UTILIZATION OF EGGSHELL WASTE AS SOLID CATALYST FOR BIODIESEL PRODUCTION FROM *JATROPHA CURCAS* OIL

IQMIL BIN HAMDAN

A thesis submitted in fulfilment of the

requirements for award of the degree of

Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

UTILIZATION OF EGGSHELL WASTE AS SOLID CATALYST FOR BIODIESEL PRODUCTION FROM *JATROPHA CURCAS* OIL

ABSTRACT

Increasing demand on the energy consumption due to modernization of the world where the major part of that energy is derived from fossil such as petroleum and natural gas where the energy-based fossil fuel has become limited resources that has drawn many researchers to look for alternative fuel which can be produced from renewable feedstock. Based on the recently research, *Jatropha curcas* oil that is derived from non-edible oil has a potential for biodiesel production. Eggshell has been investigated to utilize the composition of calcium carbonate as a heterogeneous catalyst for biodiesel synthesis. The objective for the experiment is by utilizing the eggshell waste as solid catalyst for biodiesel production from *Jathropa curcas* oil by the variation of temperature, methanol oil ratio and reaction time. The eggshell is prepared by the process of calcinations to get the calcium dioxide from the calcium carbonate. Fatty acid will be reduced to less than 1% before transesterification process by using acid catalyst of 1wt% of H_2SO_4, 60^0C, 3 hours of reaction time and 60% methanol to oil ratio. After that the process of transesterification for producing biodiesel from the refined *Jatropha* oil will be done in the batch reactor. There were several parameters that need to be considered which were; (1) reaction temperature (35°C, 45°C, 55°C, 60°C, 65°C), (2) methanol/oil ratio (1:1, 3:1, 5:1, 7:1, 9:1), (3) reaction time of 1h, 3h, 4h, 5h, 6h, The highest biodesel was found at 88.50% by the methanol oil ratio of 5:1, temperature of 60 ^{0}C reaction time for 5 hours.

PENGGUNAAN KULIT TELUR SEBAGAI PEMANGKIN PEPEJAL UNTUK PENGELUARAN BIODIESEL DARI MINYAK JATROPHA CURCAS

ABSTRAK

Permintaan yang semakin meningkat terhadap penggunaan tenaga disebabkan oleh pemodenan dunia di mana sebahagian besar tenaga yang berasal dari fosil seperti petroleum dan gas asli di mana tenaga berasaskan bahan api fosil telah menjadi sumber yang terhad yang telah menarik ramai penyelidik untuk mencari bahan api alternatif yang boleh dihasilkan daripada bahan mentah yang boleh diperbaharui. Mengikut kajian penyelidik baru-baru ini, minyak *Jatropha Curcas* yang berasal dari minyak dan mempunyai potensi untuk pengeluaran biodiesel. Kulit telur telah dikaji komposisi kalsium karbonatya sebagai pemangkin heterogen untuk sintesis biodiesel. Objektif bagi eksperimen ini adalah dengan menggunakan sisa kulit telur sebagai pemangkin pepejal untuk pengeluaran biodiesel daripada minyak *Jathropa Curcas* dengan perubahan suhu, nisbah minyak dan metanol dan juga reaksi masa. Kulit telur ini disediakan oleh proses pengkalsinan untuk mendapatkan kalsium dioksida dari kalsium karbonat. Asid lemak akan dikurangkan kepada kurang daripada 1% sebelum proses transesterifikasi dengan menggunakan pemangkin asid% 1wt H_2SO_4, 60^0C, 3 jam masa reaksi dan metanol 60% kepada nisbah minyak. Selepas itu proses transesterification untuk penghasilan biodiesel daripada minyak *Jatropha* akan ditapis dalam reaktor kelompok. Terdapat beberapa parameter yang perlu dipertimbangkan iaitu; (1) tindak balas suhu (35 ° C, 45 ° C, 55 ° C, 60 ° C, 65 ° C), (2) nisbah metanol / minyak (1:1 , 3:1, 5:1, 7:01, 9:1), (3) masa reaksi 1h, 3h, 4h, 5h, 6h, biodesel tertinggi didapati di 88,50% oleh nisbah minyak metanol daripada 5: 1, suhu 60^0C masa reaksi selama 5 jam.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The fuel consumption is increasing while the amount of crude oil decreasing over a period of time and this affect the price of the fuel together with rival between the fuel consumers. Hence some important steps must be taking into consideration to tackle this problem. The best solution recently has been talked among the researchers is by substituting the fuel of petro diesel with the biodiesel which is extracted from the vegetable oil such as Jatropha oil, corn oil, soybean oil and castor oil. The production of biodiesel would be cheap as it could be extracted from non-edible oil sources. The growing interest by using *Jatropha curcas* oil as the feedstock of biodiesel production because it is non-edible oil and thus does not compromise the edible oils, which are mainly used for food consumption (May et. al., 2011). Biodiesel can be used in diesel automotive engine in its pure form or blended with petroleum-based diesel. This product has no modification required and as a result it is less expensive, renewable resources and most importantly is clean burning fuel that will prevent the depletion of ozone. Biodiesel is an alternative diesel fuel that produced from vegetable oil and animal fats. It consists of the monoalkyl esters formed by a catalyzed reaction of the triglycerides in the oil or fat with a simple monohydric alcohol (Gerpen, 2005). The process which is from vegetables oils and animals fat to biodiesel production is called transesterification process. This process involves break down the molecules of vegetables oil into constituent molecules forming biodiesel as the main product and glycerin as the by product (Khemani, 2011)

Previously, *Jatropha curcas* was being neglected due to low demand of the oilseed crop but now, the jatropha has become the latest economic improvement among countries that has a potential to become global alternatives corporations and given a tremendous prospective as a viable and cheapest feedstock for the biodiesel production compare to other vegetables oil. Interestingly, since the jatropha fruit is non-edible, using it to produce biodiesel would not affect or be affected by demand for food, a major problem that is constantly faced by the palm oil-based biodiesel and corn “ethanol” industries (Adnan, 2009).

Jatropha Curcas is a drought-resistant perennial, growing well in marginal/poor soil. It is easy to establish, grows relatively quickly and lives, producing seeds for 50 years. *Jatropha Curcas* produces seeds with an oil content of 40-60% (Makkar et al. 1997). The important consideration for biodiesel feedstock is the content of free fatty acid (FFA) in the oil (Azhari et al. 2008). *Jatropha curcas* oil that has high FFA should purified the oil first to reduce the fatty acid by acid catalyst in esterification process so that the oil can directly be utilized in a transesterification reaction with methanol in the presence of an alkaline catalyst to avoid soap formation. It burns with clear smoke-free flame, tested successfully as fuel for simple diesel engine. The by-products are press cake a good organic fertilizer, oil contains also insecticide. It is found to be growing in many parts of the country, rugged in nature and can survive with minimum inputs and easy to propagate. Jatropha grows wild in many areas of India and even thrives on infertile soil. As a result, jatropha oil should be cheaper alternative to produce biodiesel compare to the popular edible fuels from rapeseed, corn and palm oil.

The fatty acid of *Jatropha* curcas oil consist of 34-45.8% of oleic acid, 14-15.3% of palmitic acid, 3.7-9.8% of stearic acid and 29-44% of linoleic acid (Azhari et al. 2008). As stated above, the biodiesel is generally produced by transesterification of vegetables oil or animal fats with short-chain alcohol. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol propanol, butanol, and amyl alcohol. Generally methanol is used for this process because of its low cost and physical and chemical advantages associated with being polar and the shortest chain alcohol compared to the ethanol which is derived from agricultural products and is renewable and biologically less objectionable in the environment with the presence of catalyst. The reaction time required is shorter in the methanolysis because of the physical and chemical properties of methanol. Thus the energy required is not high enough than ethanol since boiling point of methanol only 64.7 ^{0}C rather than ethanol is 78.4 ^{0}C (Hanna and Ma, 1999). The high viscosity of Jatropha oil from the extraction process could not be used directly in diesel engine because it can reduce the fuel atomization and increase fuel penetration and will cause the high engine deposits and thickening of lubricant oil. Those are the reason to go through for the transesterification process which is in the presence of catalyst.

Transesterification is required catalyst to enhance and improve the reaction rate so that the reaction can be completed in a shorter time. Heterogeneous catalyst is promising for the transesterification reaction of vegetable oils to produce biodiesel. Compare to homogenous catalyst, this heterogeneous catalyst can be used several times and does not produce a large amount of waste water in the separation step (Masoud et al. 2009). The catalyst are not consumed or dissolved in the reaction and therefore can be easilt separated from the products. As a result the product does not contain impurities of the catalyst and the final separation could be reduced.

The production of biodiesel from waste egg shell as a catalyst that has high potential of CaO derived from $CaCO_3$ made biodiesel production more economical, environmental and ecological friendly more competitive with petroleum based-diesel. Hence the usage of the eggshell as a catalyst can be considered for biodiesel production because the catalyst will give the high yield of biodiesel and low cost catalyst since the eggshell can be found from the waste. Thus it will generate waste to wealth.

1.2 Problem Statement

Nowadays, the price of petro diesel has been mouthing for many people in the world for the increasing of the price market of petro diesel consumption for the consumers. In fact, the production of diesel product keep increasing because of the raw materials used may be an expensive material. The feasibility of raw material should be looking forward to reduce the price of the diesel market. Since *Jatropha Curcas* oil can be used to produce a biodiesel, the demand for the biodiesel will be increased year by year and will overcome the problem of the petro diesel decreases by nature. The eggshell can be used for the production of biodiesel due to the high disposal of the eggshell nowadays. Optimum condition such as temperature, reaction time, methanol/oil ratio has been investigating continuously to make sure the best quality of biodiesel fuel product will be produced.

1.3 Research Objectives

The objective of this research is to produce biodiesel from *Jatropha curcas.* oil using activated egg shell waste as a solid catalyst and to investigate the effect of temperature, reaction time and methanol oil ratio to biodiesel yield.

1.4 Scope of Research

To achieve the objective of this research, scopes have been identified

1. Preparation of activated egg shell as a solid catalyst.
2. Reducing free fatty acid value in crude *Jatropha curcas* oil
3. Production of biodiesel from *Jatropha curcas* oil using activated egg shell as a catalyst in batch systems
4. Optimizing the selected parameter for biodiesel production (temperature, methanol/Oil Ratio and reaction time).
5. Analyze the biodiesel yield production using Gas Chromatography (GC).
6. Identifying affect of the temperature, reaction time, methanol/oil ratio on yield of biodiesel.

1.5 Rationale & Significance

Increasing the price of the petroleum and significantly decrease the amount of the petroleum must have an alternative fuel to face the market demand. Bio-fuel is one of the alternative renewable energy. A hectare of Jatropha may produce approximately 1892 liters of fuel and Jatropha is one of the reasons for the raw material to be used for the production of biodiesel because jatropha is non-edible oil and will not give an impact to the food price if the demand of jatropha increases with the usage of eggshell that considerable as a huge waste if not controlled well can be used as a catalyst. For the replacement of the fossil fuel, biodiesel is the best alternative way to be a replacement fuel.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel Production

All energy consumed nowadays comes from fossil sources such as petroleum; coal and natural gas which are these non-renewable resources become fatigued in the future. The search for another source of renewable and sustainable energy such as biodiesel has gained importance with the potential to solve many current social issues such as the increasing price of petroleum crude and environmental concerns like air pollution and global warming caused by combustion of fossil fuels (Demirbas, 2005). Generally, the biodiesel is the simple alkyl monoesters of long chain fatty acids derived from renewable feedstock such as vegetable oil either edible or non-edible oil which is conform the most suitable substitute to diesel (Ferrari et al. 2007). For the ecosystem review, the petroleum oil spill becomes a major problem of contamination of the ecosystem. This is the major concern for the living system, hence such effort have been through as a biodiesel production have been found as a highly biodegradable in fresh water as well as in soil and great part of it is mineralized in until 28 days under aerobic or anaerobic conditions (Zhang et al., 2003). Biodiesel is less damaging to the environment because it is made from renewable resources and has lower emissions compared to fossil diesel. Fuel grade biodiesel is produced to straight industry specification ASTM D6751 in the US in order to ensure proper combustion and will not harm the engine component.

Biodiesel sold nowadays is considerable as an expensive (Ferrari et al. 2007), since the production cost influenced by the raw materials that are using for this process such as edible oil from vegetables oil such as soy bean, corn and etc. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as non-edible oils, animal fats, and waste food oil and by products of the refining vegetables oils (Emil et al, 2009). When the production of biodiesel is in demand, the cost for the raw material will increase and the competition between "food production" and "energy production" will occur according to the available of land for the crop. (Chhetri et al., 2008). In order to reduce the production cost, the producers of the biodiesel should choose the raw material that had no competition with the food production such as non-edible oil as a *Crembe Abyssinica, Jatropha Curcas* and *Pongamia pinnata (*Madras and Rathore, 2007). High cost of biodiesel is mainly due to the cost of virgin vegetable oil (edible oil).

There are four primary ways to make biodiesel, direct use and blending, micro emulsions, thermal cracking (pyrolysis) and transesterification. The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction which is to produce alkyl esters (biodiesel) is affected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats (Hanna and Ma, 1999). The process is less complex and it is quite easy. For the direct use of vegetables oil as combustion fuel is not suitable because of high viscosity and low vitality that will cause a clogging and deposit at the fuel line. Micro emulsion has been prepared to overcome this situation of high viscosity oil. Another method of thermal cracking is not preferred for biodiesel production because will go through a complicated process and produce side product that has no commercial value.

Biodiesel is the modern fuel and economical ways to prevent the depletion of ozone due to releasing of fossil fuel to the environment. It is the product of a chemical process that replaces the glycerol in natural oils like jatropha or soybean oil with methanol. Biodiesel receiving high attention an alternative, nontoxic, biodegradable and renewable diesel fuels (Hanna and Ma, 1999). Biodiesel has a higher cetane number than diesel fuel, no aromatics, almost no sulphur and contains 10 to 11% of oxygen by weight (Lin et al. 2011). These characteristics of biodiesel reduce the emissions of carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) in the exhaust gas compared to petroleum-based diesel fuel (Gerpen and Canakci, 2001). Biodiesel can be used alone or in a blend with petroleum-based fuel in existing diesel engines with little or no modification.

2.2 *Jatropha Curcas L.*

Jatropha Curcas L. is a plant belonging to *Euphorbiaceae* family that produce a significant amount of oil from its seed. In Malaysia, wild *Jatropha curcas* tree is also known as *Jarak Pagar* particularly in Peninsular Malaysia area. Approximately, the oil content in Jatropha seed in the range of 30-50% by weight of the seed and range from 45 to 60% of the kernel itself (Pramik, 2003). Jatropha is a drought-resistant perennial tree that grows in marginal lands and can live over 50 years. The jatropha tree has several beneficial properties such as its stem is being used as a natural tooth paste and brush, latex from stem is being used as natural pesticides and wound healing, its leaf as feed for silkworms among other uses (Chhetri et al,. 2008). It can be grown below 1400 meters of elevation from sea level and requires a minimum rainfall of 250mm which is the plant can be live in the desert and optimum rainfall between 900-1200mm (Bosewell, 2003).

Approximately 1.3 million farmers in three countries of the province Guizhou, Sichuan and Yunan stated in southwest have started to produce jatropha for biodiesel production (Chhetri et. al., 2008). The jatropha seed is particularly suitable for biodiesel production because it can be harvested in the third year of plantation five or six times annually. This occurs because the lifetime of this plantation is within 50 years and this plantation can be survived at the place where less water contains. Hence, development of environmentally friendly biofuel from non-edible oils such as jatropha has great promise to the economic energy for developed countries (Chhetri et. al., 2008). In Brazil, diesel consumption is approximately around 40 billion litres per annum and providing huge opportunities for biodiesel production and it is expected that the biodiesel market will be approximately 2 billion litres by 2013. According to United States Department of Agriculture (USDA), biodiesel represents the biggest biofuel. Various provinces of Canada have adopted renewable energy portfolio standards. For example, the province of Nova Scotia had proposed regulations that stipulate the 5% of the total power generation had been met by renewable sources by 2010. Jatropha oil that has a potential to use as feedstock for biodiesel production and has a potential to be an environmental-friendly sources for alternate transportation fuel in Malaysia and other countries.

Nowadays, this plant has huge potential to produce biodiesel because it has high percentage of unsaturated fatty acid (Jumat and Rozaini, 2008). The most important characteristic of biodiesel is to determine the free fatty acid of the oil. According to May et al. (2011) high percentage of fatty acid will cause soap formation, consume catalyst that will cause a lowest yield of biodiesel thus it give a negative effects during transesterification reaction of triglycerides with alcohols. Feedstock of biodiesel production should contain lowest percentage of FA (<1%) to be used directly in transesterification reaction. Since crude *Jatropha* oil contains about 8% of FFA which is far beyond the 1% limit for promoting the transesterification reaction to occur. Pretreatment of oil should be done to decrease the value of FA itself. Esterification of FA with methanol in the presence of acid sulphuric is the most commonly pretreatment applied due to the simplest method to reduce the amount of FA (Azhari et al, 2008).

Table 2.1 Comparison of properties of diesel, neat jatropha oil and biodiesel

Properties	Diesel	Neat Jathropa Oil	Biodiesel from Jathropha
Density (kg/m3)	840	918	880
Viscosity(cSt)	4.59	49.9	5.65
Calorific value (kJ/kg)	42390	39774	38450
Flash point (^{0}C)	75	240	170

(Sources: Reddy and Ramesh, 2005)

Biodiesel produced from jatropha oil has similar characteristics as shown in table 2.1 which is petroleum diesel the jatropha oil is a strong alternative for diesel replacement (Reddy and Ramesh, 2005). Direct application of *Jatropha* oil is not possible due to its higher viscosity and due to that, reduction of this non-edible oil is urgent needed for this process. The transesterification process is commonly and widely used to reduce the viscosity and improve the fuel property of this oil (Mathiyazhagan and Ganapathi, 2011).

2.3 Egg Shell as Catalyst

Catalyst availability also affecting the price of biodiesel production. There are three types of catalyst for this production such as base acid and enzymes catalyst. Enzymatic catalyst has been chosen by many researchers for the biodiesel production due to tolerate between fatty acid and water content to avoid soap formation. However, the enzymes itself are expensive to commercialize the biodiesel production (Masoud et al, 2009). The heterogeneous catalyst have been attached to overcome the lack of homogeneous catalyst since the homogeneous seems to have a lot of disadvantages such as corrosive to equipment and also react with free fatty acid to form unwanted soap by-products that require expensive separation, while the homogeneous acid catalyst (H_2SO_4) are difficult to recycle and operate at high temperatures and also give rise to serious environmental and corrosion problems (Wei et. al 2009). Due to that issues, heterogeneous base catalyst such as egg shell (Wei et al. 2009), mollusk (Faungnawakij et al., 2010), Oyster (Sakugawa et al. 2009), etc have been purposed due to the economical and environmental friendly for biodiesel production.

According to Stadelman (2000), the egg shell as heterogeneous catalyst posses the weigh approximately 10% of the total mass of hen egg and significant solid waste produced from food processing and manufacturing plants. According to Wei et al. (2009) the egg shell has the chemical composition (by weight) of calcium carbonate (94%) magnesium carbonate (1%), calcium phosphate (1%) and balance is the organic matter. Since the amount of calcium carbonate is high in the eggshell, it is suitable to convert calcium carbonate to calcium dioxide which is used to develop an active heterogeneous catalyst. According to Wei et al. (2009), the egg shell derived catalyst can be repeated use for 13 times with no apparent loss if activity. After that, the catalyst activity reduces gradually and if it used more than 17 times, the catalyst will deactivate completely. Egg shell can be reused to reduce contamination and minimize the production cost of biodiesel and produce the biodiesel with more ecological friendly.

2.4 Pretreatment of Free Fatty Acid

In alkali-catalysed transesterification, high FFA content is unfavourable because the FFA will react with the catalyst to form soap and the separation of products will be extremely difficult. Most non-edible oil contains a high level of free fatty acids which is undesirable as it lowers the yield of biodiesel. Fatty acid of *Jatropha* oil composition was given in table 2.2.

Table 2.2 Fatty acid Composition of *Jatropha curcas* oil

Fatty acid	Formula	Systemic name	Structure	Weight (%)
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0	0-0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	14.1-15.3
Palmitoleic	$C_{16}H_{30}O_2$	*cis*-9-Hexadecanoic	16:1	0-1.3
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0	3.7-9.8
Oleic	$C_{18}H_{34}O_2$	*cis*-9-Octadecanoic	18:1	34.3-45-8
Linoleic	$C_{18}H_{32}O_2$	*cis*-9,*cis*-12-Octadecedianoic	18:2	29.0-44.2
Linolenic	$C_{18}H_{30}O_2$	*cis*-6,*cis*-9,*cis*-12-Octadecatrienoic	18:3	0-0.3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0-0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0-0.2

(Source: Gubitz et al, 1999)

Table 2.2 it shows that the highest percentage of FFA in *Jatropha curcas* oil is oleic acid followed by linoleic acid and palmitic acid. The lowest percentage of FFA in *Jatropha curcas* oil is stearic acid. Thus the *Jatropha curcas* oil can be classified as oleic-linoleic oil. According to (Marchetti and Errazu, 2008), the feedstock that has high value of FFA, much higher than the maximun amount suitable to be used with basic homogeneous catalyst will give a high amount of soap produced simultaneously. Thus the acid homogeneous catalyst is commonly being used to reduce the amount of free fatty acid (Azhari et al, 2008).

2.5 Transesterification Process

Vegetables oil was proposed as diesel fuels but was found to be a problematic due to their greater viscosity found inside the engine component. Since vegetables oil does not suitable to use directly, the process which is to reduce viscosity of the oil is called transesterification. Generally, conversion of the oils to their alkyl esters reduced the viscosity to near diesel fuel levels and produced a fuel with properties that were similar to petroleum-based diesel fuel and which could be used in existing engines without modification (Peterson et al. 1983).

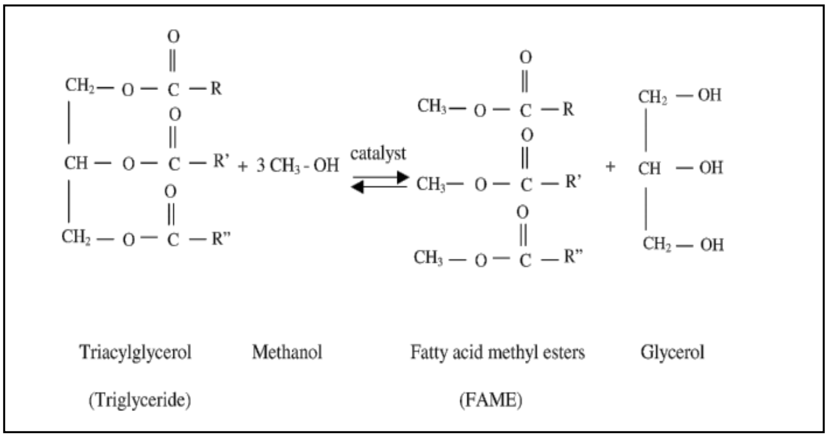

Figure 2.1 Reaction for oil transesterification

(Source: Gerpen, 2005)

By the theoretical, (Figure 2.1) transesterification refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. Triglycerides as the main component of vegetable oil consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (mainly as a methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid methyl esters (FAME). A catalyst is usually used to improve and enhance the reaction rate so that the reaction can be completed in a shorter reaction time (May et al. 2011). This study has been used calcium oxide as a catalyst for this production. Glycerol is produced as a by-product. Methanol is the most commonly used as alcohol because of it low cost compared to ethanol.

Glycerol is essentially insoluble in biodiesel so almost all of the glycerol is easily removed by the settling or centrifugation. The free glycerol must be removed because the free glycerol may remain as suspended droplets and will become a problem if the excessive free glycerol is not removed. The excessive free glycerol will create a very viscous mixture that can plug fuel filters and cause combustion problems in the engine (Gerpen, 2005).