while the bands at 1638 cm^{-1} and 1458 cm^{-1} were assigned to aromatic-like C=C stretching mode in polyaromatic sketch (Chen & Fang, 2010; Rao et al., 2011). This result is agreed with the finding of Mo et al. (2008) that incomplete carbonization of starch-derived catalyst can form a rigid carbon material that composed of small polycyclic aromatic carbon sheet with phenolic group. By comparing FTIR spectra between S400P and S400, S400 has new peak at 1700 and 1033 cm^{-1}. This is due to the stretching modes of carbonyl group of carboxylic acid group and stretching modes of sulfate groups (Shu et al, 2010) respectively. The carbon frameworks formed during high temperature carbonization have efficient IR absorption ability hence reduce the intensities of peak in FTIR spectrum (Nakajima and Hara, 2012). Hence, the intensity of FTIR spectra obtained in this analysis was low and the peaks were hardly to be identified.

a)

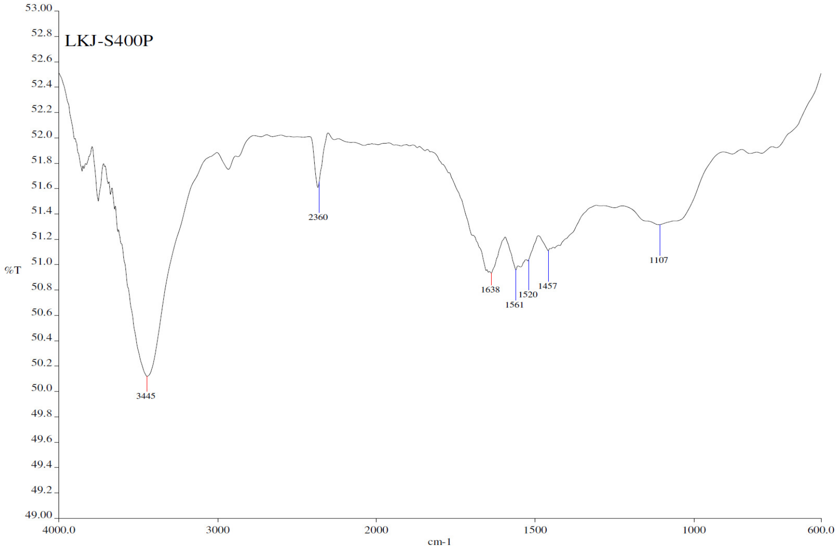


Figure 4.4: FTIR spectra of precursor, S400P

b)

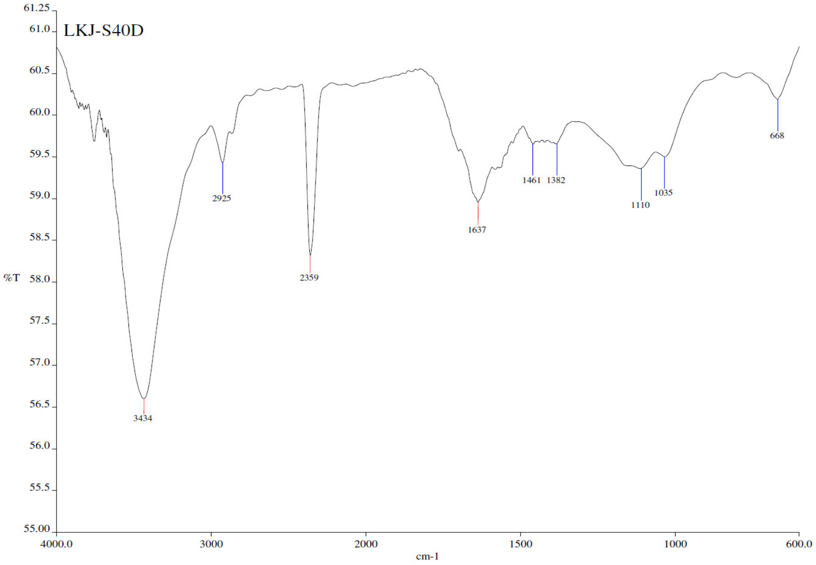


Figure4.5: FTIR spectra of sulfonated catalyst, S400

4.3 Optimization of Biodiesel

4.3.1 Optimization via One-Variable-At-A-Time

4.3.1.1 Temperature

Temperature is an important variable as it will influence the rate of the catalytic reaction. The range of temperature that used in this study was 50˚C to 100˚C. The respective conversion for each temperature was plotted and shown in the Figure 4.6. The 70°C was chosen as fix parameter for the following optimization.

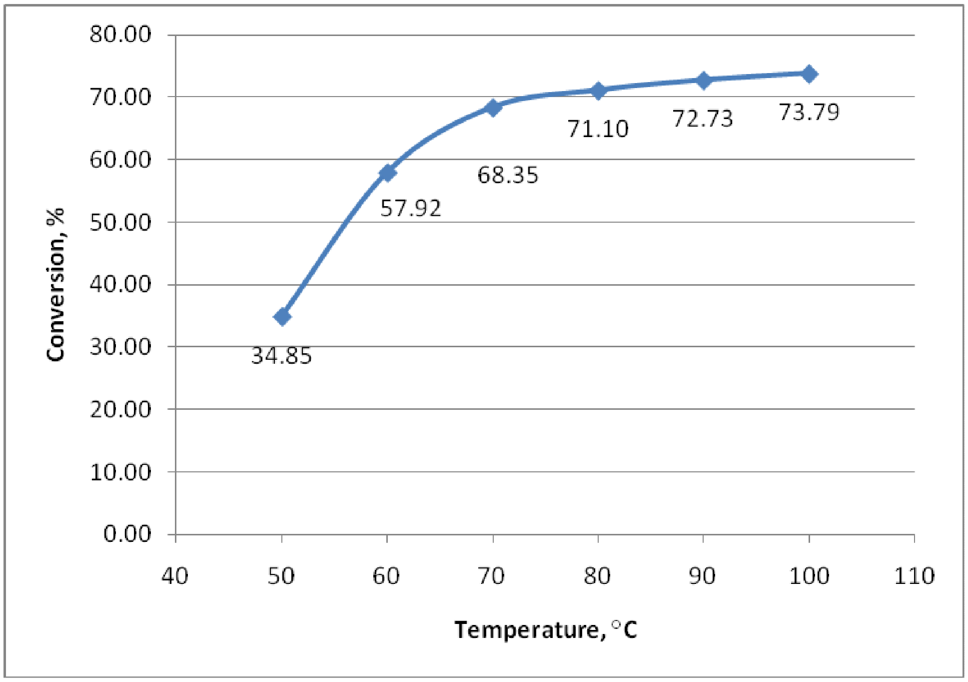


Figure 4.6: The effect of reaction temperature towards the fatty acid conversion

4.3.1.2 Reaction time

The reaction time from 30 min to 180 min was used to study its effect on conversion of PFAD to biodiesel. The respective percentage of conversion in each time interval was plotted and shown in the Figure 4.7. When the time exceeds 90 min, the percentage of conversion was increased by 2-3% per 30 min time increment. So the time range from 90-150 min was further study in the optimization method.

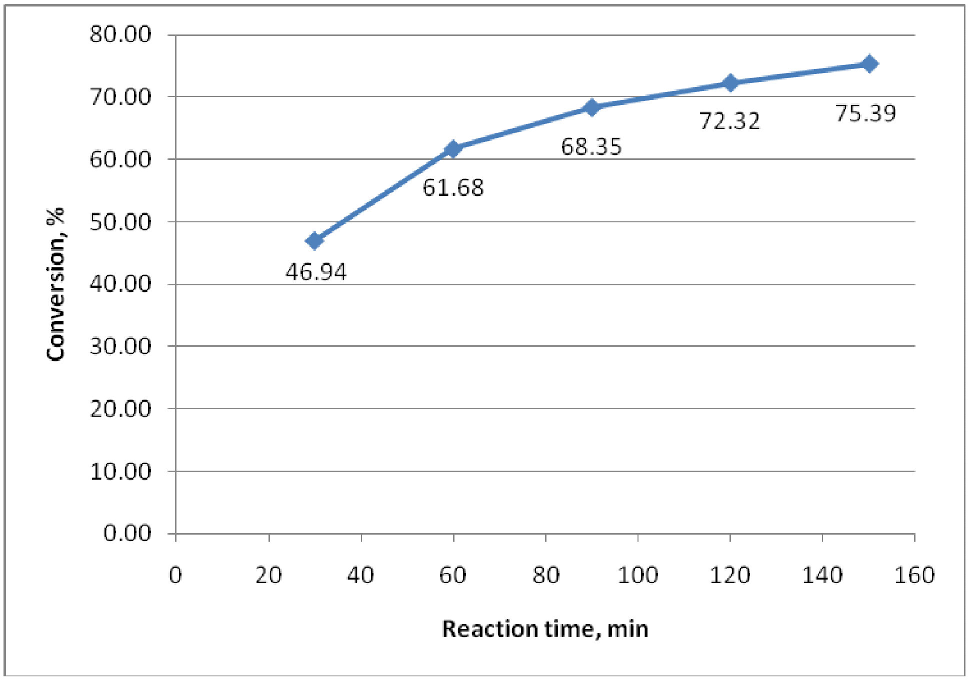


Figure 4.7: The effect of reaction time towards the fatty acid conversion

4.3.1.3 Catalyst Concentration

The catalyst concentration from 0.5 to 5 wt.% was manipulated to determine the effect on the PFAD conversion. The respective percentage of conversion for each concentration of catalyst used was plotted and shown in the Figure 4.8. When the catalyst concentration reached 4%, there was no significant increment in the conversion. Hence, the range of catalyst concentration involved in following optimization is 2 to 4 wt.%.

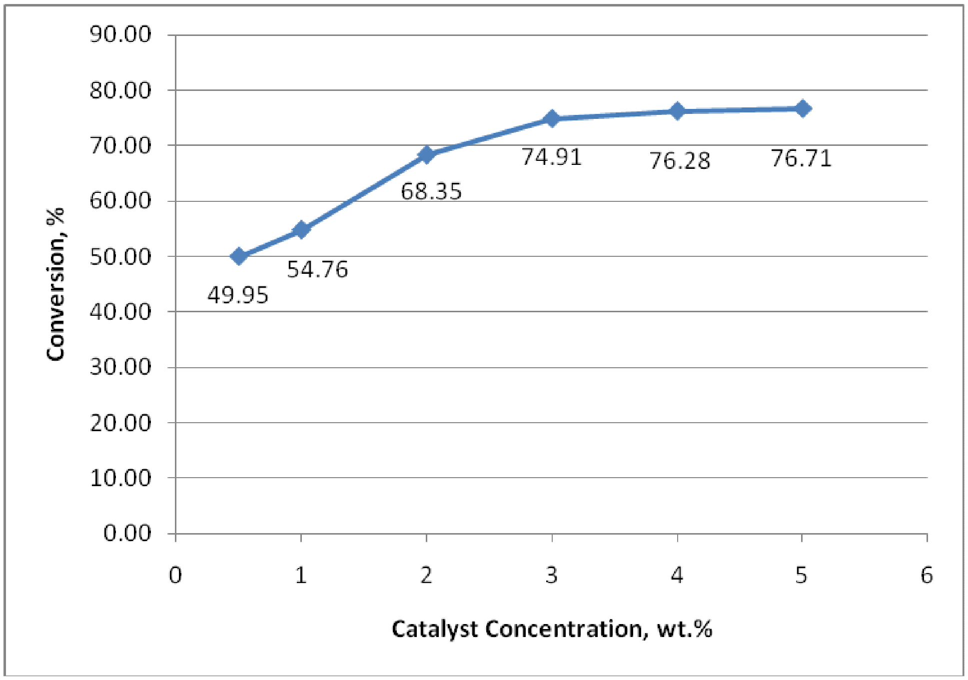


Figure 4.8: The effect of catalyst concentration towards the fatty acid conversion

4.3.1.4 Molar Ratio of Methanol to Feedstock

The molar ratio of methanol to feedstock ranged from 2.5:1 to 20:1 was used and the conversion was plotted in the Figure 4.9. From the trend result, it suggested the optimal range for molar ratio of methanol to feedstock was between 5:1 to 10:1.

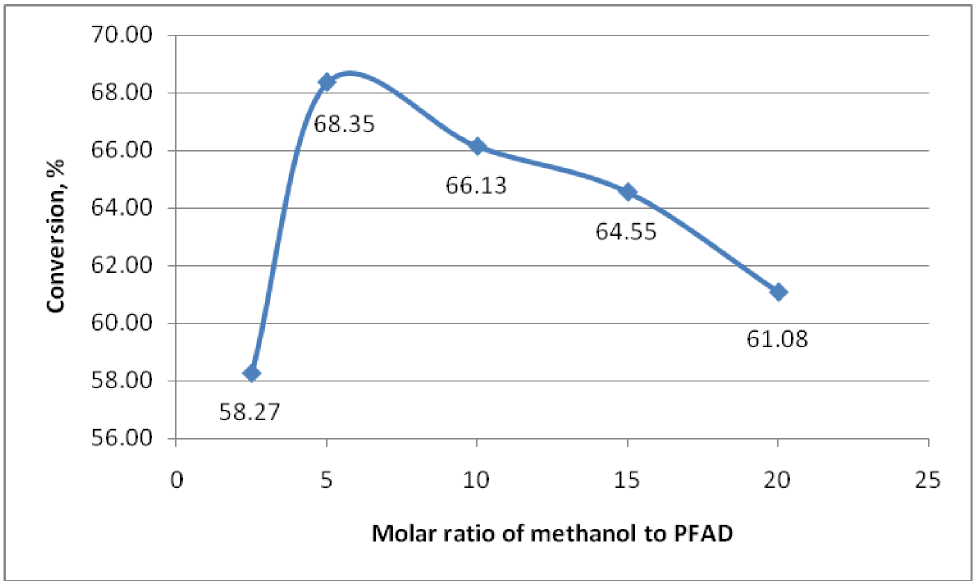


Figure 4.9: The effect of molar ratio of methanol to PFAD towards fatty acid conversion

4.3.1.5 Agitation Speed

The agitation speed with 0 rpm to 800 rpm was used to investigate its effect towards conversion of PFAD. Their respective percentage conversion with different agitation speed was plotted and shown in Figure 4.10. In this part, the biodiesel production does not have significant difference with the increase of agitation speed. The 600 rpm was selected as the fixed parameter since it has the highest percentage of conversion.

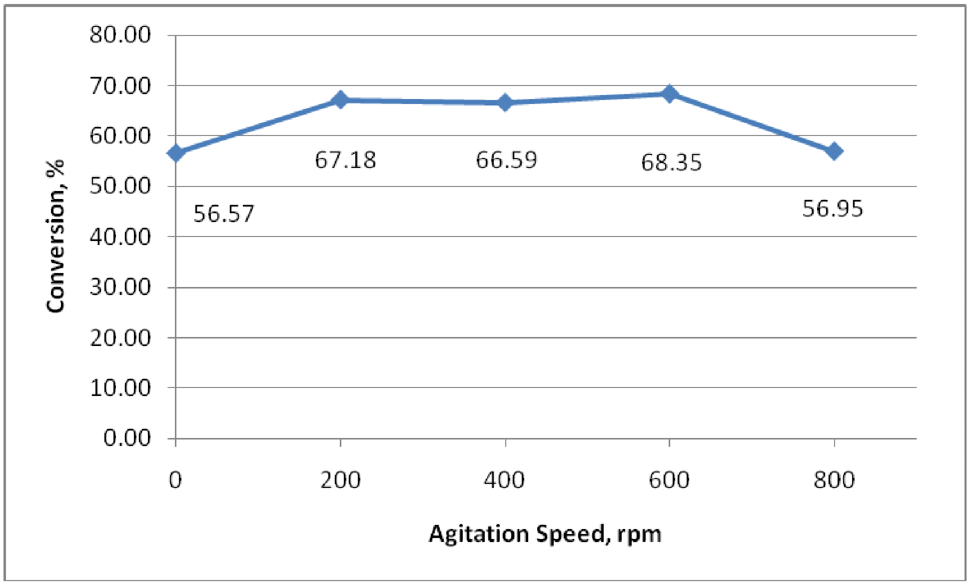


Figure 4.10: The effect of agitation speed toward fatty acid conversion

4.4 Characterization of Biodiesel

4.4.1 Acid Value Test

The volume of titration and calculation was attached on Appendix B. The acid value of PFAD was 252.56 mg KOH/g. The acid value of PFAD was brought down to 28.45 mg KOH/g after carried out esterification to synthesize biodiesel under the optimal condition. The conversion of PFAD for the biodiesel is 88.73%. This high conversion indicated that the fatty acid in PFAD was converted.

4.4.2 Thin Layer Chromatography (TLC)

TLC plate was spotted with the biodiesel, PFAD and methyl oleate ester as the standard and the TLC result was shown in the Figure 4.11. Biodiesel was spotted at the left side followed with PFAD in the middle while methyl oleate ester at the right side. According to Posada et al. (2007), PFAD contain of squalene, vitamin E, sterols, free fatty acids, glycerides and other unknown compound. Therefore, some of the spots in TLC plate were unable to identify. Based on the studies of Fedosov et al. (2011), the spot that travel further from the bottom line was FAME, followed by triglycerides, free fatty acid, diglycerides, and lastly monoglycerides. However, based on the TLC result, the spots that travelled further in biodiesel and PFAD cannot be identified and it might be due to the presence of unknown compound in PFAD. By referring to the spots developed by biodiesel on TLC plate, the second highest spot indicated the presence of FAME and this result was confirmed with the spot developed by the methyl oleate ester standard. The third spot away from the upper line was due to the presence of free fatty acid and followed with diglycerides and lowest spot was due to the presence of monoglycerides. For the spots developed by PFAD, the second spot away from the upper line was due to free fatty acid, followed by diglycerides and the spot near the bottom line was due to monoglycerides.

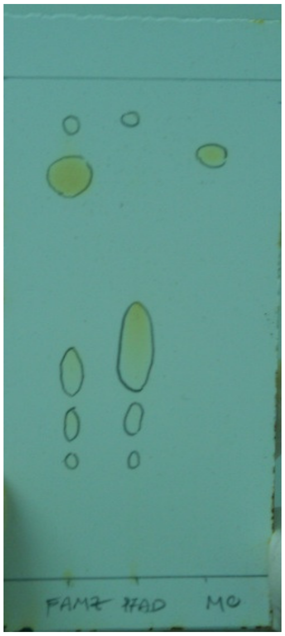


Figure 4.11: TLC plate for the Biodiesel, PFAD and Methyl Oleate Ester standard

4.4.3 Viscosity Test

The viscosity of biodiesel was measured under 40±1˚C water bath and the time for the biodiesel to drop from the upper mark to the lower mark was recorded and the calculation of viscosity test was attached in Appendix E. The viscosity of biodiesel after calculation was 6.4 mm^2/s and this property of FAME does not fulfilled the specification as stated in ASTM D6751 and EU 14214. In ASTM D6751 and EU 14214, the acceptable range of viscosity kinematic at 40°C for biodiesel is between 1.9-6.0 mm^2/s and 3.5-5.0 mm^2/s respectively. The reason that the biodiesel does not fulfill the specification is due to the conversion of fatty acid in PFAD is low resulted high content in fatty acid and low content of FAME (66.21%).

4.4.4 Liquid Infrared (IR) Spectroscopy

Figure 4.17 shows the IR spectrum for biodiesel. The spectrum of biodiesel was compared with methyl linoleate ester in the database (No. F62290). Biodiesel and methyl linoleate ester have the similar pattern. Therefore, this can indicated that biodiesel mainly containing methyl fatty acid chain ester. The sharp peak at 1741 cm^{-1} is due to the presence of carbonyl group of ester group while there has no broad peak near 3000 cm^{-1} indicated that the hydroxide group in the fatty acid was converted into ester group.

```
Peak Table:

Biodiesel 30...  3401  4000.00  600.00  2.72  100.34  4.00  %T  3  1.00

REF: 4000 99.92  2000 99.37  600
 3464.00 97.25  3004.00 66.64  2919.00  2.81  2852.00  6.42
 2681.00 91.21  2358.00 87.63  2339.00 90.53  2040.00 98.50
 1741.00  2.72  1712.00 30.24  1461.00 24.52  1436.00 23.23
 1361.00 43.76  1245.00 25.08  1195.00 13.65  1169.00  8.55
 1118.00 37.05  1096.00 50.42  1015.00 55.86   881.00 71.17
  846.00 71.25   722.00 27.18   617.00 87.44   604.00 88.22
END 24 Peaks found
```

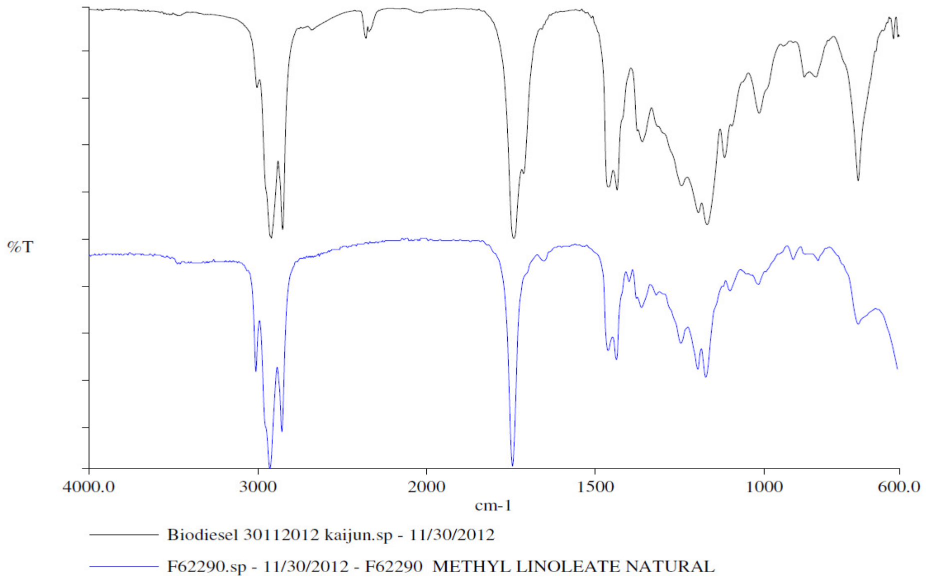


Figure 4.12: FTIR spectrum of Biodiesel

4.4.5 Water Content

The water content of the optimized biodiesel was as 0.46% and the low water content in FAME was due to the water was mainly removed during the last steps mentioned as section 3.5. The calculation for water content was attached in Appendix F.

4.5 Reusability Test of Catalyst

The conversion of PFAD and the cycle of catalyst reused was plotted and shown in the Figure 4.18. The acid value of PFAD was 252.56 mg KOH/g and after the first usage of catalyst, the acid value of biodiesel fallen to 28.45 mg KOH/g. When the catalyst was reused after the first usage, there have no significant decrease in acid value of PFAD resulted low conversion of PFAD. The conversion of PFAD drop significantly from 88.73% to 26.24% after the 1st cycle of catalyst reusability test and the conversion continuously dropped to 22.39% after the 2nd cycle of catalyst reuse.

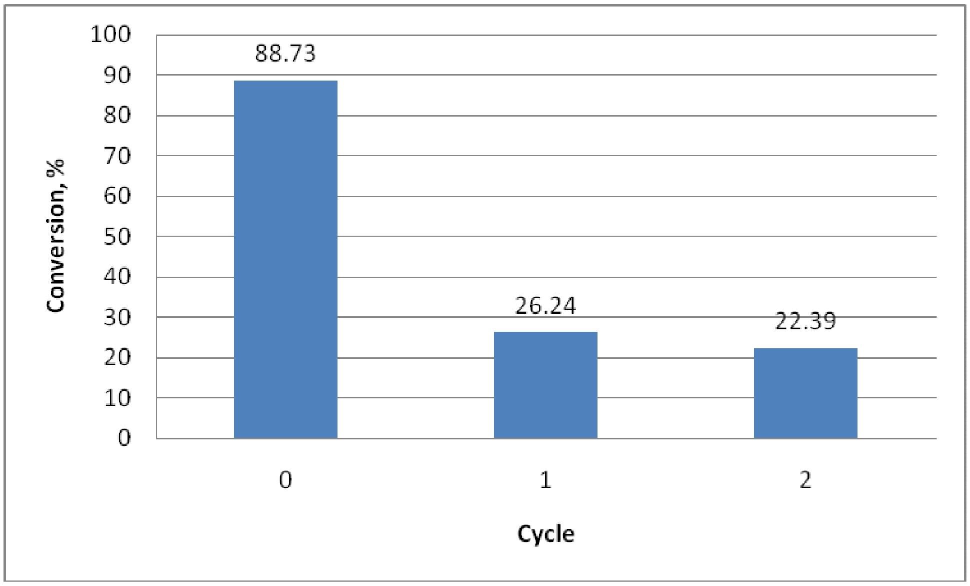


Figure 4.13: The effect of cycle of catalyst reused towards fatty acid conversion

CHAPTER 5

CONCLUSION

Sucrose was used as solid acid catalyst to synthesize biodiesel from PFAD through esterification reaction with methanol. The XRD and SEM results shown that this catalyst possess an amorphous carbon structure. FTIR result was shown that this catalyst consists of aromatic-like C=C functional group and sulfonic group. Sulfur content in the catalyst was investigated via EDS and the result indicated that sulfonic group was introduced into the precursor. The parameters such as reaction temperature, reaction time, agitation speed, molar ratio of methanol to feedstock and catalyst concentration were selected to investigate their influence towards the conversion of PFAD to biodiesel. After the One-Variable-At-One-Time, agitation speed was screened out as the less significant parameter. Three parameter involved in RSM were catalyst concentration (2 - 4 wt.%), reaction time (90 -150 min) and molar ratio of methanol to feedstock (5:1 – 10:1). The optimal condition for the conversion of PFAD was 140 min of reaction time, 10:1 of molar ratio of methanol to PFAD, 4 wt.% of catalyst concentration, 70°C of reaction time and 600 rpm of agitation speed. The predicted value for the conversion of PFAD was 86.41% and the actual value for the conversion of PFAD was 88.73%. The reusability of this synthesized catalyst was low due to the leaching of the active species from the catalyst. This result is in agreement with sulfur content of biodiesel and the EDS data of the reused catalyst.

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Appendix A

No of set	Time, min	Temperature, ˚C	Catalyst Concentration, wt%	Molar ratio of feedstock to methanol	Agitation speed, rpm
1	90	70	2	1:5.0	600
2	30	70	2	1:5.0	600
3	60				
4	120				
5	150				
6	180				
7	90	50	2	1:5.0	600
8		60			
9		80			
10		90			
11		100			
12	90	70	0.5	1:5.0	600
13			1		
14			3		
15			4		
16			5		
17	90	70	2	1:2.5	600
18				1:5.0	
19				1:15.0	
20				1:20.0	
21	90	70	2	1:5.0	0
22					200
23					400
24					800

Calculation for Acid Value of biodiesel synthesized under optimal condition.

Percentage of conversion, %	Mass of sample, g	Normality of KOH used, N	Volume of titrant used, ml	Acid value, mg KOH/g
88.73	0.5232	0.1	2.6	28.45

Appendix B

Viscosity test no	Time		Total time, t (s)
	min	second	
1	10	51.35	651.35
2	10	51.45	651.45
3	10	52.19	652.19
4	10	51.33	651.33
Average			651.58

Kinematic viscosity, v = Ct

$= (0.009821\ \text{mm}^2/\text{s}^2) \times (651.58\ \text{s})$

$= 6.3992\ \text{mm}^2/\text{s}$

Appendix C

Calculation for water content of biodiesel

	Mass, g
Beaker	34.4243
Beaker + 5g of biodiesel before heating	39.4716
Beaker + 5g of biodiesel after heating	39.4484

Water content (%) = $\frac{39.4716\text{g} - 39.4484\text{g}}{36.4716\text{g} - 34.4243\text{g}}$ x 100% = 0.46 %