ESTERIFICATION OF OLEIC ACID AND PALM FATTY ACID DISTILLATE-OLEIC ACID BLEND USING SULFATED TITANIA-SILICA CATALYST

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To Allah (SWT) my creator and sustainer

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ABSTRACT

The synthesis of biodiesel from low cost feedstocks containing high free fatty acid is gradually gaining global acceptance as a worthwhile process route capable of keeping biodiesel production cost and its product price below that of petroleum diesel. The high free fatty acid content of these feedstocks however makes them difficult to process using the conventional high activity base catalysts. Sulphuric acid has been widely employed in the esterification of oils containing high free fatty acids to produce biodiesel. However, the major demerits associated with the use of sulphuric acid are its corrosiveness and environmental unfriendliness. In this study, biodiesel was synthesized from the individual methanolysis of oleic acid, and PFAD-oleic acid blend in the ratio 8:2 using sulfated titania-silica catalyst. This catalyst was prepared by reacting 0.5M solution of titanium isopropoxide with silica and then sulfated with 0.5 M sulphuric acid. The catalyst was then characterized by FE-SEM, XRD, BET, TGA, TPD - NH_3 and FTIR respectively. The esterification was carried out in a three-neck round bottom flask and was well stirred. The variables investigated are molar ratio of oleic acid and PFAD-Oleic acid blend to methanol, catalyst loading and reaction time; while the reaction temperature and stirring rate were kept constant at 65 ^{o}C and 200 rpm respectively. The process was optimized using response surface methodology (RSM) based on Box Behnken design (BBD) to explicitly depict the interactions between the independent variables and the responses. The resulting biodiesel yield was determined using GC/FID and the conversion was determined through volumetric analysis. The optimum values predicted for methyl oleate yield and oleic acid conversion from the esterification of oleic acid are 81.04% and 92.14%. While the optimum values for methyl oleate yield, methyl palmitate yield and PFAD-oleic acid conversion obtained from the esterification of PFAD-oleic acid blend are 90.04%, 91.92% and 96.84% respectively.

ABSTRAK

Sintesis biodiesel menggunakan sumber bahan mentah berkos rendah yang mengandungi asid lemak bebas yang banyak semakin diterima pakai diperingkat antarabangsa kerana kos pengeluarannya lebih rendah daripada sintesis melalui diesel. Walau bagaimanapun, bahan mentah tersebut sukar diproses menggunakan pemangkin konvensional. Asid sulfurik telah digunakan secara meluas dalam proses esterifikasi asid lemak bebas untuk menghasilkan biodiesel namun ia mempunyai kekurangan utama yang mampu menyebabkan menghakis dan tidak mesra alam. Dalam kajian ini, biodiesel telah diproses melalui metanolisis asid oleik dan sintesis melalui campuran PFAD- asid oleik berdasarkan nisbah 8:2 menggunakan pemangkin komposit titania disulfur – silika. Pemangkin ini telah disediakan melalui tindak balas campuran 0.5 M larutan titanate tetraisopropil berserta silika dan disulfur dengan 0.5 M asid sulfurik. Pemangkin ini dikategorikan menggunakankaedah FE SEM, XRD, BET, TGA, TPD – NH_3 dan FTIR. Prosess esterifikasi dijalankan di dalam tiga leher kelalang bulat di bawah dan dikacau secara sekata. Pemboleh ubah yang dikaji adalah nisbah kepekatan asid oleik dan PFAD-asid oleic terhadap methanol, jumlah pemangkin dan tempoh tindak balas pada suhu malar 65^{o}C dan kelajuan putaran pada 200 psuingan seminit. Proses dioptimumkan menggunakan *response surface methodology* (RSM) dengan Box Behnken design (BBD) untuk melihat hubungan kait di antara setiap pemboleh ubah. Hasil biodiesel yang terhasil adalah ditentukan dengan menggunakan GC/FID dan penukaran adalah ditentukan melalui analisa volumetric. Nilai optimum yang diramalkan untuk hasil perangkap oleate dan asid oleik penukaran dari estarifikasi asid oleik adalah 81.04% dan 92.14%. Manakala nilai optimum untuk hasil perangkap oleate, hasil perangkap palmitate dan penukaran PFAD-asid oleik yang diperolehi daripada esterifikasi daripada campuran PFAD-asid oleik adalah 90.04%, 91.92% dan 96.84% telah diperolehi.

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LIST OF ABBREVIATIONS

Avi	-	Initial Acid Value
Avt	-	Final Volume of Acid
Al_2O_3	-	Alumina
ANOVA	-	Analysis of Variance
ASTM	-	American Society for Testing and Materials
BBD	-	Box Behnken Design
BET	-	Brunauer-Emmet-Teller
BF	-	Boron Fluoride
C	-	Methyl Ester Content
C_1	-	Initial Concentration
C_2	-	Final Concentration
CP	-	Cold Point
DOE	-	Design of Experiment
EIA	-	Energy Information Administration
EN	-	European Biodiesel Standard
F-Value	-	Frequency Value
FAAE	-	Fatty Acid Alkyl Ester
Fe_3O_4	-	Iron Tetra-oxide
FFA	-	Free Fatty Acid
FTIR	-	Fourier Transform Infrared
GC/FID	-	Gas Chromatography- Flame Ionization Detector
GC/MS	-	Gas Chromatography- Mass Spectrometer
H_2O	-	Water
H_2SO_4	-	Sulfuric Acid
H_3PO_4	-	Phosphoric Acid
MPOB	-	Malaysian Palm Oil Board

P-Value	-	Probability Value
PFAD	-	Palm Fatty Acid Distillate
PP	-	Pour Point
ppm	-	Parts Per Million
R & D	-	Research and Development
SD	-	Standard Deviation
Sr/ZrO_2	-	Strontium Doped with Zirconia Oxide
TiO_2	-	Titania
SiO_2	-	Silica
USDA	-	United States Department of Agriculture
V_1	-	Initial Volume of Solution
V_2	-	Final Volume of Solution

LIST OF SYMBOLS

ºC	-	Degree Celsius
CN	-	Cetane Number
CV	-	Coefficient Variation
Df	-	Degree of Freedom
MPa	-	Mega Pascal
MT	-	Metric Ton
R^2	-	Coefficient Determination
R adj ^{2}	-	Adjusted Coefficient Determination

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Petroleum is undoubtedly an important natural resource which has been a global source of energy for decades. Chemically, it is a mixture of complex hydrocarbon compounds with small amounts of nitrogen, oxygen, sulfur and compounds containing traces of metals. On refining, petroleum yields valuable products ranging from gasoline, diesel oil, asphalt, wax and a host of petrochemicals. The petrochemicals and some other products derived from petroleum are in turn used as raw materials for other industrial processes (EIA, 2013).

There is hardly a part of the human life that is not affected by petroleum energy. At present, it is estimated that petroleum and natural gas contribute up to 70% of the global energy consumption (Gary *et al.*, 2007). On the contrary, the environmental unfriendliness and unsustainable nature of petroleum like other fossil fuels discourage its continuous use. Riva Jr (1983), reported that as at 1965, only 10% of the globally produced oil (from petroleum) was consumed. However, due to the projected future demand for the product, it has been estimated that between 1965 and 2040, up to 80% of the residual reserve will be used up. Thus, only 10% of the product will be left to contend with for many more years ahead. These factors among others strongly necessitate the search for an alternative fuel. Figure 1.1 below indicate the global fossil fuel production and forecast from 1900 to 2096. It visualizes the consistent decline of the resources as they get to their respective peaks.

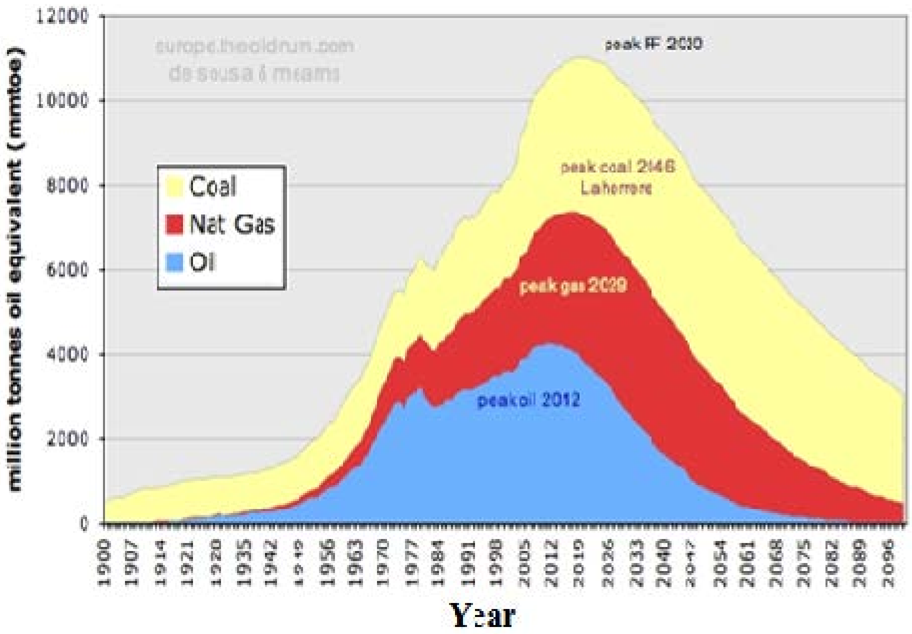

Figure 1.1 : Global Fossil Fuel Production and Forecast (imgarcade.com)

The arduous search for sustainable energy resources to meet the needs of a rapid growing global population remain one of the major challenges of this century (Armaroli and Balzani, 2007; Azadi *et al.*, 2013). Despite remarkable growth in established as well as predicted reserves of fossil fuels expected to last for many more decades, there are still far-reaching uncertainties surrounding the assertion as a result of their unsustainable and unrenewable nature (Lee *et al.*, 2014). Furthermore, continuous combustion of such large quantity of carbon based fuels cannot be accomplished without accompanying detrimental effects on the environment. Effects ranging from the discharge of greenhouse gases which leads to greenhouse effect and subsequently to global warming (Searchinger and Heimlich, 2008). It is therefore inevitable to strike a balance between meeting the target of global rising energy demands and the obligation to mitigate current carbon dioxide and associated toxic emissions all of which lead to climatic changes (EIA, 2013). The best mitigation and amelioration measure remain finding an alternative to fossil fuels. The alternative fuel should be one that is devoid of the shortcomings associated with fossil fuels. This quest however stimulates various researches in the area of biofuels to boost their production.

Biofuels are fuels derived from plant and animal sources through succession of biological processes. Depending on the desire, they could be transfigured into the liquid, solid or gaseous forms. The major advantage of biofuel over petroleum aside being renewable and sustainable is its oxygen content. The oxygen content of biofuel is within the range of 10% to 45%, compared to petroleum that has just a trace or in some cases none, depending on its origin. Biofuels are also characterized with low sulfur content and many of them have low nitrogen content as well. Biomass can conveniently be converted into liquid and gaseous fuels via thermochemical and biological means. Liquid biofuels are classified as bio-alcohols, vegetable oils and biodiesels, as well as bio-crude and bio-synthetic oils (Outlook, 2010). The advantages associated with biofuels has made it to gain increased acceptance worldwide. This is evident in its global market share index as illustrated in Figure 1.2 below showing the gradual spread of biofuels across almost all parts of the globe.

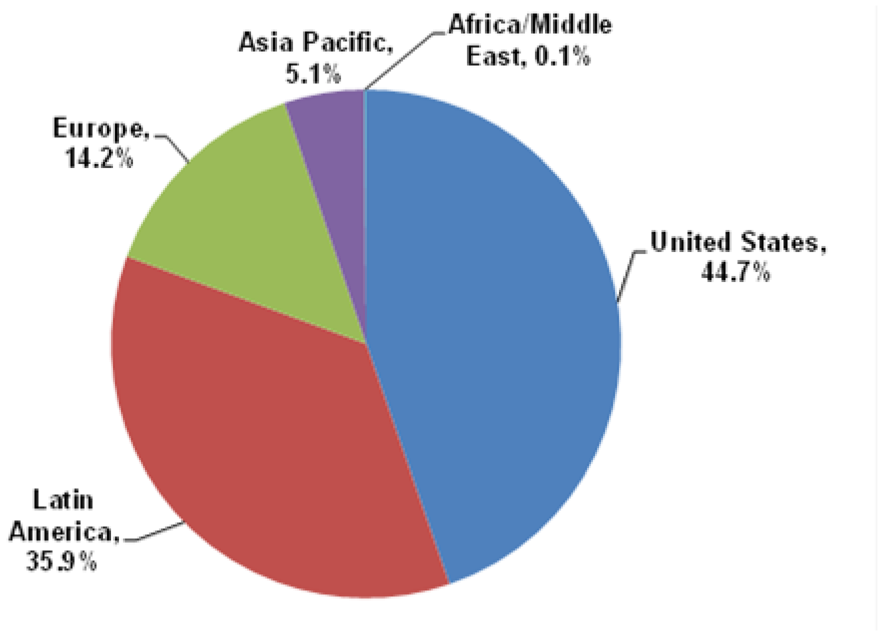

Figure 1.2 : Biofuel Market Share by Region, World Markets, 2010 (Pike Research).

Biodiesel, a liquid biofuel is defined by the American Society for Testing and Materials (ASTM) as the monoalkyl esters of long-chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fats (EIA, 2013). It has been identified as a better substitute of petroleum diesel due to its renewability, sustainability and biodegradability. In general, biodiesel is produced via transesterification of vegetable oils or animal fats or from esterification of fatty acids with short-chain alcohols using homogeneous or heterogeneous catalysts (Behzadi and Farid, 2007). The most common feedstocks used for biodiesel synthesis are refined vegetable oils such as soybean oil, cottonseed oil, palm oil, sunflower oil among others (Rashid *et al.*, 2008). The current increase in the demand of biodiesel has led to more increase in the demand for refined vegetable oils. This leads to a rise in the price of the commodity and of the biodiesel product due to increased production cost. Consequently, biodiesel inevitably become more expensive than petroleum diesel. These drawbacks have necessitated the search for alternative non-edible and cheaper feedstocks.

Low cost oils and fats are characterized with high amounts of free fatty acids (FFAs) compared to refined vegetable oils. The presence of FFAs requires the use of acid catalysts other than base catalysts to avoid soap formation and other process complexities. In order to reduce the production cost, more attention is paid to non-edible oil sources which contain higher amount of FFAs for biodiesel synthesis. Oleic acid, a fatty acid with 18 carbon atoms, is one of the fatty acid that occur naturally in lipids. Serrano-Ruiz *et al.* (2011) mentioned that oleic acid is available in high amount in many natural oils. Therefore, using oleic acid as the model compound generally describes the esterification reaction for FFAs to produce biodiesel.

Another important feedstock for biodiesel synthesis is palm fatty acid distillate (PFAD) which is in abundant in Malaysia. Oil palm industries in Malaysia produce about 16 million tons of crude palm oil per annum. About 700,000 metric tons of PFAD is obtained as a by-product in the crude palm oil refining process. At present, palm fatty acid distillate is mainly used in the animal feed, cosmetic and soap industries as a starting raw material (Sumathi *et al.*, 2008). It consist of high free fatty acid (FFA) content within the range of 85-93 wt%, about 10 wt% of triglycerides and small amounts of squalene, sterols and vitamin E (Lokman *et al.*, 2015; Refineries, 2013). The major constraint of using PFAD as biodiesel feedstock is its high FFA content. However, a suitable heterogeneous catalyst will facilitate a high FAME yield from the feedstock (Hara, 2009).

Various heterogeneous catalysts have shown remarkable activity in various industrial processes ranging from chemical to other manufacturing processes (Lee, 2014; Somorjai *et al.*, 2009). In a post petroleum period, catalysis will play a major role in breaking the existing barriers in research and development (R&D) thereby creating economically feasible path ways to other untapped sources of energy mainly in the area of bio-generated processes (Lee, *et al.*, 2014).

Generally, the activity of base catalysts is higher than those of acid catalysts in the transesterification of high purity oils with low FFA content. They are however not suitable for the transesterification of oils having high FFA content such as PFAD and its likes. The base catalyst tend to react with the acidic FFA to initiate neutralization and saponification reactions respectively. Consequently, the reactions are compensated and the catalyst is deactivated. To overcome these undesirable side reactions, an acid catalyst such as homogeneous sulphuric acid is used to esterify high FFA oils (Ayuk *et al.*, 2011). Nevertheless, the final biodiesel product will require several purification steps to be recovered from the acid catalyst. This creates additional production cost which in turn reflects on the cost of the end biodiesel. The aforementioned difficulties gave rise to the use of solid acid catalysts. These catalysts are capable of eliminating the problems caused due to corrosion, separation, emulsification and saponification respectively (Lokman, *et al.*, 2015).

Theoretically, the esterification as well as transesterification of high FFA feedstocks requires high temperature and longer reaction time due to the slow rate of reaction of the process. To overcome these challenges, a two-step process was introduced. The feedstock was first treated via an acid catalyst to reduce the amount of FFA and the remaining triglycerides is transesterified using a base catalyst (Lokman *et al.*, 2014). Subsequently, autoclave reactors were introduced and can be used to skip the two- step method; however, both methods were found to be difficult, time consuming and dissipate so much energy (Talebian-Kiakalaieh *et al.*, 2013). Similarly, enzyme-based transesterification is also carried out at moderate temperatures with high yields, but this method cannot be used in the industry today due to high enzyme costs, and the problems related to its deactivation caused by feed impurities (McLaughlin, 2011).

Despite the present challenges in biodiesel synthesis, the ultimate goal is to obtain biodiesel that is cheaper than petroleum diesel. In this study, oleic acid and PFAD-oleic acid blend in the ratio 8:2 were separately used as feedstock for biodiesel production. The esterification of each feedstock was carried out using sulfated titania-silica as catalyst. The catalyst was prepared by reacting silica with titanium isopropoxide solution which is a cheap precursor of Titania. The titania-silica composite synthesized was then impregnated with sulphuric acid to enhance the attachment of the sulphate group in order to yield the desired sulfated titania-silica composite catalyst.

1.2 Problem Statement

Depletion of natural resources and increased human population as well as environmental pollution are serious challenges confronting the world today. Therefore to improve energy security for economic development, it is imperative to search for an alternative fuel that is devoid of the problems faced with fossil-diesel.

The emergence of biodiesel as one of the topmost potential renewable energy to adequately replace fossil derived diesel was globally embraced. This is because it is found to be a promising, nontoxic and biodegradable substitute of fossil fuel. Biodiesel can be used directly or as a blend with petroleum diesel without prior modification of the engine. Other advantages of biodiesel include its sustainability and environmental friendliness; as it emits low greenhouse gases. These advantages among others has encouraged tremendous growth in the biodiesel industry. Sakai *et al.* (2009) reported that biodiesel production rose from about 25 million gallons in the early 2000s to about 1.7 billion in 2014. However, the consistent use of refined vegetable oils for biodiesel production is commercially impractical due to the high cost of feedstock (which reflects on the final product biodiesel) and undue competition with food resources. This situation poses a potential threat to the sustainability of the biodiesel industry.

Many low grade feedstocks characterized with high FFA are available for biodiesel production. Palm fatty acid distillate (PFAD) and other low-cost feed stock characterized with high FFA are abundant in Malaysia. Oleic acid has been found to be in abundant in many natural oils. It constitutes part of the high free fatty acids of most low grade oils. Therefore, its model compound demonstrates the possibility of esterifying many oils with high FFA. These oils are presently underutilized due to their FFA content which has been perceived by many to be a problem. On the contrary, proper utilization of these feedstocks could be a perfect solution to lowering biodiesel price. A suitable catalyst can enhance a high conversion as well as selectivity of PFAD, other oils with high FFA and even a blend of the oils into good and cheap FAME.

The idea of blending PFAD with oleic acid in this study is to set a pace for blending different low cost oils. This arise from the fact that various low cost oils are region or location specific. In the face of the increasing demand for biodiesel, sometimes it may be difficult to get adequate quantity of a particular oil in a particular place. It is therefore worthwhile to try different low cost oil blends for biodiesel production in order to solve the problem of dependency on a particular specie that may not be available at all or inadequate in a particular region. This could go a long way to solving the problem of the feedstock scarcity and maintenance of its price stability. It will also enhance lowering biodiesel production cost hence its overall cost. A similar approach was used by (Qiu *et al.*, 2011) in the case of soybean oil and rapeseed oil.

Various catalysts are available to catalyze biodiesel synthesis from PFAD and other high FFA oils. Homogeneous catalysts which are usually in the same phase as the reaction are characterized with formation of complexes leading to so many purification steps and difficulties in separating the catalyst from the biodiesel. Heterogeneous catalysts are in different phase as the reaction and are easily separated downstream. The activity of the solid base catalyst is more than that of the solid acid catalyst but solid base catalysts are generally unsuitable for feedstocks with high FFA such as PFAD, oleic acid and oils containing oleic acid. The solid base catalyst tend to favour neutralization and saponification reactions thereby deactivating the catalyst. The solid acid catalyst has the advantage of being less affected by the FFA content of a feedstock. It also has the advantage of eliminating the neutralization and saponification reactions and can therefore be easily separated from the biodiesel. Sulfated titania - silica composite catalyst which was used in this study is relatively cheap, environmentally friendly and has offered improved selectivity and easy catalyst separation from the reaction mixture. This reduction in process complexities and wastes go a long way to reducing the cost of production and indeed the biodiesel price.

1.2.1 Hypothesis of the Study

The hypothesis of this study is on the utilization of sulfated titania-silica catalyst to improve the responses (methyl oleate and methyl palmitate yield as well as conversions of oleic acid and PFAD-oleic acid blend) for the esterification of oleic acid and PFAD-oleic acid blend compared to the conventional homogeneous catalysts mainly sulphuric acid. It is expected that an increase in the methanol ratio, catalyst loading and reaction time will increase the conversions of oleic acid and PFAD-oleic acid blend as well as methyl oleate and methyl palmitate yields until an optimum is reached.

In addition, optimization using response surface methodology (RSM) with Box Behnken design (BBD) can predict the optimum conditions for oleic acid and PFAD-oleic acid blend with minimum error between the predicted and experimental values.

1.3 Objective of the Study

1. To prepare, characterize and screen sulfated titania-silica composite catalyst for the esterification of oleic acid and PFAD-oleic acid blend.
2. To characterize oleic acid and PFAD-oleic acid blend using GC/MS and to optimize their esterification using RSM with BBD.
3. To analyse the biodiesel produced from oleic acid and PFAD-oleic acid blend using GC/FID

1.4 Scope of the Study

The scope of this study are:

1. Preparation of sulfated titania – silica composite derived solid catalyst by reacting silica with titanium isopropoxide solution which is a precursor of titania. The TiO_2-SiO_2 particles formed was then sulfated by impregnating with sulphuric acid and calcined at various temperatures and time. The catalyst obtained was characterized by BET-surface in order to ascertain its specific surface area, pore size and pore volume, XRD to determine its crystallinity, FE-SEM and EDX to determine its morphology and elemental composition and FTIR to ascertain its consistent nature by identifying its functional groups, TPD-NH_3 to test the acid stability of the catalyst and TGA to test the thermal stability of the sulfated titania-silica catalyst.

2. Characterization of oleic acid and PFAD-oleic acid blend using GC/MS and to optimize the esterification of oleic acid and PFAD-oleic acid mixture using response surface methodology (RSM) based on Box Behnken design (BBD).

3. Analysis of the synthesized methyl oleate and methyl palmitate using GC/FID to determine their yield and volumetric analysis to obtain its conversion.

1.5 Significance of the Research

This research demonstrates the use of sulfated titania-silica catalyst as a cheap and environmentally friendly catalyst for the esterification of oleic acid and PFAD-oleic acid blend using a batch process. The high yields of methyl oleate and methyl palmitate as well as high conversions of oleic acid and PFAD-oleic acid blend achieved strongly indicates that the catalyst has a high activity and was found to eliminate the downstream process complexities encountered with homogeneous as well as heterogeneous base catalysts. On this basis, sulfated titania-silica catalyst is suitable to replace corrosive sulphuric acid in the esterification of high FFA oils. The optimum experimental variables used in this study can serve as a valuable guide in scaling up the process and will also serve as a guide for better utilization of high FFA oils in biodiesel production.

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