Faculty of Resource Science and Technology

BIODIESEL FROM FREE FATTY ACID (FFA) BY USING HETEROGENEOUS CATALYST

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Declaration

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning. I hereby declare that this project is the work of my own excluded for the references document and summaries that has been acknowledge.

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List of Abbreviations

FFA	Free Fatty Acid
PFAD	Palm Fatty Acid Distillate
CPO	Crude Palm Oil
FAME	Fatty Acid Methyl Ester
FAEE	Fatty Acid Ethyl Ester
ACC	Activated Carbon Catalyst
CaO	Calcium oxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
$CaCO_3$	Calcium carbonate
FTIR	Fourier Transform infrared spectroscopy

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Biodiesel From Free Fatty Acid (FFA) By Using Heterogeneous Catalyst

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ABSTRACT

Biodiesel refers to non-petroleum based fuel obtained from transesterification of vegetable oil. This study was conducted to produce biodiesel from palm fatty acid distillate (PFAD), crude palm oil (CPO) and palm stearin. Biodiesel is produced from waste material by using transesterification process in the present of catalyst. The heterogeneous catalysts were prepared from natural resources as a source of calcium oxide (CaO) and activated carbon catalyst (ACC) to produce a low cost biodiesel production catalyst. CaO was prepared from mussel shell while ACC prepared from plant under calcination at 1000 ^{o}C. Both biodiesel and catalyst were characterized by Fourier Transform Infrared (FTIR). Biodiesel production from PFAD was produced by two step reactions of esterification as pre-treatment using H_2SO_4 and transesterification using CaO as catalyst. CPO and palm stearin was produced using 30% methanol as minimum requirement for industrial purposes.

Keyword: Biodiesel, Palm Fatty Acid Distillate, Crude Palm Oil, Free fatty acid, Transesterification.

ABSTRAK

Biodiesel merujuk kepada bahan api berasaskan bukan petroleum diperolehi daripada transesterifikasi minyak sayur-sayuran. Kajian ini dijalankan untuk menghasilkan biodiesel daripada palm fatty acid distillate (PFAD), crude palm oil (CPO) dan palm stearin. Biodiesel dihasilkan daripada bahan buangan dengan menggunakan proses transesterifikasi. Pemangkin heterogen disediakan daripada sumber semulajadi sebagai sumber kalsium oksida (CaO) dan activated karbon (ACC) untuk menghasilkan biodiesel kos rendah. Kalsium oksida dihasilkan daripada kepah manakala ACC dihasilkan daripada tumbuhan dibawah pengkalsinan pada 1000^{o}C. Kedua-dua biodiesel dan pemangkin telah dicirikan oleh Fourier Transform Infrared (FTIR). Biodiesel daripada PFAD telah dihasilkan melalui dua proses tindakbalas, esterifikasi sebagai pra-rawatan menggunakan H_2SO_4 dan transesterifikasi menggunakan CaO sebagai pemangkin. CPO dan palm stearin telah dihasilkan dengan menggunakan 30% methanol sebagai keperluan minimum untuk tujuan perindustrian.

Kata kunci: Biodiesel, palm fatty acid distillate, crude palm oil, free fatty acid, transesterifikasi.

CHAPTER 1

Introduction

Petroleum-based fuels are important in the energy sector as it is essential for transportation. However, due to the depleting of this non-renewable natural source, the alternative fuel which is renewable and non-toxic energy becoming important to replace petroleum-derived diesel oil. Biodiesel is a biodegradable and non-toxic as it is made from renewable resources and it has properties that similar to petroleum-based diesel oil. Biodiesel is an alternative fuel for diesel engine and can be used directly in most diesel engine without require any engine modifications. It can be produced from vegetable oil and animal fat that is transesterified with simple alcohol to produce fatty acid methyl ester (FAME) or known as biodiesel (Boey *et al*., 2009). The advantages of using biodiesel are it is a renewable fuel and have low toxicity compared to diesel. It can minimize the environmental pollution as it degrades more rapidly than diesel fuel. Furthermore, it has excellent properties as a lubricant where it can be used in a conventional diesel engine (Romano & Sorichetti, 2011).

1.1 Sources of Biodiesel

Biodiesel can be produced from raw materials such as cooking oils, vegetable oils and fat residues (Romano & Sorichetti, 2011). The vegetable oil extracted from plant is used due to high triglycerides content that is similar in properties to diesel (Arifin, 2009). Vegetable oils include edible and non-edible oil is promising feedstock for biodiesel. More than 95% of biodiesel production feedstock comes from edible oil. Common edible oils used in biodiesel production are soybean, palm oil, rapeseed and sunflower. The examples of non-edible oil that has been used are castor oil, tung, cotton and jojoba (Romano & Sorichetti, 2011). Vegetable oils have become attractive research because of their environmental friendly and made from renewable resources (Abdul Rashid, 2008). Currently, Asian countries are exploring palm oil as FAME feedstock and since crude palm oil is the world's cheapest vegetable oil, it presents a potential alternative as feedstock for FAME (Yee & Lee, 2008). There are many types of palm oil products such as palm fatty acid distillate (PFAD), crude palm oil (CPO) and palm stearin.

1.2 Transesterification

Biodiesel can be produced by a chemical process known as transesterification which it is formed by replacing the glycerol molecule with methyl from methanol molecule. Transesterification is a reversible reactions and proceeds by mixing the reactants. This reaction of oil with an alcohol in the presence of catalyst produced mono-alkyl esters and glycerol. Glycerol are then separated and purified. The transesterification reaction requires a catalyst in order to obtain reasonable conversion rates (Meher *et al*. 2004).

1.3 Catalysts

Catalyst is very important in the production of biodiesel to complete the reactions. The catalysts used for the transesterification may be classified as heterogeneous and homogeneous base, acid and enzymatic catalyst.

1.3.1 Homogeneous catalyst

The widely used homogeneous alkali catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH) while homogeneous acid catalyst is sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). All homogeneous alkali and acid catalyst can easily soluble in methanol for the conversion of oil to ester (Arifin, 2009). The advantage of using homogeneous catalyst is simple usage and less time required for oil conversion (Borges & Diaz, 2012). Although homogeneous catalyst is cheaper and can provide high yield of biodiesel, it produced a large amount of water resulting from washing by water and neutralization by acid or alkali (Sharma *et al*., 2010). This lead to higher production costs as the processes involves washing and purification steps to meet the specific biodiesel quality and glycerol separation process needs improvements (Semwal *et al*., 2011). Besides that, the formations of soaps during separation also cause the loss of triglycerides molecules that can be used in production of biodiesel (Yee & Lee, 2008). This problem can be overcome by using heterogeneous catalyst (Sharma *et al*., 2010).

1.3.2 Heterogeneous catalyst

Heterogeneous catalyst act in a different phase from the reaction mixture while homogeneous act in the same phase as reaction mixture (Sharma *et al*., 2010). Heterogeneous solid base used in biodiesel synthesis are enzymes, basic zeolites, alkaline earth metal oxides and hydrotalcites (Pandey *et al.*, 2011). The example of enzyme catalyst is lipase. The use of enzyme catalyst for production of biodiesel has attracted much attention as enzyme can tolerate with free fatty acid and water content. This can lead to easy purification of biodiesel and glycerol. However, enzyme catalyst has some drawbacks where it is expensive and has long residence time (Chouhan & Sarma, 2011). The heterogeneous base catalysts that are abundantly used are magnesium oxide (MgO) and calcium oxide (CaO) (Thanh *et al.*, 2012). These catalysts are identified as a good option to replace homogeneous catalyst because it can exhibit alkaline properties (Pandey *et al*., 2011). It also more environment-friendly as heterogeneous catalyst can be recycle and exhibits a less corrosive character (Romero *et al.*, 2007).

1.4 Problem statement

This study was conducted to produce biodiesel from waste by transesterification processes on palm fatty acid distillate (PFAD), crude palm oil (CPO) and palm stearin as a raw material. The problem with processing this raw material was that it contains a large amount of free fatty acid and homogeneous alkali catalyst cannot directly be used due to formation of soap (Hillion *et al*., 2003). This cause lower yield of the biodiesel and inhibits the separation of the esters from the glycerol (Leung *et al*., 2010). This also causes higher costs for the production of biodiesel. From previous study, biodiesel from PFAD and CPO were produced using H_2SO_4 and KOH as a catalyst in two step reactions of esterification and transesterification (Boonnoun *et al*., 2008). In this study, the biodiesel was produced by single step reaction of transesterification using heterogeneous catalyst prepared from mussel shell and plant. This single step reaction subtracting the double step reactions which need a longer time and unfavourable for industries. Biodiesel was also produced using commercial CaO and activated carbon catalyst (ACC) as comparison. In the transesterification process, methanol was used as alcohol solvent because it is cheaper from other alcohol solvent. Different catalyst and ratio of methanol to oil were used to compare the yield of biodiesel production.

1.5 Research objectives

The objectives of this study are:

i. To prepare heterogeneous catalyst from natural resources.
ii. To compare biodiesel production from palm fatty acid distillate (PFAD), crude palm oil (CPO) and palm stearin.
iii. To characterize biodiesel using Fourier Transform Infra-Red (FT-IR)

CHAPTER 2

Literature Review

2.1 Biodiesel

Biodiesel refers to a diesel-equivalent and processed fuel which derived from biological sources. Biodiesel is monoalkyl esters of long chain fatty acids which can be obtained from renewable feed stocks like vegetable oil or animal fats (Romano & Sorichetti, 2011). Vegetable oils and animal fats contain triglycerides is the main components which are esters of free fatty acid with glycerol. Different free fatty acid can be attached to the glycerol backbone as triglyceride contains several free fatty acids (Thanh *et al.*, 2012).

2.2 Raw materials

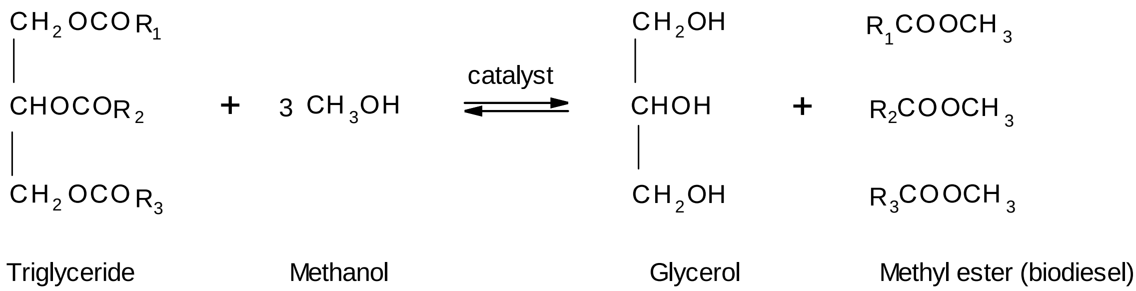
There are many types of raw materials reported for the production of biodiesel. The raw materials are important to a major portion in the cost of biodiesel production. The examples of edible oil are rapeseed, soybean, palm oil and sunflower oil (Encinar *et al*., 2010). Rapeseed is most important raw material in the European and soybean is basically important for biodiesel production in Argentina (Romano & Sorichetti, 2011). In Malaysia and Indonesia, the coconut oil is utilized for the production of biodiesel (Encinar *et al*., 2010). The biodiesel from soybean yields other valuable sub-products besides glycerin such as soybean meal and pellets. Most of the biodiesel is synthesized from edible oil causes problems arise as food resources are actually being converted into automotive fuels. These lead to global imbalance to the food supply and demand market for large-scale production of biodiesel from edible oil.

In order to overcome the devastating phenomenon, the non-edible oil such as castor oil, tung, cotton, jojoba and Jatropha are used in the production of biodiesel. The advantages of non-edible oils for biodiesel production are lower cost and no foodstuffs are spent to produce fuel. Non-edible oil also can be grown in waste lands which are not suitable for food crops (Leung *et al*., 2010). Besides that, microalgae is one of other alternative for biodiesel as it can produce very high yield of oils but only some species can be used for biofuel production (Romano & Sorichetti, 2011). In the presence of sunlight, microalgae convert carbon dioxide into sugar and protein but they produced oil when they starved of nitrogen (Encinar *et al*., 2010).

Palm oil are obtained from the fruit can produce high oil yield product is currently important in Asian for biodiesel production. Palm Fatty Acid Distillate (PFAD) is a by-product which obtains from palm oil refinery that contains the major component of 90-93% free fatty acid (FFA) and 10% of triglyceride (Boonnoun *et al*., 2008). Palm stearin is a mixture of fats that fractionated from palm oil and contains a mixture of different fully natural ingredients. It is mainly used as an edible, trans-fat free and a healthy alternative to partially hydrogenated plant oils. Crude Palm Oil (CPO) is the raw oil product that obtained from the extraction process of the palm and it is the most potential oil that can be used as a raw material to produce biodiesel (Alkabbashi *et al*., 2009).

2.3 Transesterification

Transesterification or alcoholysis is a process used to convert oils to biodiesel. There are two methods to produce biodiesel from oils and fat which is base catalyzed and acid catalyzed transesterification of the oil (Maqbool, 2010). Transesterification is the process where triglyceride molecules react with an excess alcohol in the presence of catalyst such as KOH, NaOH and CaO to produce glycerin and fatty esters. The simplified form of transesterification reaction is presented in the equation as shown below:



Scheme 1: The Transesterification Reaction.

Transesterification consists of three reversible reactions. There are conversion of triglyceride to diglyceride, diglyceride to monoglyceride and monoglyceride to fatty ester and glycerol (Chouhan & Sarma, 2011). There are two liquid phases that are formed in the transesterification process. The upper phase contains methyl or ethyl ester while the lower phase consists of glycerol and some catalyst. The intermediate products and residual free fatty acids in the oil are water and soap (Joshi, 2008). The stepwise reactions are reversible and to shift the equilibrium towards the formation of ester, a little excess of alcohol is used. Transesterification is faster when using alkaline catalyst (Arifin, 2009). Mixing efficiency is the most important factors to produce high yield of transesterification as alcohol and oil are immiscible. The mechanical stirring method is used because it is suitable for homogeneous and heterogeneous catalysts (Thanh *et al.,* 2012).

2.4 Esterification

Esterification is applied to biodiesel production where a free fatty acid reacts with an alcohol to produce an alkyl ester and water. Acid catalyst sulfuric acid and phosphoric acid normally used in esterification step. This method is suitable for feedstock that contains high level of free fatty acid (FFA) (Altic, 2010). Besides that, acid-catalyzed esterification of FFA is faster than acid-catalyzed transesterification reaction as the molecule of FFA are smaller compared to the molecules of triglyceride. Industrially, two step reactions of esterification and transesterification involve in biodiesel production. The first step is to convert the FFA into alkyl esters and then convert the remaining triglycerides into methyl esters where base catalyst is added to transesterify the remaining triglycerides (Altic, 2010). The esterification of FFA with alcohol using acids catalyst will produce ester and water. The esterification reaction is shown as below:

$$\underset{\text{Free fatty acid}}{RCOOH} + \underset{\text{Methanol}}{CH_3OH} \xrightarrow{\text{acid catalyst}} \underset{\text{Ester}}{RCOOCH_3} + \underset{\text{Water}}{H_2O}$$

Scheme 2: The Esterification Reaction.

2.5 Catalyst

Catalyst is a substance that can be used to accelerate the rate of reaction by lowering its activation energy. There are three types of catalyst that being used in transesterification of tryglycerides. There are homogeneous, heterogeneous and enzyme catalyst. The acid catalyst is good for higher free fatty acid but the reaction is slow to convert tryglycerides to fatty acid methyl ester (Lee *et al.*, 2009). The transesterification catalyst depends on the amount of free fatty acid and raw material.

2.5.1 Homogeneous Catalyst

Homogeneous catalyst is the catalysts that act in the same liquid phase as the reaction mixture (Borges & Diaz, 2012). Homogeneous catalyst involves processes in which catalyst is in solution with at least one of the reactant. Two types of homogeneous catalyst that are commonly used in transesterification are acid catalyst and alkali catalyst. The examples of acid catalyst are H_2SO_4 and HCl while KOH and NaOH are in group of alkali catalyst (Arifin, 2009). The most common used of alkaline catalyst is NaOH due to wide availability and low costs (Lotero *et al.*, 2005). The high purity and yield of biodiesel product in a short time can be achieved from the alkali catalysed process (Abdul Rashid, 2008). However, the reaction of alkali catalyst such as NaOH will form soap when reacted with free fatty acid thus lower the yields of biodiesel and inhibits the separation of the ester (Leung *et al.*, 2010).

Raw materials containing high amount of FFA such as Jatropha and tobacco oils usually used an acid catalyst because the reaction does not form soap. However, acid catalyst is very sensitive to water content of raw material (Canacki & Gerpen, 2003). The small amount of water can affect the fatty acid methyl ester (FAME) yield of the transesterification. The disadvantage of using acid as a catalyst is corrosion problem to the equipments, higher temperature and longer time is needed for the reaction. Moreover, a large amount of methanol is needed to increase the conversion of triglycerides. Acid catalyst is used as a pre-treatment step to reduce the reaction time (Thanh *et al.*, 2012).

2.5.2 Heterogeneous catalyst

Heterogeneous catalyst is catalysts that act in a different phase from the reaction mixture usually a solid (Borges & Diaz, 2012). Metal oxides are commonly used as heterogenous catalyst. Examples of metal oxides used are calcium oxide, magnesium oxide, strontium oxide, mixed oxides and hydrotalcites. The most favourable heterogenous base catalyst is calcium oxide, CaO (Borges & Diaz, 2012). CaO can be prepared from cheap and natural resource like lime stone and commonly used to replace homogeneous base catalysts for production of biodiesel (Pandey *et al.*, 2011). The other sources of calcium oxide are from egg shell, mollusk shell and crab shell (Viriya-empikul *et. al*, 2010). These natural resources can be used to produce catalyst for biodiesel production as it is low cost. Basically, $Ca(NO_3)_2$ and $Ca(OH)_2$ is the raw material to produce CaO (Viriya-empikul *et. al*, 2010). Heterogeneous catalyst has advantages due to easy separation from the reaction and it can be reused, non-toxic, cheap price, low solubility in methanol, high activity, longer catalyst life and requires a moderate reaction condition (Chouhan & Sarma, 2011).

2.6 Alcohol

Alcohol that is short chains can be used in biodiesel production such as methanol, ethanol, butanol and amylic alcohol. Ethanol is preferred alcohol because it is derived from agricultural product and environmental friendly (Abdul Rashid, 2008). However, among primary alcohols, methanol is favoured for transesterification reaction as it is high reactive and the least expensive alcohol. The boiling point of methanol is low and excess methanol from glycerol phase can be recovered easily (Thanh *et al.*, 2012). Methanol has less of an affinity to atmospheric moisture absorption and retention. The moisture removal can be achieved by simple distillation. Besides that, methanol is commonly used because of its physical and chemical advantages as well as its low cost (Abdul Rashid, 2008). Methanol can react with triglycerides quickly and alkali catalyst can easily dissolve in it. When methanol is used as a reactant, the product of the reaction will be fatty acid methyl esters (FAME) mixture while a fatty acid ethyl esters (FAEE) mixture will be obtained if ethanol is used in biodiesel production (Borges & Diaz, 2012).

2.7 Glycerin

Glycerin also called glycerol or glycyl alcohol is the usual name of 1,2,3-propanetriol is obtained from the chemical reaction of transesterification. Glycerin has no commercial value and not of high quality. It is a good solvent and a polar substance that can be mixed with water and alcohols (Romano & Sorichetti, 2011). Glycerin is obtained as a sub-product of soap or biodiesel production and it is purified to eliminate the contaminants such as catalyst and methanol from biodiesel production. Recently, the production of glycerin has increased due to the biodiesel production and there are many researches to produce high value added product using glycerin for example the raw material for the production of detergent and the production of other biofuels such as biogas (Romano & Sorichetti, 2011).

CHAPTER 3

Materials and Methods

3.1 Materials

Palm fatty acid distillate (PFAD), crude palm oil (CPO) and palm stearin were obtained from Eco-Green Technology. All chemicals including 99% methanol (MeOH), dichloromethane (DCM), 98% sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and calcium oxide (CaO) are commercial grade that obtained from Robert Scientific Sdn. Bhd and Modern Scientific Sdn. Bhd. Activated Carbon Catalyst (ACC) prepared from plant. CaO catalyst from mussel was obtained from market.

3.2 Measurement

Instruments that were used in this research are Perkin Elmer Thermoscientific Smart Omni Transmission Nicolet IS10 Fourier Transform Infrared Spectrometer (FTIR). The spectra were obtained in the 400-4000 cm^{-1} and average of 12 scans were recorded. The separation of biodiesel and glycerol was done using Centrifuge Machine (Model: Himac CR 21G).

3.3 Methodology

3.3.1 Preparation of heterogeneous catalyst

I. Calcium Oxide (CaO) from mussel

Mussel which obtained from market was cleaned and washed thoroughly with warm water. It was dried in an oven for overnight and heated in a furnace for 8 hours at 1000 ^{o}C. The catalysts were cooled to room temperature and crushed using mortar and pestle.

II. Activated Carbon Catalyst (ACC) from plant

The plant was dried under direct sun for 48 hours until the color turn to brown. The plant was calcined at 1000^{o}C for overnight and the ash produced was soaked in 20% NaOH for 2 h. Then, the ash was washed using distilled water and dried in the oven for overnight. 20% concentrated HCl was added and the ash was filtered, followed by washed using distilled water until the pH is 7 and dried in the oven. NaOH was added into a crucible containing ash in the ratio of 1:1 and heated in the muffle furnace. Petroleum ether (5ml) was added and the ash was filtered. The catalyst containing NaOH was calcined in the muffle furnace for 7-10 min and grinded using mortar and pestle.

3.3.2 Transesterification of Palm Fatty Acid Distillate (PFAD)

I. Using CaO from mussel

Methanol (24.21 g) and (1.21 g, 5%) of CaO catalyst from mussel were added to a three-necked round-bottom flask and the reaction mixture was stirred and heated to reflux in 1h. Melted PFAD (24.21 g) was added to the flask and continue refluxed for overnight. After the reaction was completed, the mixture was filtered using filter paper to remove the catalyst.

Then, the methanol was removed by a rotary evaporator and the mixture was centrifuged at 5000 rpm for 30 min to remove the glycerol.

II. Using commercial CaO

Methanol (24.21 g) and (1.21 g, 5%) of commercial CaO catalyst were added to a three-necked round-bottom flask and the reaction mixture was stirred and heated to reflux in 1h. Melted PFAD (24.21 g) was added to the flask and continues refluxed for overnight. After the reaction was completed, the mixture was filtered using filter paper to remove the catalyst. Then, the methanol was removed by a rotary evaporator and the mixture was centrifuged at 5000 rpm for 30 min to remove the glycerol.

III. Using ACC

Methanol (9 g) and (0.45 g, 5%) of ACC were added to a three-necked round-bottom flask and the reaction mixture was stirred and heated to reflux in 1h. Melted PFAD (24.21 g) was added to the flask and continues refluxed for overnight. After the reaction was completed, the mixture was filtered using filter paper to remove the catalyst. Then, the methanol was removed by a rotary evaporator and the mixture was centrifuged at 5000 rpm for 30 min to remove the glycerol.

3.3.3 Transesterification of Crude Palm Oil (CPO)

I. Using commercial CaO

Methanol (7.8 g) and (1.3 g, 5%) of commercial CaO catalyst were added to a three-necked round-bottom flask and the reaction mixture was stirred and heated to reflux in 1h. Melted CPO (26.00 g) was added to the flask and continues refluxed for overnight. After the reaction