IN SITU TRANSESTERIFICATION OF BIODIESEL FOR POSSIBLE BIODIESEL PRODUCTION

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ABSTRACT

The production of fatty acid methyl ester (FAME) by direct in situ alkaline-catalyzed transesterification of the triglycerides (TG) in castor seeds will be examined.

The Reaction was conducted through in situ trasesterification processes using methanol and in associated with basic catalyst; calcium oxide. The reaction was studied to obtain the conditions where the product of biodiesel start forming, then obtained the effect of catalyst\seed ratio to production rate.

10 g of grinded castor seed was mixed with methanol; 1:5 seed\methanol mole ratio, and calcium oxide; in different percentage. The mixture was mixed for 4h under 60 ^{o}C. The effects of co-solvent; hexane, to the reaction is investigated as well. The product of biodiesel was quantified using GC, and characterized using GC & MC.

Experimental results showed that the amount of castor oil was converted to biodiesel (FAME) started after mixing 4h under 60 ^{o}C, but it was in low yield compared to the total oil presented in the seed, and the conversion which obtained via in situ transesterification is lower than conversion which obtained via conventional transesterification in the present of the same conditions. In another hand, the present percentage of the catalyst has an effect to the conversion, whereby the conversion increase as the catalyst weight catalyst increase till it reach an equivalent with alcohol then start to decrease. Furthermore, the effects observed for the co-solvent; hexane and petroleum ether, were as purification of the product and had no effects towards product yield or conversion. In conclusion, the yield that obtained of biodiesel production from castor oil via in situ process is lower than that obtained via conventional process.

ABSTRAK

Pengeluaran asid lemak metil ester (FAME) oleh langsung dalam transesterification situ alkali bermangkinkan trigliserida (TG) dalam biji kastor akan diperiksa.

Reaksi ini telah dijalankan melalui dalam proses situ trasesterification menggunakan metanol dan dalam dikaitkan dengan pemangkin asas; kalsium oksida. Reaksi telah dikaji untuk mendapatkan keadaan di mana produk biodiesel mula membentuk, kemudian mendapat kesan pemangkin \ nisbah benih kepada kadar pengeluaran.

10 g biji kastor kisar bercampur dengan metanol, benih 01:05 \ nisbah mol metanol, dan kalsium oksida; dalam peratusan yang berbeza. Campuran telah bercampur untuk 4h bawah 60 oC. Kesan bersama pelarut; heksana, reaksi disiasat juga. Produk biodiesel telah kuantitinya menggunakan GC, dan dicirikan menggunakan GC & MC.

Keputusan eksperimen menunjukkan bahawa jumlah minyak kastor telah ditukar kepada biodiesel (FAME) bermula selepas mencampurkan 4h bawah 60 oC, tetapi ia adalah hasil yang rendah berbanding dengan jumlah minyak yang dibentangkan di dalam benih, dan penukaran yang diperolehi melalui di transesterification situ adalah lebih rendah daripada penukaran yang diperolehi melalui transesterification konvensional pada masa kini keadaan yang sama. Di tangan lain, peratusan sekarang pemangkin mempunyai kesan kepada penukaran, di mana peningkatan penukaran sebagai peningkatan pemangkin pemangkin berat sehingga ia mencapai setara dengan alkohol kemudian mula berkurangan. Tambahan pula, kesan diperhatikan untuk bersama-pelarut; heksana dan petroleum eter, adalah seperti pembersihan produk dan tidak mempunyai kesan terhadap hasil produk atau penukaran. Kesimpulannya, hasil yang diperolehi pengeluaran biodiesel daripada minyak kastor melalui dalam proses situ adalah lebih rendah daripada yang diperolehi melalui proses konvensional.

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GC	Gas Chromatography
GC&MC	Gas Chromatography and Mass Spectrophotometer
FFA	Free Fatty Acid

CHAPTER 1

INTRODUCTION

Energy is defined as the ability to do work, and found in different forms such as heat, light motion and sound. Today, most of the energy we use comes from fossil fuels; petroleum, coal and natural gas, but this resource caused environmental issues as well as they are non-renewable resource which limited with time.
As a replacement for fossil fuels, different types of renewable resource of energy are in use such as biomass. Biomass is nowadays resource of biodiesel; which is the future replacement of petroleum diesel, such as production of biodiesel from castor oil. In this chapter briefly description of biodiesel and it production from castor oil will be illustrated. In other hand, the aims of this research and the problem which is going to focus on are clearly explained in this chapter. In the end of this chapter, the contribution of this research to the cementite will be illustrated.

1.1 Background of Research

Most energy which used nowadays by the world is derived from un-renewable resource such as petroleum diesel, which use as fossil fuel, that has a great impact on environments .The demand of fossil fuels is increasing very rapidly and it is estimated that the remaining world reserves will be exhausted by the year 2020, with the current rate of consumption (Ismail et al., 2010). There is an urgent need to seek for an alternative fuels to substitute the diesel due to gradual depletion of world crude oil reserves. Research is, therefore oriented for alternative energy. Biodiesel got a high interest as a replacement of petroleum diesel due to that biodiesel is environmental friendly, because biodiesel has a lower percentage of sulfur and carbon oxides. As well as, biodiesel produced from renewable resources.

Biodiesel is produced through transesterification of vegetables' oil such as Soybean (Guo et al., 2010), Jatropha (Shuit et al., 2009), Sunflower (Georgogianni et al., 2007), Castor oil (Hincapié et al., 2011) ECT. In two major techniques which are conventional transesterification and in situ transesterification of vegetables' oil.

Ricinus communisis or normally known as The castor bean plants are species of flowering plant in the spurge family that belong to a monotypic genus, Ricinus, subtribe, and Ricininae (Williams, 1995). According to Salimon (2010), Ricinus communisis is responsible to produce castor bean for the purpose of mass biodiesel production and also act as intermediate product for various chemical processes. The seeds contain between 40% to 60% oil that is rich in triglycerides, mainly ricinolein (Hincapié et al., 2011). As reported by C/O Clixoo Company (2010), the seed contains ricin, a toxin, which is also present in lower concentrations throughout the plant.

The oil extracted from the castor seed can be characterized as viscous, pale yellow, non-volatile and non-drying oil (Williams, 1995). With comparison to other vegetables' oil, it is characterized for its partial solubility in alcohol, high hygroscopicity and high viscosity (Hincapié et al., 2011).

Castor oil is the best feedstock to produce biodiesel compared to other vegetables' oil due to a high content of oil, a low percentage of toxic, and it is non-edible.

The production of biodiesl via conventional transesterification is applicable in industry nowadays, but it considers a high cost methods. Therefore, many researches are established to consider in situ-transesterification of castor oil for biodiesel production. Among those research is this research which will construct the possibility of biodiesel production from castor oil through in situ transesterification of castor oil using methanol and present of basic catalyst; calcium oxide.

1.2 Problem Statement

In the last few years, a major concern about using biodiesel as petroleum diesel for transportation. The main resource for biodiesel production is an edible-oil, whereby edible-oils aren't the suitable choice to produce biodiesel such as Palm oil, corn, cottonseed, rape seed , ECT because the production effect the food cycle. To overcome this problem, there are several non-edible oil seed species which can be used as a better source for biodiesel production, among those castor seed (Hincapié et al., 2011).

In the current time, conventional transesterification of castor oil is widely used in production of biodiesel. This technique is considered costly due to the extraction, and takes long time as well. To overcome this problem, in situ transesterification of castor oil has been presented so as to minimize the time and to reduce the cost.

Acidic catalyst is wildly used for in situ transesterification of vegetables' oil seed (Hincapié et al., 2011). The acidic catalyst is not recommended in industry due to corrosion and the catalyst is hard to be removed from the product. To overcome this problem, a basic catalyst; calcium oxide, will be in used for in situ transesterification of castor oil due to it wildly availability, low cost, and easy to be removed from the product.

1.3 Research Objectives

1- To investigate the yield of in situ transesterification of castor oil to produce biodiesel in present of basic catalyst. And to compare the yield obtained with the conventional transesterification of castor oil for biodiesel production in present of the same catalyst.

2- To investigate the effects of co-solvent petroleum ether, hexane.

3- To characterize the biodiesel produced through in situ transesterification of castor in present of basic catalyst; calcium oxide.

1.4 Scope of the study

This research presents the production of biodiesel from crude castor seeds having a high content of free fatty acid (FFA) by in situ transesterification. The process will be in presence of basic catalyst; calcium oxide, and methanol. The process will be run under different conditions; by manipulating the temperature and time of reaction to obtain the highest yield which can be produced by in situ transesterification of castor oil in present of the basic catalyst. The quality and quantity of the biodiesel will be analyzed using a Gas Chromatography.
The biodiesel obtained by in situ transesterification of castor oil; in present of the basic catalyst, will be characterized, then compared with in situ transesterification of

castor oil; in present of acidic catalyst, to obtain the best quality and compare the yield.

Lastly, the yield of in situ transesterification of castor oil will be compared with conventional transesterification, to obtain the highest yield and the economically method of tranesterification of castor oil.

1.5 Significant of the Research

Energy is the main concern nowadays for the world so researchers and countries tend to find a resource for energy in lowest cost and environmental impact. The lower percentage of sulfur and carbon oxide in biodiesel comparing to petroleum diesel make it environmental friendly. In other hands, biodiesel is produced from renewable resources; vegetables' oil and animal fat, which make it sustainable and good resource for energy.

Production of biodiesel through tranesterification of edible vegetables' oil has affected the food cycle. To overcome this issue, tranesterification of non-edible vegetables' oil has been presented whereas it still considered costly comparing to petroleum diesel due to the extraction steps, and the toxic presented in the non-edible vegetables' oil.

In situ transesterification of non-edible vegetables' oil such as castor oil has been presented, to reduce the cost with high yield of a sustainable and friendly energy resource which is biodiesel.

CHAPTER 2

LITERATURE REVIEW

According to Demirbas.A (2007), “the scarcity of conventional fossil fuels, growing emissions of combustion generated pollutants, and their increasing costs will make biomass sources more attractive. On the other hand, biomass use, in which many people already have an interest, has the properties of being a biomass source and a carbon neutral source. Experts suggest that current oil and gas reserves would suffice to last only a few more decades. To meet the rising energy demand and replace reducing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of alternative technologies. Accordingly the viable alternative for compression-ignition engines is biodiesel”. This chapter will perused of biodiesel, castor oil and the production techniques of biodiesel based on previous studies. Additionally, this chapter will touch on the different catalysts which used in biodiesel production, and detailed on calcium oxide as transesterification catalyst.

2.1 Biodiesel

Biodiesel is composed of long-chain fatty acids with an alcohol attached, often derived from vegetable oils. Biodiesel fuel can be defined as medium length (C16± 18) chains of fatty acids, and is comprised mainly of mono-alkyl fatty acid esters (Hofman.V, 2003). Technical properties of biodiesel is listed in **Table 2.1**

Table 2.1: Technical properties of biodiesel (Demirbas, 2008)

Common name	**Biodiesel**
Common chemical name	Fatty acid (m)ethyl ester
Kinematic viscosity range (mm^2\s, at 313k)	3.3-5.2
Density range (kg\m^3, at 288k)	860-894
Boiling point range , k	>475
Flash point range, k	430-455
Distillation range, k	470-600
Vapor pressure (mmHg, at 295k)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty\soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high viscosity for use in most existing diesel engines as a straight replacement fuel oil (Hincapié et al., 2011). There are a number of ways to reduce vegetable oils' viscosity. Dilution, micro-emulsification, pyrolysis and transesterification are the four techniques applied to solve the problem encountered with high fuel viscosity (Demirbas, 2008). One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification.

Transesterification (also called alcoholysis) is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. **Figure 2.1** shows the transesterification reaction of triglycerides. A catalyst is usually used to improve the reaction rate and yield.

Different types of alcohol have been used in transesterification such as methanol and ethanol. Whereby, methanol is more preferable due to the availability of methanol, and has lower cost comparing to ethanol (Hofman, 2003). However, Different types of catalyst have been used in transesterification such as acid-catalyst H_2SO_4 (Hincapié et al., 2011), basic catalyst NaOH, KOH (Soetaredjo et al., 2010), and CaO (Manuel.S et al., 2012), and enzyme. The catalyst could be heterogeneous or homogenous. **Table 2.2** shows the comparison of various methanol transesterification methods. Whereas, Sodium hydroxide is very well accepted and widely used due to high yield production and its low cost (Demirbas, 2008).

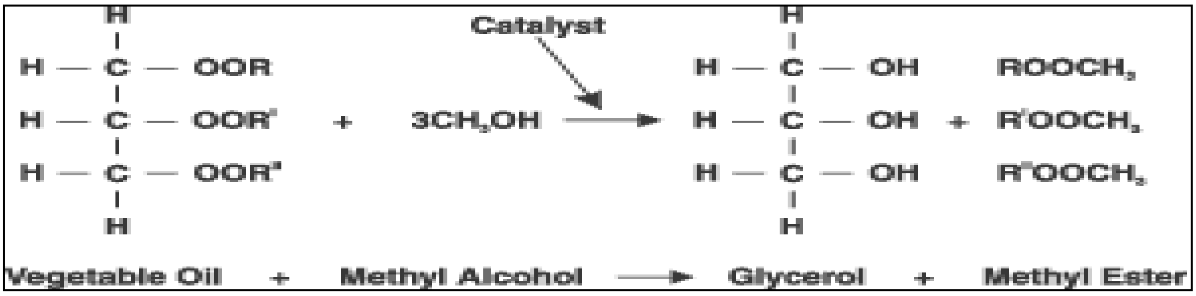

Figure 2.1: Transesterification reaction of triglycerides

Table 2.2: Comparison of various methanol transesterification methods (Demirbas, 2008)

Method	Reaction temperature, (K)	Reaction time, (min)
Acid or alkali catalytic process	303-338	60-360
Boron trifluoride-methanol	360-390	20-50

Sodium methoxide-catalyzed	293-298	4-6
Non-catalytic supercritical methanol	523-573	6-12
Catalytic supercritical methanol	523-573	0.5-1.5

According to Fukuda et al. (2002), the production of biodiesel by transesterification of vegetables' oil has two major techniques:

- Conventional transesterification. This method starts by extracting the oil from the seed, then proceeding with two steps process. Two-step process has been investigated for feed stocks with a high FFA content, the first step of the process is the acid-catalyzed esterification for reducing the FFA content of the oil and the second step is the basic catalyzed transesterification.
- In situ transesterificaton. In situ transesterification differs from the conventional reaction in that the oil-bearing material contacts with acidified or alkalized alcohol directly instead of reacting with pre-extracted oil and alcohol. That is, extraction and transesterification takes place simultaneously, the alcohol acts as an extraction solvent and an esterification reagent.

Biodiesel is the best candidate for diesel fuels in diesel engines due to that biodiesel fuel has the benefits of being non-toxic, biodegradable and essentially free of sulfur and carcinogenic ring components (Hincapié et al., 2011). Additionally, biodiesel produced from renewable resources, a comparison between biodiesel and petroleum diesel as in **Table 2.3.**

Table 2.3: Comparison between Biodiesel and Petroleum diesel.

Area of comparison	**Biodiesel**	**Petroleum diesel**
Availability, (Demirbas, 2008).	• Currently : Moderate • Future : Excellent	• Currently : Excellent • Future: Moderate-poor
Resource	Renewable resource	Non-renewable resource
sulfur content	No sulfur content	A percentage of sulfur content
Oxygen content	10-20% greater than petroleum diesel.	Less than biodiesel.
Cost	Expensive	Cheap comparing to biodiesel

Biodiesel is low toxic emissions and particulate, biodegradable and greenhouse gas neutral. Additionally, biodiesel is all natural, renewable, and dissolves in water faster than sugar. It is 11 % oxygen by weight and contains no sulfur. In other hand, biodiesel is easy to store and has high flash point. The main advantage of biodiesel is that it doesn't require any modification for the engine, as well as does not affect engine performance (Demirbas.A, 2007).

The biodiesel, as other energy resource, got disadvantages which are its higher viscosity, lower energy content, higher could point and pour pint and higher nitrogen oxide emission. Additionally, it causes to lower the engine speed and power, injector coking, engine compatibility, high price and higher engine wear

(Demirbas.A, 2007). The main disadvantage of biodiesel is that it affects the food cycle.

Biodiesel burns like petroleum diesel as it involves regulated pollutants. On other hand, biodiesel probably has better efficiency than gasoline (Demirbas, 2008). Considerable research has been done on vegetable oils as diesel fuel. That research includes palm oil (Kansedo et al., 2007), soybean oil, sunflower oil (Siler-Marinkovic et al., 1998), rapeseed oil (Biktashev et al., 2010), and cotton oil (Qian et al., 2008), castor oil (Manuel.S et al., 2012).

Biodiesel is pure or 100% biodiesel, and referees in industry as B100. Additionally, biodiesel is blend with diesel and refered as BXX, whereby XX refer to the biodiesel percentage in the fuel such as B80 where, the biodiesel is 80% and 20% is petroleum diesel (Demirbas, 2008).

The main raw materials for Biodiesel production in industries nowadays are coming from edible vegetables' oil via both technics. This kind of production effects the food cycle, so the research is looking for other resource for biodiesel production among the non-edible-vegetables' oil such as castor oil.

In the past years, castor oil got a high interest in the production of biodiesel due to it's contain of oil, and low concentration of toxic.

2.2 Castor seed's oil

2.2.1 Castor seed plantation

Ricinus communis (castor plant) is a species that belongs to the Euphorbiaceous family and it is commonly known as castor oil plant, and Palma Christi. This plant originates in Africa but it is found in both wild and cultivated states in all the tropical and subtropical countries of the world. In wild conditions this plant is well-adapted to arid conditions and is able to stand long periods of drought (Forero, n.d).

According to Forero (n.d), Ricinus communis plants can present precocious, median and delayed cycles. The precocious cycle is that in which flowering occurs about 45 days after sowing. The median cycle presents lowering at an intermediate time between the precocious and delayed cycle, which has a flowering time of 90 to 120 days after sowing. The castor oil plant can vary greatly in its growth habit and appearance. The variability has been increased by breeders who have selected a range of cultivars for leaf and flower colors, and for oil production. It is a fast-growing, suckering perennial shrub which can reach the size of a small tree (around 12 meters / 39 feet), but it is not cold hardy.

The flowers of castor plant; as in **Figure 2.2**, are borne in terminal panicle-like inflorescences of green or, in some varieties, shades of red monoecism flowers without petals. The male flowers are yellowish-green with prominent creamy stamens and are carried in ovoid spikes up to 15 centimeters (5.9 in) long; the female flowers, born at the tips of the spikes, have prominent red stigmas.

Figure 2.2: Castor flowers

The fruit of castor plant; as in **Figure 2.3,** is a spiny, greenish (to reddish-purple) capsule containing large, oval, shiny, bean-like, highly poisonous seeds with variable brownish mottling. Castor seeds have a warty appendage called the caruncle, which is a type of elaiosome. The caruncle promotes the dispersal of the seed by ants (myrmecochory).

Figure 2.3: Castor fruit.

Castor seed; as in **Figure 2.4,** is the source of castor oil, which has a wide variety of uses. The seeds contain between 40% and 60% oil that is rich in triglycerides, mainly ricinolein. The castor bean is the natural source of castor oil. Unfortunately, it also contains ricin, a highly toxic protein (Plante et al., n.d).

Figure 2.4: Castor seed

2.2.2 Castor oil

Castor oil is extracted from the seeds of Palma Christi. Castor seeds consist of approximately 46% of oil (Hincapié et al., 2011), and the rest is water and solid moisture (Plante et al., 2010).

Physically, castor oil is highly viscous, pale yellow in room temperature, it has a soft and faint odor, and it has highly unpleasant taste (Forero et al., n.d), non-volatile and non-drying oil (Hincapié et al., 2011). Those above properties differs castor oil from other vegetables' oil. Castor oil is a clear liquid at room temperature (27^oC) and showed no solid fat content at 0^oC (Salimon et al., 2010), this behavior due to hydrogen bonding of its hydroxyl groups (Ogunniyi, 2006). As well as Castor oil dissolves easily in alcohol, ether, glacial acetic acid, chloroform, carbon sulfide, and benzene.

According to Hincapié et al. (2011), castor oil; as another vegetables' oil, made up mainly of triglycerides which consist of three fatty acids and one molecule of glycerol, as shown in **Figure 2.4**, which show the chemical structure for castor oil.

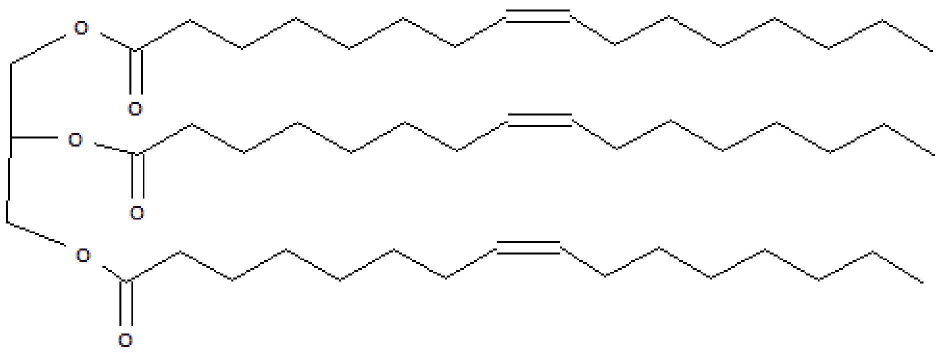

Figure 2.5: castor oil chemical structure (G.R.O'shea company).

The fatty acids of this oil consist of approximately Ricinoleic acid, Linoleic acid, Stearic acid, and Dihydroxystearic acid ,as shown in **Table 2.4**.

Table 2.4: Properties of castor oil (G.R.O'shea company).

Acid Name	**Average Percentage Range**		
Ricinoleic acid	95	to	85%
Oleic acid	6	to	2%
Linoleic acid	5	to	1%
Linoleic acid	1	to	0.50%
Stearic acid	1	To	0.50%
Palmitic acid	1	To	0.50%
Dihydroxystearic acid	0.5	To	0.30%
Others	0.5	To	0.20%

Mainly, castor oil consists of Ricinoleic acid; chemical structure of Ricinoleic acid ;as shown in **Figure 2.5**, a monounsaturated, 18-carbon fatty acid, which is unusual in that, it has a hydroxyl functional group on the twelfth carbon. According to C/O Clixoo Company report (2010), this functional group causes Rinoleic acid (and castor oil) to be unusually polar, and also allows chemical derivation that is not practical with most other vegetables' oil. It is the hydroxyl group which makes castor