BIODIESEL PRODUCTION FROM OLEIC ACID AND PALM FATTY ACID DISTILLATE/ OLEIC ACID USING SULFONATED CARBON

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A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

MARCH 2016

To my beloved husband, mum and siblings for their endless support and encouragement

ACKNOWLEDGEMENT

Alhamdulillah. I would like to take this opportunity to express my utmost gratitude to Allah Subhanahu Wa Ta'ala, without whom this Thesis would not have been possible, for his guidance throughout the journey that I have embarked on in which I have been opportuned to gain a lot of experience, academically, socially and morally.

First, my sincere gratitude goes to my supervisor, Prof. Dr. Nor Aishah Saidina Amin for the continuous support of my M.Sc. study and related research, for her patience, motivation and immense knowledge. Her endless guidance in the supervision of my thesis has helped me a lot from the lab work to the writing of the thesis. I could not having imagined having a better supervisor for my M.Sc. study. Besides my supervisor, i would also like to express my appreciation to members of the Chemical Reaction Engineering Group (CREG, UTM) for their valuable support of my work. My sincere appreciation also goes to Mr Latfi, Mrs Zainab, and Mr Izzad for their assistance in the analysis and characterization of my products.

I would also like to express my utmost appreciation to my husband, Mohammed Ahmed Hayatu, my mum, and siblings for their endless support and encouragement morally, financially and spiritually. Their support and prayers have helped a lot in making this research possible.

Lastly, I am indebted to the Government of Malaysia and Universiti Teknologi Malaysia for accepting me to study in the school and providing a conducive environment for my research.

ABSTRACT

Biodiesel has been globally accepted as a substitute to diesel fuel, and is an ongoing subject for research. It is a fuel obtained from renewable sources such as vegetable oils, animal fat, and algal oil. Biodiesel is non- toxic, biodegradable, inflammable, and has a good combustion emission profile. Recently, the application of edible sources in the production of biodiesel has caused a lot of debate due the insecurity on food. Hence, the use of inedible and industrial waste sources such as palm fatty acid distillate (PFAD) and oleic acid (OA). Although, they could be the answer to a more economic biodiesel production due to their availability and low cost, their high free fatty acid (FFA) content causes biodiesel production to be expensive when homogeneous catalysts are used. Hence, the need for a heterogeneous acid catalyst, which is the most economically viable catalyst in the production of biodiesel from low cost feedstocks. In this work, the production of biodiesel (FAME) from oleic acid and PFAD/oleic acid mixed feed using a sulfonated carbon catalyst derived from glycerol was investigated. The synthesized catalyst was characterized using FTIR, BET, FESEM, XRD and TPD-NH_3 to determine its catalytic activity. Simultaneous esterification/ transesterification of oleic acid, and PFAD/oleic acid mixed feed were carried out using the synthesized catalyst. In addition, Response Surface Methodology (RSM) using Box-Behnken Design was used in optimization of the process variables to study the influence of molar ratio of methanol to oleic acid, and PFAD/Oleic acid mixed feed, catalyst loading and reaction time on the conversion and yield of FAME. For oleic acid conversion and yield, 99% and 97% were obtained respectively. While 98%, 94% and 96% were obtained as PFAD/oleic acid conversion, methyl oleate yield and methyl palmitate respectively.

ABSTRAK

Biodiesel diterima secara meluas sebagai pengganti kepada bahan api fosil, dan merupakan subjek penyelidikan semasa. Ia menghasilkan kurang karbon monoksida berbanding diesel petroleum. Walau bagaimanapun, penggunaan sumber-sumber yang boleh dimakan dalam pengeluaran biodiesel menyebabkan banyak perdebatan kerana ketidakkukuhan makanan. Oleh itu, penggunaan sumber sisa yang tidak boleh dimakan dan perindustrian seperti sulingan asid lemak sawit (PFAD) dan asid oleik (OA) digunakan. Sumber-sumber ini merupakan pengeluaran biodiesel yang lebih ekonomi kerana ketersediaan dan kos rendah. Walau bagaimanapun, kandungan tinggi asid lemak bebas (FFA) adalah halangan utama. Oleh itu, pemangkin asid heterogen diperlukan, iaitu pemangkin yang paling ekonomikal dalam pengeluaran biodiesel. Dalam kajian ini, pengeluaran biodiesel (FAME) daripada asid oleik dan PFAD/asid oleik campuran menggunakan pemangkin karbon-sulfurnat dikaji. Pemangkin yang telah disintesis dicirikan dengan menggunakan FTIR, BET, FESEM, XRD dan TPD-NH3 untuk menentukan aktivitinya sebagai pemangkin. Esterifikasi serentak dan transesterifikasi asid oleik, dan PFAD/asid oleik campuran telah dikaji dengan menggunakan pemangkin yang telah disintesis. Metodologi *Response Surface* (RSM) yang menggunakan *Box-Behnken Design* digunakan dalam pengoptimuman pembolehubah proses untuk mengkaji pengaruh nisbah molar metanol kepada asid oleik, dan PFAD/asid oleik campuran, jumlah pemangkin dan tindak balas masa dalam penghasilan FAME. Untuk penukaran asid oleik dan kadar hasil, 99% dan 97% telah diperolehi. Manakala 98%, 94% dan 96% diperolehi sebagai PFAD/penukaran asid oleik, kadar hasil metil oleat dan metil palmitat.

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LIST OF ABBREVIATIONS

BET	-	Brunauer- Emmett- Teller
BBD	-	Box-Behnken Design
DOE	-	Design of Experiment
EDX	-	Energy Dispersive X-ray Spectrometer
FAME	-	Fatty Acid Methyl Ester
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
GC	-	Gas Chromatography
GC-FID	-	Gas Chromatography Flame Ionization Detector
GC-MS	-	Gas Chromatography- Mass Spectrometer
PFAD	-	Palm Fatty Acid Distillate
RSM	-	Response Surface Methodology
TPD-NH_3	-	Temperature Programmed Desorption-NH_3.
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

%w/w		Weight/weight percent
AV_i	-	Initial acid value
AV_f	-	Final acid value
C	-	Methyl ester content
g	-	Gram
g/cm	-	Gram per cubic centimetre
h	-	Hour
J/Kmol	-	Joule per Kelvin mole
m^3	-	Cubic metre
mgKOH/g	-	Milligram potassium hydroxide per gram
min	-	Minute
ml	-	Millilitre
mm^2/s	-	Square millimetre per second
mol	-	Mole
N	-	Normality
^0C	-	Degree Celsius
R^2	-	Coefficient of determination
V_f	-	Final volume of alkali used in the titration
V_i	-	Initial volume of alkali used in the titration
W	-	Weight of sample
wt%	-	Weight percent
wt/vol	-	Weight per volume
Y_{1o}	-	Oleic acid conversion
Y_1	-	Methyl oleate
Y_2	-	Methyl palmitate

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

1.1.1 Biofuel

For several decades, the world has been undergoing a crisis in energy as a result of the excessive use of the world's depleting oil reserves, by the ever-increasing human population. The depletion in fossil fuels, the ever- increasing prices of fuels, and environmental pollution, have driven scientists to look for alternative fuels from renewable energy sources. Sources that are inexhaustible, and have less negative effects on the environment. These renewable energy sources are those obtained from natural sources such as the wind, rain, biomass, etc. They are cheap, inexhaustible, easy to obtain, and greatly reduce greenhouse gas emissions. Presently, biomass energy is the largest source of renewable energy, as it has a versatile range of feedstocks (obtained from plants), and it represents 77.4% of global supply of renewable energy. Biomass, as a renewable fuel, are converted into biofuels to be used in our vehicles for transportation.

Biofuels have existed for as long as civilization itself, because the first automobiles were made to function on them, rather than fossil fuels. However, the discovery of huge petroleum deposits kept gasoline and diesel cheap for decades, and biofuels were forgotten. Recently, the growing concern about global warming, decline in fossil fuels, and the recent rise in prices of oil made biofuels regain their popularity.

They have the potential to minimize green house gases, and also replace petroleum based fuels.Their emergence has been projected to contribute 40-60% of world energy demand by 2050 (Beatrice *et al*., 2014). Presently, biofuels such as bioethanol and biodiesel, are being used in countries such as United States, Germany, England, and Brazil, some parts of Asia, and Africa (Dorado *et al*., 2006). Figure 1 shows the steady growth of biofuel production in Asia and Africa from 2007, and its projection up till 2020.

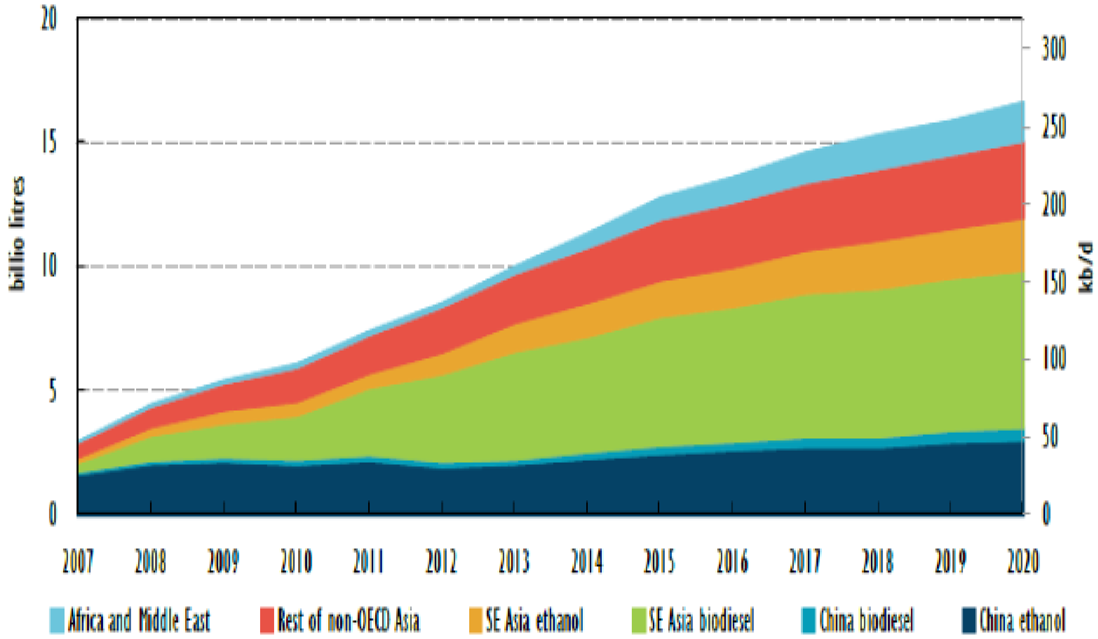

Figure 1.1 Biofuel production in Asia and Africa (Renewable Energy Market Report, 2014)

1.1.2 Biodiesel

Biodiesel is a biofuel that has strongly gained acceptance worldwide, especially in the transportation system. It is of great importance for the economic and social development of any country. Millions of barrels of oil equivalent are produced daily, with almost 1.5 million barrels per day in 2014 (BP., 2015). It is a natural and renewable fuel that can be synthesized from vegetable oils, fats or micro-algal oil, (Abbaszaadeh *et al*., 2012). It is conventionally produced through the transesterification process of triglycerides, and also esterification of free fatty acids (FFA) with an alcohol. It can also be produced through pyrolysis, dilution with petroleum-based fuel and emulsification. The properties of biodiesel are almost similar to that of diesel fuel. Therefore, it can be used directly in the diesel engine with little modification or blended with diesel fuel. The benefits of substituting diesel fuel with biodiesel are numerous. It has a low emission profile, it is biodegradable, non-toxic and is a renewable source. In addition, it does not contribute to the increase in carbon dioxide levels in the atmosphere. Instead, carbon dioxide from plants are converted into organic compounds via photosynthesis process. These crops are used to produce biodiesel, and as engine combustion produces carbon dioxide, it is returned to the atmosphere for the plants to use them up again (Mohammad, 2013).

The production of biodiesel is being faced with a major challenge as a result of the use of edible oils, because almost 70-85% of the overall production depends on the raw materials used for its production (Singh and Singh, 2010). This has brought up a lot of debates lately, as a result of which researchers have turned to inedible feedstocks such as Palm Fatty Acid Distillate (PFAD), algae, waste cooking oil, waste sludge, oleic acid, stearic acid etc., which are promising alternatives for biodiesel production. Malaysia, with a worldwide production of 19,800,000 metric tonnes of palm oil as at 2014, and an annual production of 700,000 metric tonnes of PFAD has a great potential of using PFAD, as a promising low cost alternative to vegetable oils. Oleic acid, as an alternative feedstock is also in abundance, because it occurs naturally in lipids. However, both PFAD and oleic acid have high fatty acid content, which poses a threat to the cost of biodiesel production, especially when using homogeneous catalysts. Therefore, the development of an efficient process for the conversion of PFAD, and other feedstocks with high FFA content to biodiesel is needed in order to reduce the cost of biodiesel production.

The application of base catalysts in the transesterification of PFAD is almost impossible (Lokman *et al*., 2015), as it results in a saponification process which deactivates the catalyst. Therefore, acid catalysts such as sulfuric acid have been used in its esterification (Chongkhong *et al*., 2007). However, the final product needed several steps of purification processes in order to recover the product from the acid catalyst (Nakpong, 2010). Hence the introduction of heterogeneous acid catalysts in order to eliminate corrosion, separation, emulsification and saponification problems.

Heterogeneous acid catalysts have been widely accepted over the conventional homogeneous catalysts for the efficient conversion of FFA to biodiesel, due to several advantages it has over it. These advantages include the recyclability of the catalysts, minimal wastewater generation, and ease in handling. Recently, heterogeneous catalysts such as carbon catalysts, have been studied for the improved production of biodiesel. Catalysts such as carbohydrate-derived solid acid catalyst (Chen and Fang., 2011), ferric alginate (Boey *et al*., 2012), and so on. Sulfonated carbon catalyst from glycerol is a relatively cheap catalyst which will be used in this study in the simultaneous esterification/transesterification of oleic acid and PFAD/oleic acid mixed feed. It is readily available, and will offer improved selectivity and easy catalyst separation from the product obtained. Thereby, reducing the cost of production.

1.2 Problem Statement.

The depletion in fossil fuels, environmental pollution, and high cost in prices of petroleum products has led scientists to look for alternative fuels such as biofuels, obtained from sources that can be renewed. Biodiesel, as a biofuel, has the potential to be used as substitute to diesel fuel because it is biodegradable, non-toxic, inflammable, produces less emission of carbon monoxide, sulfur dioxide, and unburnt hydrocarbons when compared to diesel fuel. Biodiesel is a fuel obtained from vegetable oils or fats and methanol. However, the use of edible oils is not practical as this brings shortage in food, and a hike in food prices. This limitation can be overcome by the use of inedible feedstocks. Feedstocks such as Jatropha curcas, PFAD, waste cooking oil, and triglycerides such as oleic acid, stearic acid, palmittic acids and so on. All of which are low-cost feedstocks. PFAD and oleic acid are the most promising alternative low cost feedstocks as they are abundant in Malaysia, cheap and readily available.

However, due to their high FFA content, a suitable catalyst is required for their esterification and transesterification.

Solid acid catalysts are promising heterogeneous catalysts that have a great influence in reducing the cost of biodiesel production as a result of its effectiveness in promoting the conversion of FFA to biodiesel (FAME). They are insensitive to FFA, which makes them economically viable. The ease in which they are separated from the end product also adds greatly to its advantages. Unlike homogeneous catalysts which pose a threat economically, and environmentally. For high FFA content feedstocks, heterogeneous acid catalysts have been found to be more viable economically, as they are insensitive to FFA. Therefore, using a PFAD/oleic acid mixed feed and sulfonated carbon based catalyst as a heterogeneous acid catalyst generally describes esterification and transesterification reaction for FFAs to produce biodiesel.

In biodiesel synthesis, the output depends on the interaction between variables during the reaction. The variables commonly varied for biodiesel synthesis include: molar ratio of oil to alcohol, time, temperature, and catalyst loading. Determining the optimum conditions in biodiesel production brings about a better utilization of resources. The conventional method of process optimization considers the effect of one variable at a time which is expensive and time consuming. To overcome this problem, design of experiment (DOE) is used to study multiple variables in the same experiment. Response Surface Methodology (RSM) is one of the suitable tools for optimizing biodiesel production process. It is a statistical tool used to predict a mathematical model based on the fitness of experimental data obtained in relation to experimental design (Bezerra *et al*., 2008).

The reaction conditions for biodiesel production using different catalysts have been optimized using RSM by many authors (Dwivedi and Sharma., 2015; Lokman *et al*., 2015). However, little or no work has been carried out on the production of biodiesel from oleic acid and PFAD/oleic acid mixed feed using sulfonated carbon based catalyst. Therefore, the researcher intends to study the simultaneous esterification/transesterification of oleic acid and PFAD/oleic acid mixed feed using a sulfonated carbon catalyst. The researcher also intends to study the activity of the catalyst on the production of biodiesel from PFAD, and its reusability. And also, optimization of the esterification/transesterification of oleic acid and PFAD/oleic acid mixed feed using Response Surface Methodology (RSM).

1.3 Research Hypothesis

The hypotheses of this study are

i. The application of sulfonated carbon as a catalyst in the esterification of oleic acid, PFAD/oleic acid mixed feed can increase its conversion. It can also increase methyl oleate and methyl palmitate yield as compared to the conventional catalyst (H_2SO_4).
ii. The application of RSM as a design technique can help to predict the optimum conditions for oleic acid and PFAD/oleic acid esterification with minimum errors between the predicted and experimental values.

1.4 Research Objectives

The objectives of this research are:

1. To synthesize and characterize a sulfonated carbon (SO_3H-C) catalyst for the simultaneous esterification/transesterification of oleic acid, and PFAD/oleic acid mixed feed.
2. To optimize the esterification/ transesterification of oleic acid, and PFAD/oleic acid mixed feed using Response Surface Methodology (RSM).
3. To analyze the feed, and FAME obtained using gas chromatography (GC), and test the reusability (recycling) of the catalyst for the esterification/transesterification of oleic acid, and PFAD/oleic acid mixed feed.

1.5 Scope of the Research.

The research was carried out to synthesize a sulfonated-carbon (SO_3H-C) catalyst for the production of biodiesel from oleic acid and PFAD/oleic acid (low cost feedstocks), which can improve the efficiency of production when low quality feedstocks with high FFA are used as raw materials. The scope of the research involved:

i. Synthesis of sulfonated carbon catalyst for simultaneous esterification/ transesterification of oleic acid, and PFAD/oleic acid mixed feed.
ii. Characterization of sulfonated carbon catalyst for simultaneous esterification/ transesterification of PFAD/oleic acid mixed feed. The characterization of the catalyst was done using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM), Brunauer-Emmett-Teller (BET).
iii. Three parameters were controlled during the experiments. These include: molar ratio of oleic acid, and PFAD/oleic acid mixed feeds to methanol, catalyst loading, and time.
iv. Optimization of the process variables using Response Surface Methodology.
v. The reusability of the catalyst was tested.
vi. The oleic acid, mixed feed and biodiesel produced was analyzed using Gas Chromatography analysis.

1.6 Significance of the Study

The research will utilize a sulfonated carbon catalyst (SO_3H-carbon) derived from glycerol as a benign catalyst for the esterification/transesterification of PFAD biodiesel, which is one of the main processes in biodiesel synthesis. The utilization of such catalysts can help in reducing the risks associated with usage of homogeneous catalysts. And determining the optimum conditions of process variables can aid in an efficient and better utilization of resources, in both small and large scale industries.

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