TRANSESTERIFICATION OF CASTOR OIL TO BIODIESEL BY USING MAGNESIUM OXIDE AS SOLID-BASE CATALYST

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ABSTRACT

All these years fossil fuels are the main resources of energy that meets the world requirements. Gasoline, petrodiesel and natural gas are the fossil-based resources which are limited and insufficient for the future world's energy demands. Therefore, the search of renewable fuels is a big concern nowadays. Biodiesel is a renewable, environmental friendly and biodegradable fuel that it may substitute conventional fuel with none or very minor engine modification. Environmental issue is one of the concern about the fossil-based fuels because of the emission of total hydrocarbons and carbon monoxide which is contrast with biodiesel due to more complete combustion caused by the increased oxygen content in the flame coming from the biodiesel molecules. Biodiesel is the product from the chemical reaction called transesterification between vegetable oil or animal fat with an alcohol to produce a fatty acid alkyl ester. Methanol is the common alcohol used due to its low cost.Biodiesel can be produced from use waste edible oil or non-edibles oil such as jatropha, castor,and rubber seed. Mostly, the biodiesel today is produced by base-catalyzed transesterification. In this study, the parameters were: methanol to oil ratio of 3:1 and 4:1; and time of 1 hour, 2 hour and 3 hour. For every experiment done, castor oil was heated at 50°C and mixed with methoxide (methanol and Magnesium Oxide) according to the considered parameters. The agitation speed was set at 400 rpm. After the transesterification process completed, the hot mixture was left to settle down for at least one day in a separating funnel. After one day, there were two layers formed. The lower layer of glycerine and catalyst and the upper layer of castor oil methyl ester. The product of castor oil methyl ester was washed with 60°C hot tap water for few times. Next, the product was transferred into a rotary evaporator to remove excess methanol. Then, the product was transferred to a universal bottle and some Magnesium Sulphate was added into it. The mixture was shaken vigorously and was left to settle down for one day. The final product was sucked by using a pipette and then analyzed by using Gas Chromatography-Mass Spectrocopy (GC-MS). The highest yield of biodiesel from the research was found to be 78% at methanol to oil ratio of 4:1, reaction time of 3 hours and temperature of 60°C. This study also proved that biodiesel can be produced from castor oil because the GC-MS analysis showed that all the products contained methyl ricinoleate.

TRANSESTERIFIKASI MINYAK CASTOR KEPADA BIODIESEL MENGGUNAKAN MAGNESIUM OKSIDA SEBAGAI PEMANGKIN BERASASKAN PEPEJAL

ABSTRAK

Selama beberapa tahun ini bahan api fosil merupakan sumber utama tenaga yang memenuhi keperluan dunia. Petrol, petrodiesel dan gas asli adalah merupakan sumber berasakan fosil yang terhad dan tidak mencukupi untuk menampung permintaan tenaga dunia pada masa hadapan. Oleh itu, mencari bahan api yang boleh diperbaharui adalah satu tumpuan utama pada masa kini. Biodiesel adalah bahan api yang boleh diperbaharui, mesra alam dan boleh dihapuskan yang menjadikan ia pengganti bagi bahan api konvensional dengan tiada atau pengubahsuaian enjin yang sangat kecil. Isu alam sekitar merupakan salah satu daripada kesan buruk daripada bahan api berasaskan fosil kerana pelepasan jumlah hidrokarbon dan karbon monoksida yang sama sekali berbeza dengan biodiesel di mana pembakaran adalah lebih lengkap disebabkan oleh kandungan oksigen meningkat dalam bara yang datang dari molekul biodiesel. Biodiesel adalah produk daripada tindakbalas kimia yang dipanggil *transesterification* yang berlaku antara minyak sayuran atau lemak haiwan dengan alkohol untuk menghasilkan alkil ester asid lemak. Metanol adalah alkohol yang biasa digunakan dalam proses ini kerana kosnya yang rendah. Biodiesel boleh dihasilkan daripada sisa minyak masak atau minyak bukan untuk dimakan seperti jatropha, kastor/jarak dan biji getah. Kebanyakkan biodiesel pada hari ini dihasilkan dengan *base-catalyzed transesterification.* Dlam kajian ini, parameter yang dikaji adalah seperti: nisbah metanol kepada minyak 3:1 dan 4:1; dan masa tindakbalas 1 jam, 2 jam dan 3 jam. Minyak kastor telah dipanaskan pada suhu 50°C dan dicampurkan dengan *methoxide* (metanol dan magnesium oksida) mengikut parameter yang telah ditentukan. Kelajuan pergolakan telah ditetapkan pada 400 rpm. Selepas proses *transesterification* selesai, sebatian yang panas itu dibiarkan di dalam *separating funnel* selama sekurang-kurangnya satu hari. Selepas satu hari, dua lapisan akan terbentuk. Lapisan bawah adalah campuran *glycerin* dan pemangkin

manakala lapisan atas adalah *methyl ester castor oil*. Produk tersebut kemudiannya dibasuh dengan air paip dipanaskan pada suhu 60°C untuk beberapa kali. Seterusnya, produk akan dipindahkan ke dalam *rotary evaporator* untuk menyingkirkan lebihan metanol. Selesai proses menyigkirkan lebihan metanol, produk dipindahkan ke dalam botol universal dan dicampurkan beberapa gram Magnesium Sulfat. Campuran tersebut digoncang beberapa kali dabn dibiarkan untuk satu hari. Produk akhir disedut dengan menggunakan pipet dan kemudian dianalisis menggunakan *Gas Chromatography-Mass Spectrocopy (GC-MS)*. Hasil tertinggi biodiesel daripada penyelidikan ini adalah 78% pada parameter metanol kepada nisbah minyak iaitu 4:1, masa tindak balas 3 jam dan suhu 60 ° C. Kajian ini juga membuktikan bahawa biodiesel boleh dihasilkan dari minyak kastor kerana analisis GC-MS menunjukkan bahawa semua produk mengandungi *methyl ricinoleate*.

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LIST OF SYMBOLS

%	Percentage
°C	Degree celcius
g	Gram
L	Litre
mL	Mililitre
rpm	Revolution per minute
y1	weight of oil before (g)
y2	weight of oil after (g)

LIST OF ABBREVIATIONS

GC-MS	Gas chromatography/Mass Spectrometry
GC	Gas chromatography
MgO	Magnesium Oxide
FFA	Free fatty acids
FAME	Fatty acid methyl ester
et al.	And others

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Castor bean plant or its scientific name Ricinus communis is belong to Euphorbiaceae family. Its origin are from Africa but it is found in both subtropical and tropical countries all around the world including Malaysia. Castor oil had been proven to be the potential source that can contribute to biodiesel production eventhough it contains the ricin toxin that are harmful to human beings. Biodiesel is one type of the renewable, biodegradable and efficient source of energy needs. It is defined as medium length (C16 to C18) chains of fatty acids. Besides, it also comprised mainly of mono-alkyl fatty acid esters.

People commonly used base-catalyzed transesterification because it is the most economical process (Singh et al., 2006). This is usually done by stripping the glycerin from the fatty acids with a catalyst such as sodium or potassium hydroxide, and then replacing it with methanol. Then, the raw product is centrifuged and washed with water to cleanse it of impurities. Finally, it yields methyl or ethyl ester or commonly named as biodiesel with some small amounts of glycerol as the by-product. In the other hand, there are another method to produce biodiesel. It is called the use of heterogeneous (solid) catalysts in transesterification process. This is because it is easy to separate from the reaction medium and it is also reusable. Neither catalyst recovery nor aqueous treatment steps are required in the process. Moreover, the purification steps of products are much simple and yield of methyl esters is very high (Cao et al., 2008).

The overall process is normally a sequence of three consecutive steps which are the reversible reactions. Firstly, diglyceride is obtained from triglycerides. Second, monoglyceride is produced from diglyceride. Lastly, glycerine is obtained from monoglyceride. Esters are produced in all these reactions. According to P. Rosaura et al (2009) the stoichiometric ratio of alcohol/oil has been studied in range of 1:1 and 6:1. According to Liu et al (2007) the order of activity among alkaline earth oxide catalysts is BaO>SrO>CaO>MgO. MgO has low activity in transesterification of vegetables oils to biodiesel. CaO.MgO provided higher catalytic activity than CaO powder to transform rapeseed oil to biodisel. MgO made soap formation in the reaction process.

1.2 Problem Statement

The major concern is the depletion of fossil-fuel source. Hence, the search for the alternative become critical nowadays. Besides that, this study is important to find out whether the vegetable non-edible oil which is castor oil can be a source to produce biodiesel. According to Refaat (2011), heterogeneous catalyzed transesterification generally requires more severe operating conditions which are relatively elevated temperatures and pressures. The main problems with heterogeneous catalysts is their deactivation with time and then resulted to many possible phenomena such as poisoning, coking, sintering and leaching (Sivasamy et al., 2009). According to Lam et al (2010), poisoning is particulary evident when the process involves used oils. Catalyst leaching increase the operational cost as a reeult of replacing the catalyst. Hence, it leads to product contamination. The examples of best qualities of catalyst are catalyze both transeterification and esterification, stable, not activated by water, do not give rise to leaching, active at low temperature and high selectivity (Di Serio et al., 2008).

1.3 Objectives

This research obejectives are:-

a) To produce biodiesel from castor oil

b) To investigate yield of biodiesel in transesterification of castor oil by using MgO base catalyst

1.4 Scope of Study

In this research, the scopes are to find the alternative to fossil-based fuel from natural resources and the use of vegetable non-edible oil which is castor oil for biodiesel production.

1.5 Rationale and Significance

Generally, the significance of my research is to use non-edible vegetable oil as source of production of biodiesel in order to maintain the important of food oil(edible oil). Besides that, the search for the alternative for the depletion of the fossil-fuels source become critical nowadays to support the world energy demand. From past research by Romero (2011), biodiesel derived from vegetable oil has been shown to be a potential alternative replacing petroleum-derived diesel oil for diesel engine. Forero (2010), also reported that biodiesel is obtained by the transesterification of oil triglycerides. These triglycerides are converted to the corresponding alkyl ester and glycerol by transesterification with short chain alcohols typically methanol. Traditional homogeneous catalysts which are mainly in sodium or potassium hydroxide dissolved in methanol. But, they possess advantages of high activity whereby they complete reaction within one hour and mild reactions conditions which are from 40 to 65°C and at atmospheric pressure (Romero, 2011).

Sharma (2011) also reported that oxides of magnesium and calcium (Mg0 and CaO) have been tried as solid base catalyst because of their easy availability, low cost and non-corrosive nature. MgO was found to work efficiently in batch reactor at ambient temperature during the transesterification reaction with production of 500 tonne of biodiesel. The overall cost of production is reduced since it not required heating during the batch process.

CHAPTER 2

LITERATURE REVIEW

2.1 Castor Oil

According to Casa Kinabalu (2012), castor oil is a vegetable non-edible oil obtained from the castor bean in which its scientific name is Ricinus Communis. Castor oil (CAS number 8001- 79-4) is a colorless to very pale yellow liquid with mild or no odor or taste. Its boiling point is 313 °C (595 °F) and its density is 961kg/m3. It is a triglyceride in which approximately ninety percent of fatty acid chains are ricinoleic acid. Oleic and linoleic acids are the other significant components. In addition, its molecular formula is CH3-(CH2)5-CH(OH)-CH2-CH=CH-(CH2)7-COOH which contains a fatty acid with 18 carbon atoms, a double bond between the ninth and tenth carbons, and is known as Dodecahydroxyoleic Acid. No other vegetable oil contains such a diverse and high proportion of fatty hydroxyacids.

According to Forero (2004), we can get castor oil by extracting the seeds of Palma Christi. The seeds are approximately 46% oil. The oil is viscous, pale yellow nonvolatile and non-dry oil. The oil dissolves easily in alcohol, ether, glacial acetic acid, chloroform, carbon sulfide, and benzene. It is made up of triglycerides: 91-95% ricinoleic acid, 4-5% linoleic acid and 1-2% palmitic and stearic acids. Besides that, castor oil also possess a hydroxyl functionality that is rarely found in vegetable oils. Rosaura et al. (2009) found that the functionality give an extra stability to the oil and its derivatives by preventing the formation of hydroperoxides.

2.2 Biodiesel

The main aim of this study is to produce biodiesel from castor oil by base-catalyzed transesterification process. The term biodiesel here is synonyms to that of methyl ricinoleate or ricinoleic methyl ester. Biodiesel is a vegetable oil processed to resemble diesel fuel. Sagar and Sarda (2011) found that biodiesel is technically vegetable oil methyl ester or called fatty acid methyl ester (FAME). Liu et al. (2006) reported that biodiesel is synthesized from direct transesterification of vegetable oils, whereby the corresponding triglycerides react with a short-chain alcohol in the presence of a catalyst.

Table 2.1: Properties of methyl ricinoleate. (ACME Synthetic Chemical, 2012).

Parameters	Range
Synonyms	Ricinoleic acid methyl ester, methyl ester of ricinoleic acid
CAS no.	141-24-2
Formula	$C_{19}H_{36}O_3$ $CH_3(CH_2)_5$ $CH(OH)CH_2$-CH=$CH(CH_2)_7$ $COOCH_3$
Mol. Wt	312.45
Purity	Min. 85% Ricinoleate by GC
Appearance & Colour	Pale yellow to dark brownish yellow liquid
Acid Value	3 Max.
Moisture	0.5% Max.
Uses	Methyl ester of castor oil is used in place of castor oil in the production of hydraulic fluids. Methyl ricinoleate is found to be of use in ethyl cellulose, nitrile rubber, nitrous and polivinyl butyral lacquers.

2.3 Transesterification

Transesterification is also known as alcoholysis. It is reversible reaction although in the production of biodiesel the back reaction is negligible because glycerol is not miscible with the product later lead to a two-phase system (Romero et al., 2011). To improve their reaction rate and yield, a catalyst is used (Sagar & Sarda, 2011). The ester group from the triglyceride is detached to form three alkyl ester molecules. Catalyst is not needed for biodiesel synthesis when alcohol and oil are used in supercritical conditions (Sharma et al., 2011).

Transesterification of vegetable oils to biodiesel with methanol or ethanol can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) catalysts (Liu et al., 2007). Methanol or ethanol are used due to their low cost and physical and chemical advantages. The transesterification reaction occurs between alcohol adsorbed on catalyst and ester of the reactant by Eley-Rideal mechanism. Liu et al. (2007) also reported that homogeneous base catalyst provide much faster reaction rates than heterogeneous catalysts. Homogeneous catalysts are such as sodium hydroxide, potassium hydroxide and sodium methoxide formed an alkoxide group on reaction with alcohol which then attacks carbonyl carbon atom of the triglyceride molecule.

2.4 Heterogeneous Catalysts

Sharma et al. (2011) reported that homogeneous catalysts act in the same phase as the reaction mixture while heterogeneous catalysts act in a difference phase from the reaction mixture. Hence, being in the different phase have give the advantage of easy separation and reuse. At the moment, the biodiesel industrial plants are using homogeneous alkaline catalysts (Romero et al., 2011) although it is highly cost because they cannot be reused. Indeed, those homogeneous aci and alkali catalysts provide high yield and conversion of biodiesel but we need to wash it with a lot amount of water and neutralize it by respective acid or alkali. These needed extra water and in other way also generate excess wastewater (Sharma et al., 2011). The biodiesel must then be dried to remove the resultant moisture content.

Those limitations can be avoided by using a heterogeneous (solid) catalyst which should not leach into the reaction medium and can be reused other than have high selectivity for the desired product and also high yield and conversion to biodiesel. Sharma et al. (2011) found that the characteristics of the fuel depend on the feedstock used in the synthesis of biodiesel. Solid catalysts can be whether solid base or solid acid catalyst and they are classified as Bronsted or Lewis catalysts (Di Serio et al., 2008). The mechanism are similar to the homogeneous catalysts. Heterogeneous basic Bronsted or Lewis catalyst react similarly with alcohol to form homogeneous alkoxide group. Bronsted or Lewis acid is suitable for esterification reaction whereby the acid gets deactivated due to the water formed. Therefore, it is preferred for transesterification reaction. The reaction mechanism proceeds by protonation of carbonyl group which increasing its electrophilicity hence it is easy to nucleophilic attack (Sharma et al., 2011).

Sharma et al. (2011) reported that the past research shows that calcium and magnesium oxides (alkaline earth metal oxides) were succesfully developed to attain high yield and conversion of biodiesel. 92% yield has been achieved using 12:1 methanol to oil molar ratio with 5wt% of catalyst in one hour (Di Serio et al., 2008). The less consumption of solid catalyst in the reaction, the more the benefit of the solid catalyst. According to Romero (2011) in transesterification of rapeseed oil catalyzed by MgO, CaO, SrO and BaO at same reaction conditions resulted in <5%, 58%, 60% and 86% of FAME content respectively. Verziu et al. (2008) found that in the transesterification of sunflower oil by using nanocrystalline MgO give 90% yield at 70oC and 4:1 methanol to oil molar ratio. However, there was the detachment of magnesium caused by saponification.

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, the detailed description of the materials, equipments and methods was discussed. Besides that, the materials used which are castor oil, methanol , Magnesium Oxide (powder) ,Magnesium Sulphate (anhydrous) and hot tap water and the equipments which are 500 mL 3-necked round-bottom glass flask equipped with a reflux condenser with tubes, rubber stopper and a thermometer, 500 mL separating funnel, hot plate with stirrer, rotary evaporator, pH meter, magnetic stirrer, analytical weight balance, beaker 250 mL, aluminium bowl and 100 mL measuring cylinder. The research method used are :

i. Preparation of Sample

ii. Performing Experiment

iii. Product Analysis

3.2 Materials

3.2.1 Castor Oil

The raw material used in this research was castor oil. The castor oil was bought from an indian shop located in Kuantan, Pahang.

3.2.2 Methanol

The alcohol used in this study was methanol because the reaction time time will be faster compared to ethanol because methanol can quickly react with the triglycerides (polar and shortest chain alcohol). Besides, methanol is cheaper than ethanol. The methanol was supplied by the FKKSA laboratory.

3.2.3 Magnesium Oxide

The catalyst used in this research was Magnesium Oxide (powder) which is a solid-base heterogeneous catalyst. Magnesium oxide was available at FKKSA laboratory.