UNIVERSITI PUTRA MALAYSIA

FATTY ACID METHYL ESTER PRODUCTION FROM PALM FATTY ACID DISTILLATE USING SULFONATED CARBON-BASED CATALYST FROM PALM KERNEL SHELL AND BAMBOO

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By

AHMAD FARABI BIN MOHAMAD SAMAN

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

FATTY ACID METHYL ESTER PRODUCTION FROM PALM FATTY ACID DISTILLATE USING SULFONATED CARBON-BASED CATALYSTS PREPARED FROM PALM KERNEL SHELL AND BAMBOO

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March 2018

Chairman: Prof. Taufiq Yap Yun Hin, PhD
Faculty: Science

Excessive use of petroleum and concerns on the energy security along with the uncontrolled emission of greenhouse gases have made the world's involuntarily to turn towards the utilization of environmental friendly and renewable biofuels. In this work, sulfonated carbon based solid acid catalysts were synthesized using two types of biomass sources which is from the palm kernel shell and bamboo. The catalysts were studied for its physico-chemical properties and applied as catalysts to convert the palm fatty acid distillate (PFAD) into fatty acid methyl esters (FAMEs). Solid acid catalysts prepared were derived from the palm kernel shell, bamboo and biochar. The sulfonated (-SO_3H) group was attached on the surface of catalyst by hydrothermal process of carbon source with the chlorosulfonic acid ($ClSO_3H$) under 70 °C for 4 hours with stirring rate of 500 rpm. Activated palm kernel shell was used in determining the optimum acid to biomass weight ratio for the sulfonation process.

The resultant catalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray (SEM-EDX), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET), Fourier transform infrared (FTIR), temperature programed desorption (TPD-NH_3). Meanwhile, the acid value for PFAD and percentage reduction of FFA were calculated using standard AOCS method (Cd 3d-63). From the characterization results, it was found that the carbon based catalysts (PKS, Bamboo and Biochar) have been successfully functionalized with –SO_3H group that attached on the carbon structure. Different parameter (catalyst loading, methanol to oil ratio, reaction temperature and reaction time) was used in analyzing the performance of the prepared catalysts in assisting the esterification reaction of PFAD. The catalytic activity of PKS-SO_3H, Bamboo-SO_3H and Biochar-SO_3H demonstrated the highest conversion of PFAD to biodiesel under the following reaction condition: catalyst loading of 4 wt. %, methanol-to-PFAD molar ratio of 15:1, reaction temperature of 65 °C and the reaction time was 1 h. PKS-SO_3H catalyst managed to produce the highest FAME yield and FFA conversion which is 95.1% and 97% respectively, meanwhile Bamboo-SO_3H show the lowest FAME yield and FFA conversion which is 94.2% and 95.8% respectively. The catalysts can be reused for 4 cycles before complete deactivation of the catalytic active

phase. It can be concluded that the carbon based solid acid catalyst derived from palm kernel shell and bamboo had high potentials in esterify high free fatty acid feedstock.

Abstrak tesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENGHASILAN ASID LEMAK METIL ESTER DARIPADA ASID LEMAK SAWIT SULINGAN MENGGUNAKAN MANGKIN BERASASKAN-KARBON TERSULFONASI DARIPADA TEMPURUNG ISIRUNG SAWIT DAN BULUH

Oleh

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Penggunaan petroleum yang berlebihan dan keprihatinan terhadap keselamatan tenaga serta pelepasan gas rumah hijau yang tidak terkawal telah menjadikan dunia secara tidak sengaja beralih ke arah penggunaan biofuel yang lebih mesra terhadap alam sekitar dan boleh diperbaharui. Di dalam kajian ini, mangkin asid pepejal yang berasaskan karbon bersulfur telah disintesis menggunakan dua jenis sumber biojisim yang berasal daripada tempurung isirung sawit dan buluh. Sifat fizikokimia mangkin dikaji dan digunakan sebagai mangkin bagi menukar asid lemak sawit sulingan (PFAD) kepada asid lemak metil ester (FAMEs). Mangkin asid pepejal yang disediakan diperolehi daripada tempurung isirung sawit, buluh dan bioarang. Kumpulan sulfur (-SO_3H) disangkutkan pada permukaan mangkin melalui proses hidroterma karbon dengan menggunakan asid klorosulfonik ($ClSO_3H$) di bawah suhu 70 °C selama 4 jam dengan kadar kacauan 500 rpm. Tempurung isirung sawit teraktif yang diperolehi telah digunakan bagi menentukan nisbah optimum asid kepada berat biomas untuk proses sulfonasi.

Mangkin yang dihasilkan dicirikan dengan menggunakan kaedah pembelauan sinar-X (XRD), mikroskop imbasan elektron-penyebaran tenaga sinar-X (SEM-EDX), analisis termogravimetri (TGA), analisis penjerapan-nyahjerapan nitrogen menggunakan kaedah Brunauer-Emmet-Teller (BET), spektroskopi inframerah transformasi Fourier (FTIR), aturcara-suhu-nyahjerapan (TPD-NH_3). Sementara itu, nilai asid untuk PFAD dan pengurangan peratus FFA dikira menggunakan kaedah piawai AOCS(Cd 3d- 63). Hasil pencirian menunjukkan bahawa mangkin berasaskan karbon telah berjaya difungsikan dengan kumpulan -SO_3H yang melekat pada struktur karbon. Kepelbagaian parameter (muatan mangkin, nisbah minyak kepada metanol, suhu dan masa tindak balas) telah digunakan dalam menganalisis prestasi mangkin yang disediakan bagi membantu tindak balas estrifikasi PFAD. Aktiviti pemangkinan bagi PKS-SO_3H, Buluh-SO_3H and Bioarang-SO_3H menunjukkan penukaran PFAD yang paling tinggi dibawah keadaan berikut: muatan mangkin 4 wt. %, nisbah kemolar methanol kepada PFAD 15:1, suhu tindak balas 65 °C dan masa tindak balas selama 1 jam. PKS-SO_3H mampu menghasilkan FAME dan penukaran FFA yang paling tinggi iaitu sebanyak 95.1% dan 97%., manakala

Buluh-SO_3H menunjukkan hasil FAME dan FFA paling rendah iaitu sebanyak 94.2% dan 95%. Mangkin boleh digunakan semula untuk 4 pusingan tindak balas sebelum penyahaktifan fasa aktif mangkin berlaku sepenuhnya. Secara ringkas, dapat disimpulkan bahawa mangkin asid berasaskan karbon yang diperolehi dari tempurung isirung sawit dan buluh mempunyai potensi yang tinggi dalam proses esterifikasi bahan suapan asid lemak bebas tinggi.

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-Alhamdulillah-

I certify that a Thesis Examination Committee has met on 20 March 2018 to conduct the final examination of Ahmad Farabi bin Mohamad Saman on his thesis entitled "Fatty Acid Methyl Ester Production from Palm Fatty Acid Distillate Using Sulfonated Carbon-Based Catalysts from Palm Kernel Shell and Bamboo" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABREVIATIONS

P_c	Critical pressure
T_c	Critical temperature
MW	Molecular weight
T	Reaction temperature
t	Reaction time
S_{BET}	BET surface area
°C	Degree Celsius
R	Alkyl group
h	Hour
Min	Minutes
µL	Microliter
mg	Milligram
PFAD	Palm Fatty Acid Distillate
ASTM	American Society for Testing and Materials
EN	European standard
TG_s	Triglycerides
FFA	Free fatty acid
FAME	Fatty acid methyl ester
GC-FID	Gas Chromatography- Flame Ionization Detector
AV	Acid value
SV	Saponification value
XRD	X-ray Diffraction analysis
TG-DTG	Thermal Gravimetric- Differential Thermal Gravimetric
SEM-EDX	Scanning Electron Microscopy- Energy Dispersive X-ray
NH_3-TPD	Ammonia- Temperature Programmed Desorption
HCl	Hydrochloric acid
GHG	Life-cycle Greenhouse gas
CHNOS	Carbon Hydrogen Nitrogen Oxygen Sulphur elemental analysis
PP	Pour Point

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Energy is one of the basic necessities of the modern world and plays significant role in determining the economic growth in a particular country (Islam *et al.*, 2014; Kumar & Ram, 2013). For the last few decades, fossil fuels have been the major sources of the energy for all types of consumers which takes about 35 % of total energy sources (Atabani *et al*., 2012). Furthermore, around 90 % of vehicles nowadays are powered by the fossil fuel based energy. In addition, petroleum based product are known to be used as the major source material for the chemical industry producing pesticides, fertilizers, pharmaceutical, plastics and solvent (Simanzhenkov & Idem, 2003). Figure 1.1 shows the consumption of petroleum around the world which exceed the total petroleum production by thousands barrels per year. With the growing of world population along with rapid development in the manufacturing and transportation industry, the energy demand predicted to be escalated significantly. As a result, the fossil fuel reserve will depleted drastically.

Excessive usage of fossil fuel energy does not only affect the world oil reserve, in fact it will bring irreversible damages to the environment. Total dependency on fossil fuel energy will lead to the enormous of harmful gas being released to the environment. Carbon dioxide (CO_2) is one of the main gas component that was released into the environment during the combustion of petroleum based energy. This type of harmful gas will increase the formation of greenhouse gas (GHG).

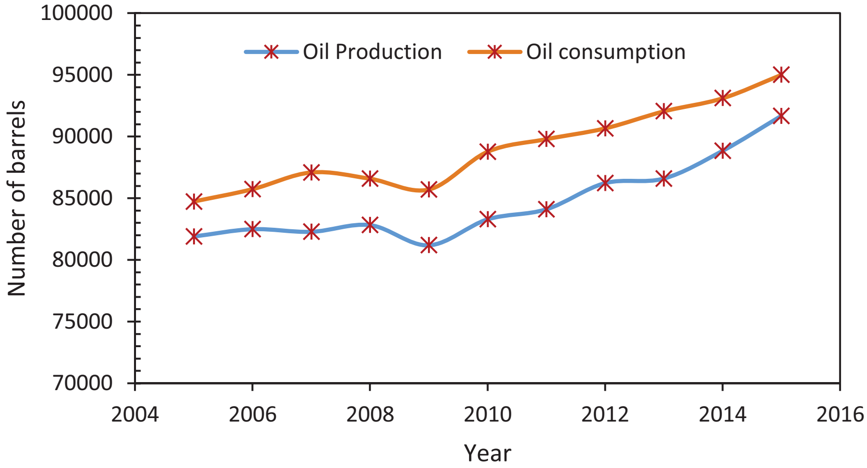

Figure 1.1: World Oil Production and Consumption (Barrels per day) 2005-2015
(British Petroleum, 2015)

The effect of increasing in greenhouse gas layer can be seen through the increasing in natural phenomena disturbance such as flash flood, heat waves, windstorms and sudden drought (Lam & Lee, 2011). To prevent this issue from protracted, world nowadays are shifting from the fossil fuel based energy into different type of energy that are green and renewable such as energy generated from wind turbines, solar panels, river dams, geothermal and biofuels which need to be utilized in replacing fossil fuel based energy. Along with the advancement of research and technology sector, production of bio-ethanol and biofuel are significantly increased and became the most common alternative energy. Generally, biofuels can be referred as liquid or gaseous fuels used as energy sources which principally produced from biomass. Nowadays, biofuels is one of the alternative sustainable burning fuels that had been successfully tried and used by majority of the consumers in replacing non-sustainable fossil fuel energy. The utilization of biofuels as energy sources meet wide range of social and environmental sustainable criteria including the limitation on deforestations, the competition with food production, an adverse impact on biodiversity, soil erosion and nutrient leaching (Alam *et al.*, 2012).

1.2 Catalyst

Catalyst is typically defined as substance or material that speed up the rate of chemical reaction by lowering the activation energy without affecting its equilibrium (Figure 1.2). Generally the catalyst will assist the reaction without being consumed, however there are some cases that the catalyst will be consumed by the reaction but can be regenerated (Ertl *et al*., 2008). Ertl *et al*., (2008) also refer to Laidler (1985), the alternative definition of a catalyst is a substance which is able to enhance a chemical reaction without affecting its equilibrium.

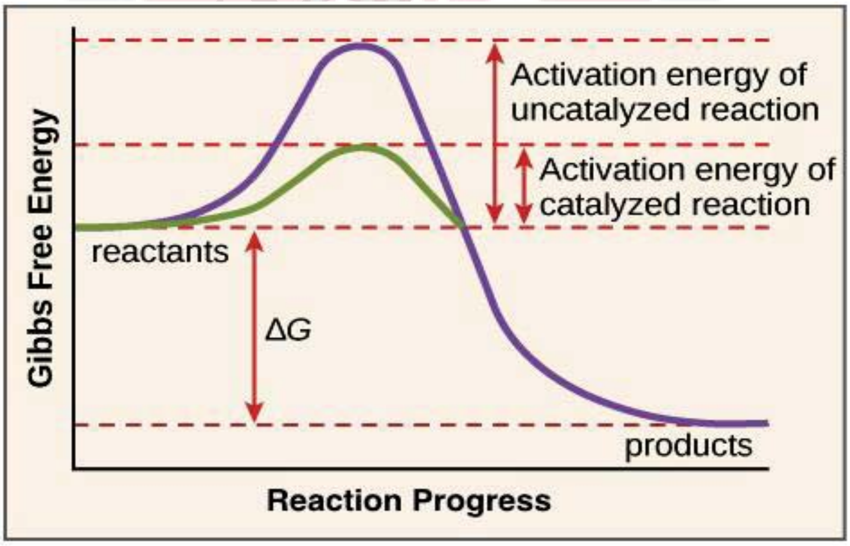

Figure 1.2: The Effect of Catalyst on the Activation Energy of the Reaction
(Brinkley, 2012)

In biodiesel production, catalyst are basically used in order to increase the fatty acid methyl ester (FAME) yield and at the same time to improve the production process. Previously, homogenous catalyst are widely utilized in biodiesel production. However due to the complexity in purification step after the completion of reaction which eventually generate large volume of wastewater thus increase the production cost, heterogeneous catalyst was introduced. The non-corrosive, easily separate and reusability properties of heterogeneous catalyst is the biggest advantages in assisting the production of biodiesel (Liu *et al.,* 2008). Furthermore Refaat, (2010) reported that utilization of heterogeneous catalyst produced soap free and high glycerol purity product.

1.3 Biodiesel: Benefits and Challenge

Generally, fossil fuel based energy plays crucial roles in most of the industries since mid of nineteen century. About 90 % of the transportation industry today are related to the petroleum based energy (Simanzhenkov & Idem, 2003). For the past few decades, due to the distress on the depletion of world petroleum reserves coupled with environmental concerns have drove the researchers to find a cleaner and renewable energy sources.

For the past few years, biomass and biofuels have the possibilities to become the main providers of energy in the next century. Biomass has taken the fourth place as largest energy source after coal, natural gas and petroleum based energy. Even though the utilization of biomass as new energy source cannot wholly support world energy consumption, it still can be considered as the largest and most versatile renewable energy source as it can be used in different ways such as for energy and chemicals production. Biomass is produced naturally by photosynthesis and during this process it stores solar energy in the form of chemical energy. Intermediate fuels can be produced from biomass using different process i.e. chemical (transesterification), biochemical (fermentation) and thermochemical (pyrolysis and gasification).

Biodiesel or scientifically known as FAME can be derived from vegetable oil or animals fat by either esterification of fatty acid or transesterification of triglycerides.(Rashid *et al.,* 2015). The conversion of starting material to FAME is possible in the presence of alcohol. Biodiesel is a promising alternative fuel which has close similarity with the conventional fossil diesel in term of chemical structure and energy content that can be used directly in standard engine diesel or blended with petroleum diesel (Lam & Lee, 2011). Nowadays, there are several types of biodiesel in the market such as B5 (blended with 5 % of biodiesel), B20 (blended with 2 % of biodiesel) and B100 (100 % of biodiesel).

Agarwal *et al.* (2007) reported that biodiesel is differ from the petroleum diesel on several important aspect such as sustainability, renewability, biodegradable and environmental friendly (less carbon monoxide and sulphur emission). Table 1.1 described the differences in oil properties between petroleum diesel and biodiesel. The utilization of biodiesel as fuel source can reduce the net carbon emission up to 78 % on a lifecycle basis compared to petroleum diesel. This phenomena can lead to the elimination of greenhouse effect due to the decreasing of the CO_2 concentration in the atmosphere.

Table 1.1: Comparison of Diesel and Biodiesel According to the American Standard for Testing and Materials (ASTM)

Property of the fuel	Diesel	Biodiesel
Standard method	ASTM D975	ASTM D6751
Fuel composition	Hydrocarbon (C_{10}-C_{21})	FAME (C_{12}-C_{22})
Density (g/cm^3)	0.848	0.878
Pour point (ºC)	-30 to -15	-15 to 16
Cloud point (ºC)	-15 to 5	-3 to 12
Flash point (ºC)	60-80	100-170
Cetane number	40-55	48-60
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulphur (wt %)	0.05	0.05

However, for the biodiesel to be commercially feasible there are several issues and challenges need to be solved. Production cost, availability of feedstock, and technology need to be thoroughly investigate before large scale production can happen. Today, one of the main obstacles in large scale biodiesel production is come from the cost and availability of feedstock. About 80 % of the production cost is came from the cost of the feedstock itself. In the beginning of the biodiesel production, people are debating about the food vs fuel issues. This is due to the most of the feedstock are coming from an edible oil (Figure 1.3). Henceforward, in order to reduce the feedstock cost and to gain the social acceptance biofuel feedstock, the biodiesel need to be derived from non-edible feedstock. For the past few years, researchers are coming with second generation feedstock which are comes from non-edible oil. However, the usage of non-edible oil as biodiesel feedstock still have limitation due to the high production cost (Atabani *et al*., 2012).

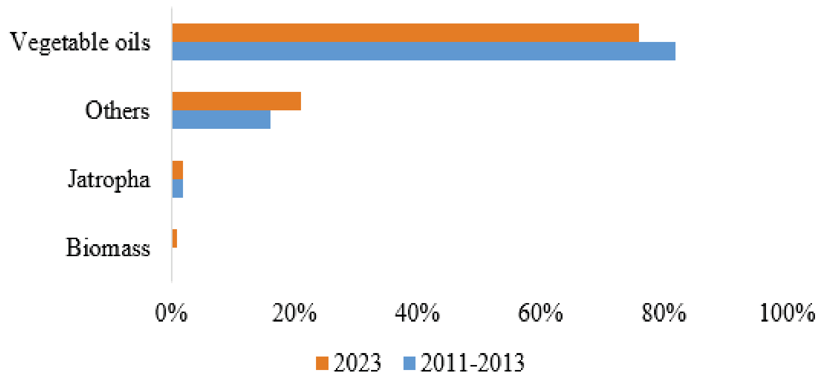

Figure 1.3: Share of Feedstock Used for Biodiesel Production (OECD-FAO, 2009)

1.4 Problem Statement

Continuously growing on energy demand along with the depletion on fossil fuel resources and pressured by the major environmental pollution concerns, world are being pushed into finding alternative fuels that can overcome all these issues. Nowadays, replacing fossil fuel based energy with green bio-fuel energy become major interest in energy sector. However, bio-fuel (biodiesel) come with several issues such as high price tag due to the expensive feedstock, expensive and high maintenance reactor. Developing an environmental benign process for biodiesel production using cheap feedstock become global need. The use on second generation non edible feedstock instead of first generation edible feedstock helps in reducing the production cost of biodiesel. In this study, palm fatty acid distillate (PFAD) was used as a starting material, which is believed to have a significant potential in becoming sustainable biodiesel feedstock due to the availability and low-cost feedstock.

Catalyst plays major role in production of biodiesel in optimizing the rate of the process and percentage yield. However, stability and cost of catalyst production plays important role in choosing the suitable catalyst sources for the reaction. Thus, this study focuses on the catalyst development by introducing poly aromatic carbon based solid acid catalyst which the carbon precursor comes from the palm kernel shell, bamboo and biochar. These carbon precursor was choose due to the availability and the influence of these catalyst towards the production of biodiesel from PFAD.

1.5 Objectives

The objective of this study are:

1. To synthesis the heterogeneous carbon based solid acid catalyst derived from the palm kernel shell, bamboo and biochar.
2. To characterize the physico-chemical of the synthesized catalyst by various techniques such as X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area, Thermogravimetric analysis (TGA), Scanning emission microscopy – Energy dispersive x-ray (SEM-EDX), Fourier-transform infrared spectroscopy (FT-IR) and Temperature programmed desorption of Ammonia (TPD-NH_3).
3. To optimize the condition for the esterification of palm fatty acid distillate (PFAD) by using catalyst loading, methanol to oil ratio, reaction temperature and rate of reaction parameter.

1.6 Scope of Study

This study covers the synthesis of heterogeneous carbon based solid acid catalyst derived from the biomass. Palm kernel shell and bamboo was choose as the biomass sources for both of them can be found abundantly in Malaysia. Prior to the sulphonation process, the raw biomass was calcined for 5 hours under the nitrogen flow to produce the incomplete carbonized carbon catalyst. The performance of the sulphonated carbon catalyst was carried out for esterification reaction of palm fatty acid distillate (PFAD). The relationship between concentration of sulphate agent and number of acid sites present on the catalyst was investigate and discussed. Detail characterization analysis of the catalyst and optimization process of the catalytic reaction were carried out and discussed in this thesis with the main purpose to understand the behaviour of the catalyst toward the production of biodiesel. Meanwhile, the biodiesel produced from this study have been analysed through the quality assessment analysis according to the American Society for Testing and Materials (ASTM) and European standard methods (EN).

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