SYNTHESIS OF BIODIESEL FROM VARIOUS SOURCES OF PLANT OILS

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved:

Dr. Lukman Bin Ismail
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

June 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Dang Dinh Thang

ABSTRACT

"The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time as important as the petroleum and coal tar products of the present time" (Rudolf Diesel, 1912). Nowadays, environment has been affected seriously by the industrialization. Many effects such as green house effect, undegradable materials are slowly causing harmful to environment and human lives. Every country suggest of using bio-diesel due to its degradability, safety with environment and also many advanced properties compared with mineral-based fluids. The main resources for synthesis of bio-based diesel are various and we decided to choose palm kernel oil, jatropha curcus oil and canola curcas oil as the base oils, and also sodium hydroxide and potassium hydroxide as main catalysts. The aim of this research is to study the advance of the bio-based diesel and also the kinetics of reactions and characteristics of diesel produced from different bio-based oil feed stocks.

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LIST OF ABBREVIATIONS

PKO	Palm Kernel Oil
ASTM	American Society for Testings and Materials
CI Engine	Compression Ignition Engine
CPO	Crude Palm Oil
USEIA	United States Energy Information Administration
FDA	Food and Drug Administration
USDA	United States Department of Agriculture
AAFC	Agriculture and Agri-Food Canada's
AOCS	The American Oil Chemists' Society
LSD	Least Square Difference
MR	Molar Ratio
SR	Stirring Rate
ME	Methy Ester
PET Bottle	Polyethylene Terephthalate Bottle

CHAPTER 1:

INTRODUCTION

1.1 Background

Nowadays, people are using diesel in massive amount for their mechanical equipments. But the used mineral takes decades to degrade; it is the big problem to environment. So, the global drive towards the use of biodegradable products in increasing despite early commercial resistance due to their cost and performance consideration (Davidson and LaPierre, 1998). Modern biofuels have been reported as a promising longterm renewable energy source which has potential to address both environmental impacts and security concerns posed by current dependence on fossil fuels (Alamu et al., 2007a; Gupta et al., 2007). Fossil fuels such as petroleum, coal and natural gas, which have been used to meet the energy needs of man are associated with negative environmental impacts such as global warming (Munack et al., 2001; Saravanan et al., 2007). Besides, supply of these non-renewable energy sources is threatening to run out in a foreseeable future (Sambo, 1981; Munack et al., 2001). It has been widely reported that not less than ten major oil fields from the 20 largest world oil producers are already experiencing decline in oil reserves. Recently published data also revealed a total of 29 major world oil producing countries already experiencing declining oil reserves from year 2005 to 2007 (EIA, 2007; Alamu et al., 2007a).

In comparison to petroleum-based fuels, biodiesel offered reduced exhaust emissions, improved biodegradability, reduced toxicity and higher cetane rating which can biodiesel produces about 65% less net carbon monoxide, 78% less carbon dioxide, 90% less sulphur dioxide and 50% less unburnt hydrocarbon emission (Margaroni, 1998; Ryan et al., 1982; Knothe and Steidley, 2005; Krahl et al., 2006). The search for renewable energy resources continues to attract attention in recent times. It has been reported that in diesel engines, vegetable oils can be used directly as fuel, or as blend with petroleum diesel (Gupta et al., 2007; Math, 2007). However, due to high viscosity of these oils, poor fuel atomization occurs in CI engines resulting in improper fuel-air mixture and inefficient combustion (Bari et al., 2002; Saravanan et al., 2007). The problem also manifests in injector coking, engine deposits and thickening of lubricants during extended operation of the engine (Ryan et al., 1982; Alamu et al., 2007a). The high viscosities of vegetable oils are however reduced through the process of transesterification. Satisfactory results have appeared in the literature on production of biodiesel through transesterification of different kinds of vegetable oil from different parts of the world. Such feedstock include soybean (US), rapeseed (Europe), oil palm (South-East Asia), jatropha curcus and rice bran oil (India). Biodiesel from canola, waste restaurant oil as well as animal fats have also been used in the existing CI engines without any modification (Al Widyan and Al Shyoukh, 2002; Chitra et al., 2005; Krahl et al., 2006; Gupta et al., 2007; Saravanan et al., 2007).

The fluids have excellent thermal stability, better lubricity, low volatility, and resist hydrolysis better than other esters (Kohashi, 1990). However, these esters suffer the disadvantages of seal-swelling tendencies due to their high degree of polarity. Nonetheless, there are applications where ester-based fluids are inevitable to overcome the high or low temperature limitations of vegetable oil-based diesels. For instance, long-chain polyol esters have been used successfully in the steel-rolling industry, hydraulic fluids and outdoor lubricants, particularly in forestry, waterways and construction (Remmelmann and Murrenhoff, 1998).

The sources of oils and fats are various vegetable and animal raw materials with the vegetable raw materials such as soybean, palm, rapeseed and sunflower oil being the most important one regarding the amounts involved. The composition of the fatty acids contained in the oil determines the further use of the oils. At the moment, a special attention was given to palm kernel oil and coconut oil, because of their high share of medium chain length fatty acid (Hill, 2000). Indonesia as a tropical country has wide variations in climatic and soil condition and thus has a wide variety of domestic plants that produce oil-bearing materials. (Barlow *et al.*, 2003).

1.2 Problem Statement

At the moment, from more than hundred types of plants that produce oil-bearing material, palm oil becoming prime of the Indonesian oils and fats scenes and contributed 1.5 – 2 % of the country's gross domestic product (Barlow *et al.,* 2003). To date, due to its high value and demand, oil palm producers give also special attention to the palm kernel oil (which was formerly just looked as a 'by product' of oil palm industry).

Beside palm oil, palm kernel oil, and coconut oil, many of Indonesian plants oil sources have been identified, but their potential as oil source has not been assessed. Among them such as rubber seed oil, candle nut oil, saga seed oil, and fenugreek oil could become good source of oils with special fatty acids composition and used as alkyl esters raw material.

In comparison to petroleum-based fuels, biodiesel offered reduced exhaust emissions, improved biodegradability, reduced toxicity and higher cetane rating which can biodiesel produces about 65% less net carbon monoxide, 78% less carbon dioxide, 90% less sulphur dioxide and 50% less unburnt hydrocarbon emission (Margaroni, 1998; Ryan et al., 1982; Knothe and Steidley, 2005; Krahl et al., 2006). The search for renewable energy resources continues to attract attention in recent times. It has been reported that in diesel engines, vegetable oils can be used directly as fuel, or as blend with petroleum diesel (Gupta et al., 2007; Math, 2007). However, due to high viscosity of these oils, poor fuel atomization occurs in CI engines resulting in improper fuel-air mixture and inefficient combustion (Bari et al., 2002; Saravanan et al., 2007). The problem also manifests in injector coking, engine deposits and thickening of lubricants during extended operation of the engine (Ryan et al., 1982; Alamu et al., 2007a). The high viscosities of vegetable oils are however reduced through the process of transesterification. Satisfactory results have appeared in the literature on production of biodiesel through transesterification of different kinds of vegetable oil from different parts of the world. Such feedstock include soybean (US), rapeseed (Europe), oil palm (South-East Asia), jatropha curcus and rice bran oil (India). Biodiesel from canola, waste restaurant oil as well as animal fats have also been used in the existing CI engines without any modification (Al Widyan and Al Shyoukh, 2002; Chitra et al., 2005; Krahl et al., 2006; Gupta et al., 2007; Saravanan et al., 2007).

Limited studies were however found in the literature on production and testing of biodiesel from Nigerian lauric oils. Abigor et al. (2000) produced biodiesel from palm kernel oil and coconut oil by transesterification of the oils with different alcohols using PS30 lipase catalyst. From a few recent works published on this subject, potassium hydroxide catalyst was used for the transesterification process (Alamu et al., 2007a, b; Alamu et al., 2008). In this work, biodiesel was produced through transesterification of PKO, canola oil, rapeseed oil with ethanol or methanol using NaOH or KOH (alkali) catalyst. The biodiesel produced was further characterized as alternative diesel fuel through ASTM standard tests for basic fuel properties such as specific gravity, viscosity, pour point and cloud point.

1.3 Objective and Scope of Study

- To study the kinetics of different reaction from different bio-oil feed stocks with different catalysts.
- To study the characteristics of bio-diesel produced from different bio-oil feedstocks.

CHAPTER 2

LITERATURE REVIEW

There is an increased interest in chemical derived from renewable resources such as vegetable or plant oils, animal fats, fish oils and microalgae oils rather than non-renewable petroleum. In 2002 - 2003 worldwide production of the major oils and fats was approximately 121.61 million metric tons; by far the largest share was used in human foodstuffs (Gunstone, 2003). In 2000, about 14 million tons of vegetable oils were used as starting material for synthesis of valuable intermediates in oleo chemistry and in recent years, the amounts produced have continuously increased by approximately 3% per year (Hill, 2000).

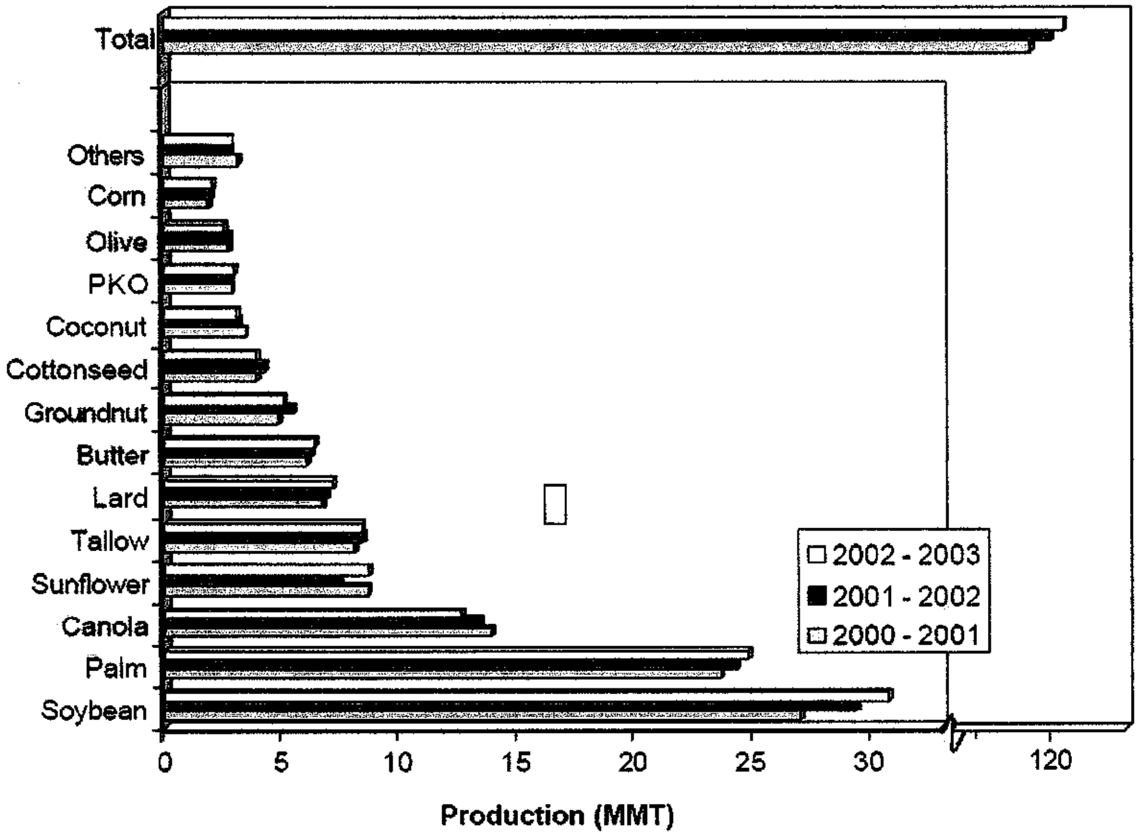


Figure 1: World Production of the Major Oils and Fats by Commodities
Others: sesame, fish, linseed, and castor oil (Source: Gunstone, 2003)

2.1. Palm *(Elais guineensis)* Kernel

2.1.1 Palm Kernel Oil

Among the 17 major oils and fats in world trade, there are only two lauric oils source, coconut oil and palm kernel oil. Palm kernel oil is very similar to coconut oil in fatty acid composition and properties. It constitutes about 45% of palm nut of palm oil. On a wet basis, the kernel contains about 45 – 50% of oil. Although it lies within the palm nut, palm kernel oil and palm oil differ greatly in their characteristics and properties. Palm kernel oil is rich in lauric acid (C12 about 48%) and other major fatty acids are myristic (C14 about 16%) and oleic acid (C18:1 about 15%). No other fatty acid is present at more than 10% (Rossel *et al.*, 1985; Pantzaris, T.P. *et al.*, 2001).

Crude palm oil - also referred to as "CPO" comes from the mesocarp (the fleshy portion of the fruit wall) and depending on the variety and age of the palm. The CPO to bunch ratio is about 25 to 28 percent.

Refined palm oil - after crude palm oil is refined, it is then referred to as Refined Palm Oil, and can then be used in a number of applications, including as a substitute for petroleum diesel - which is known as Palm Oil Biodiesel. Additionally, Palm Oil Biodiesel can be blended with petroleum diesel.

Recent estimates ranked Nigeria as the 11th largest oil producer in the world with 36 billion barrels oil reserves (USEIA, 2007). Also, global ranking by the US Energy Information Administration places Nigeria as having the seventh largest natural gas reserves in the world, with an estimated 182 trillion cubic feet of proven natural gas reserves (Alamu *et al.*, 2007a). Enormous as these energy sources appear, the global consensus is that fossil energy sources are finite (Sambo, 1981; Fluck, 1992; Jekayinfa and Bamigboye, 2004; Eleri *et al.*, 2005). This is evident from available statistics on oil reserves of world oil producers.

Table 1: World oil producers with declining oil reserves

Country	Oil (billion barrels) Year-end 2005	January 1, 2007
Mexico	13.670	12.352
United States	29.922	21.757
Ecuador	5.060	4.517
Peru	1.097	0.930
Trinidad and Tobago	0.809	0.728
Italy	0.731	0.600
Norway	9.691	7.849
United Kingdom	3.998	3.875
Kazakhstan	39.620	30.000
Russia	74.436	60.000
Iran	137.490	136.270
Oman	5.572	5.500
Saudi Arabia	264.211	262.300
Syria	3.000	2.500
Angola	9.035	8.000
Congo (Brazzaville)	1.784	1.600
Egypt	3.720	3.700
Equatorial Guinea	1.765	1.100
Gabon	2.205	2.000
Sudan	6.405	5.000
Tunisia	0.681	0.400
Australia	4.045	1.592
Brunei	1.120	1.100
China	16.038	16.000
India	5.919	5.625
Indonesia	4.301	4.300
Malaysia	4.200	3.000
Thailand	0.527	0.290
Vietnam	3.119	0.600

Source: USEIA,2007

2.1.2 Palm Oil Biodiesel

Palm Oil Biodiesel is an environmentally- friendly, renewable energy source that could also produce cost savings for taxpayers and private businesses and is produced from palm trees. The Palm Oil that is "harvested" and produced from palm trees is referred to as "Crude Palm Oil." The crude palm oil is then shipped to be refined by a palm oil refinery. The output is then referred to as Refined Palm Oil which is then suitable to be used as a biodiesel fuel, or blended with petroleum diesel.

Palm oil with an estimated global (annual) production of 25-27 million tons, is the second most produced oil in the world. By country, the leading producers of palm oil are Malaysia (13 million tons) and Indonesia (10 million tons), and together they have provided about 80% to 90% of the world's palm oil. Approximately 80% (21-23 million tons) of the global production of palm oil is exported to other countries. Malaysia exports about 12 million tons annually and Indonesia exports about 7 million tons annually to the major importers of palm oil, which include; India, China and the European Union.

2.2 Canola curcus

2.2.1 Canola Oil

Canola oil contains both omega-6 and omega-3 fatty acids in a ratio of 2:1 and is second only to flax oil in omega-3 fatty acid. Canola oil's proponents claim that it is one of the most heart-healthy oils and has been reported to reduce cholesterol levels, lower serum tryglyceride levels, and keep platelets from sticking together.

Canola oil has been claimed to promote good health due to its very low saturated fat and high monounsaturated fat content, and beneficial omega-3 fatty acid profile. The Canola Council of Canada states that it is completely safe and is the "healthiest" of all commonly used cooking oils. Traditional rapeseed oil contains higher amounts of erucic acid and glucosinolates than the commercially-sold consumer variety, both of which were deemed undesirable for human consumption by the United States Food and Drug Administration (FDA). Erucic acid may be involved with cancer and rancidity and glucosinolates may be goitrogenic. Canola oil contains only 0.5 to 1% erucic acid, well below the 2 percent limit set by the USDA (Klahorst, 1998).

Table 2: Fatty Acid Composition of Canola Oil.

Compound	Family	% of Total
Oleic acid	ω-9	55%
Linoleic acid	ω-6	25%
Alpha linoleic acid	ω-3	10%
Saturated fatty acid		4%

Source: Klahorst, 1998

The main product of the crop is the oil. To get it, it is necessary to separated the straw from the rapeseed, which ones are pressing obteining rape meal and rapeseed oil (ingeneral, raw rapeseed is approximately 60% meal and 40% oil). The later needs to be refined before be employed in the biodiesel production. These are the steps to get the rapeseed oil but depending the source elected, we have different yields.

2.2.2 Canola biodiesel

Canola biodiesel is an environmentally- friendly, renewable energy source that could also produce cost savings for taxpayers and private businesses and is produced from farmers that grow canola.

Initial research conducted by the University of Saskatchewan and the AAFC Saskatoon Research Centre has found that each ton of renewable biodiesel fuel saves five times its weight in diesel fuel. As well, engines using biodiesel demonstrate wear rates as much as 50% lower than those using regular commercial fuels – effectively doubling engine life.

Canola is a member of the Brassica Family, which includes broccoli, cabbage, cauliflower, mustard, radish, and turnip. It is a variant of the crop rapeseed. Grown for its seed, the seed is crushed for the oil contained within. After the oil is extracted, the by-product is a protein-richmeal used by the intensive livestock industry.

Canola is a very small seed, which means sowing depth must be controlled. The current sowing practice is to cover the seed lightly with soil, which provides more protection from drying out after germination. Canola is generally sown in autumn and develops over winter, with flowers emerging in the spring and is harvested early summer. With a growing period of around 180-200 days climatic effects such as sudden heat waves can reduce yields and hot dry conditions can limit its oil content. Summer weather ensures low moisture (less than 6%) at harvest. Carry-in stocks of canola are minimal because of a lack of on-farm storage. Canola is a good rotational crop, acting as a break crop for cereal root diseases. However for disease-related reasons, a rotation period of 3-5 years is required for canola crops of iodine in grams absorbed per 100 ml of oil is then "the IV". The higher the IV, the more unsaturated (the greater the number of double bonds available) is the oil and the higher the potential to 'gum up' when used as a fuel in an engine. Though some oils have a low IV and are suitable without any further processing other than extraction and filtering, the majority of vegetable and animal oils have an IV which does not permit their use as a neat fuel. Generally speaking, an IV of less than about 25 is required if the neat oil is to be used in unmodified diesel engines and this severely limited the types of oil that can be used.

The IV can be easily reduced by hydrogenation of the oil (reacting the oil with hydrogen), the hydrogen breaking the double bond and converting the fat or oil into a more saturated oil and reducing the tendency of the oil to polymerise. However this process also tends to increase the melting point of the oil and converts the oil into margarine. Only coconut oil has an IV low enough to be used without any special precautions in a unmodified diesel engine. However with a melting point of 25°C, the use of coconut oil in cooler areas would obviously lead to problems.

Linseed oil could be mixed with petroleum diesel at a ratio of up to 1:8 to give an equivalent IV in the mid-twenties. Likewise coconut oil can be thinned with diesel or kerosene to render it less viscous in cooler climates. Obviously the solubility of the oil in petroleum also needs to be taken into account. Another method is to emulsify the oil or fat with ethanol. Most vegetable oils are a mixture of different esters such as oleic acid (main constituent of olive oil), ricinoleic acid (main constituent of castor oil), linoleic acid (main constituents of linseed oil), palmitic acid (main constituent of palm kernel oil) and so on. In an analogous way to that in which crude oil is refined to make a useable automotive fuel, canola oil needs to be transesterified to make an automotive fuel that is useable in unmodified diesel engines.

When the oil is processed in a transesterfication process, the various fatty acids react with the alcohol to form a mixture of lighter esters and glycerol. The name of the specific fuel is called after the plant (or animal) source plus the alcohol. Made from rapeseed oil and methanol, the biodiesel is called Rapeseed Methyl Ester (RME), from canola oil and ethanol, Canola Ethyl Ester (CEE), and from used McDonald's cooking oil and ethanol or methanol, ("McDiesel").

2.3 Jatropha curcus

2.3.1 Jatropha curcus

Jatropha curcus (Linnaeus), a non-edible oil-bearing and drought-hardy shrub with ecological advantages, belonging to the *Euphorbiaceae* family, was found to be the most appropriate renewable alternative source of biodiesel. The seeds of this perennial shrub are used to extract oil with 30 to 40 % recovery (Kandpal and Madan, 1995).

The extracted oil could not be used directly in diesel engines because of its high viscosity. High viscosity of pure vegetable oils would reduce the fuel atomization and increase fuel spray penetration, which would be responsible for high engine deposits and thickening of lubricating oil (Silvio et al., 2002). The use of chemically altered or transesterified vegetable oil called biodiesel does not require modification in engine or injection system or fuel lines and is directly possible in any diesel engine. The stoichiometric equation requires one mole of triglyceride and three moles of alcohol to form three moles of methyl ester and one mole of glycerol in the presence of a strong base or acid (Muniyappa et al., 1996).

2.3.2 Jatropha biodiesel

The important factors that affect the transesterification reaction are the amounts of methanol and sodium hydroxide, reaction temperature and reaction time (Demirbas, 2003). The molecular weight of Jatropha curcus oil with major chemical constituents was determined as 870 (Ramesh, 2004). Since the oil also contains other minor constituents, the approximate molecular weight of Jatropha curcus oil was taken as 900. As per the transesterification reaction, 3 moles of methanol were required to react with 1 mole of vegetable oil (Kavitha, 2003). The molecular weight of methanol is 32 and hence 96 g of methanol were required for the transesterification of 1 mole (or 900 g) of Jatropha curcus oil, which amounted to 10.67 % methanol.

In order to optimize the amount of methanol required for the reaction, experiments were conducted with four different percentages of methanol (10, 15, 20 and 25 %), keeping the catalyst concentration, reaction temperature and reaction time constant.

Most researchers have used 0.1 to 1.2 % (by weight of oil) of NaOH for biodiesel production (Ma et al., 1999; Alacantara et al., 2000). If acid value is greater than 1, more NaOH is required to neutralize free fatty acids (Wright et al., 1944). In the present study, three different catalyst concentrations were used (0.5, 1.0 and 1.5 % NaOH), keeping methanol concentration, reaction temperature and reaction time constant in order to optimize the concentration of NaOH. For the preparation of sodium methoxide solution, sodium hydroxide (NaOH) pellets were completely dissolved in methanol and added into the oil, since NaOH pellets would react with CO2 and water present in the atmosphere and yield sodium carbonate, which would affect the performance of the catalyst during the transesterification reaction.

The reaction temperature influences the reaction rate and the yield of esters (Ma et al., 1998). The reaction temperature should always be maintained below the boiling point (65°C) of methanol (Freedman et al., 1984; Van Gerpen, 2004). Hence for the transesterification of Jatropha curcus oil with methanol, three different temperatures were used (30, 45 and 60°C), keeping alcohol and catalyst concentrations and reaction time constant in order to optimize the reaction temperature. The methyl ester conversion rate increases with the reaction time (Ma et al., 1998). Different researchers have reported different reaction times for the transesterification process. The process required 3 h for making ester (Senthil Kumar et al., 2003) and the reaction mixture was stirred for 90 min before it was transferred to a separation funnel (Foidl et al., 1996). Hence four different reaction times were selected for the process of transesterification of Jatropha curcus oil (30, 60, 90 and 120 min), keeping alcohol and catalyst concentrations and reaction temperature constant in order to optimize the reaction time. The following experimental procedure was adopted for the production of biodiesel. Some 200 g of Jatropha curcus oil was taken in a three-necked round-bottomed flask. A water-cooled condenser and a thermometer with cork were connected to the side openings on either side of the round-bottomed flask. The required amount of catalyst NaOH was weighed and dissolved completely in the required amount of methanol by using a stirrer to form sodium methoxide solution in the case of base/alkali catalyst. Meanwhile, the oil was warmed by placing the round-bottomed flask in the water bath maintained at the selected temperature mentioned above. The sodium methoxide solution or acid catalyst solution was added into the oil for vigorous mixing by means of a mechanical stirrer fixed into the flask. The required temperature was maintained throughout the reaction time and the reacted mixture was poured into the separating funnel. The mixture was allowed to separate and settle overnight by gravity settling into a clear, golden liquid biodiesel on the top with the light brown glycerol at the bottom. The next day, the glycerol was drained off from the separating funnel, leaving the biodiesel/ester at the top. The raw biodiesel was collected and water-washed to bring down the pH of biodiesel to 7. This pure biodiesel gives the ester yield measured on weight basis and the important fuel and chemical properties were determined and compared with the properties of raw oil and BIS standards. The emulsion that comes out during washing of ester was also collected and weighed.

After having optimized the concentration of methanol, NaOH and the time required for transesterification of Jatropha oil, experimental studies on large-scale production of biodiesel were carried out in the biodiesel pilot plant. The best treatment with higher yield of ester/biodiesel was analysed and selected for biodiesel production in the pilot plant among the various treatments. The pilot plant consists of a biodiesel reactor with heating and agitating devices, catalyst mixing tank, glycerol settling tanks and biodiesel washing tank. The pure ester yield was determined after settling the glycerol and washing the ester. The fuel properties of Jatropha curcus oil help in assessment of its suitability as fuel in diesel engines. The chemical properties of raw oil give an idea of the possibility of biodiesel production and its effect on biodiesel yield. The fuel properties such as kinematic viscosity (ASTM 445-72 method) and specific gravity (IS: 1448- 1972) and chemical properties such as free fatty acid and acid value (AOCS Official Method Ca 5a-40) were determined for raw oil and transesterified Jatropha oil according to standard test methods. A statistical tool, completely randomised design (AGRES) with single factor analysis, was used to predict optimal conditions for maximum biodiesel production from alkali-catalysed transesterification of Jatropha curcus oil. The parameters considered to find out higher biodiesel production were percentage of methanol, catalyst amount, reaction time and reaction temperature. The significance was tested using least square difference (LSD).

2.4 Transesterification process

Transesterification process is one of the most successful and promising processes to convert vegetable oils into diesel-like liquid, biodiesel. Chemically, biodiesel is mono-alkyl esters (fatty esters) of long chain fatty acids (falls in carbon range from C12-C20) derived from renewable biological sources such as vegetable oils or animal fats.

The monoesters commonly known as biodiesel are usually produced through the transesterification of vegetable oils or animal fats. Both oils and fats are triglycerides or fatty esters of glycerin. Fat usually refers to the triglycerides which are solid at room temperature while oils are liquid at room temperature. The triglyceride molecule has the chemical tructure shown in Figure 2 , where R_1, R_2, and R_3 represent long chain fatty acids.

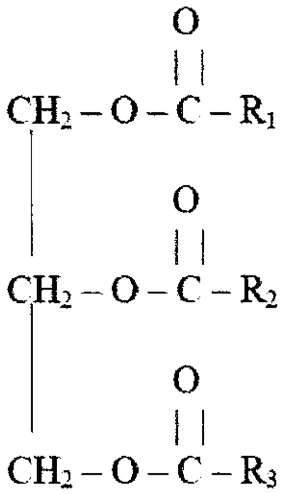
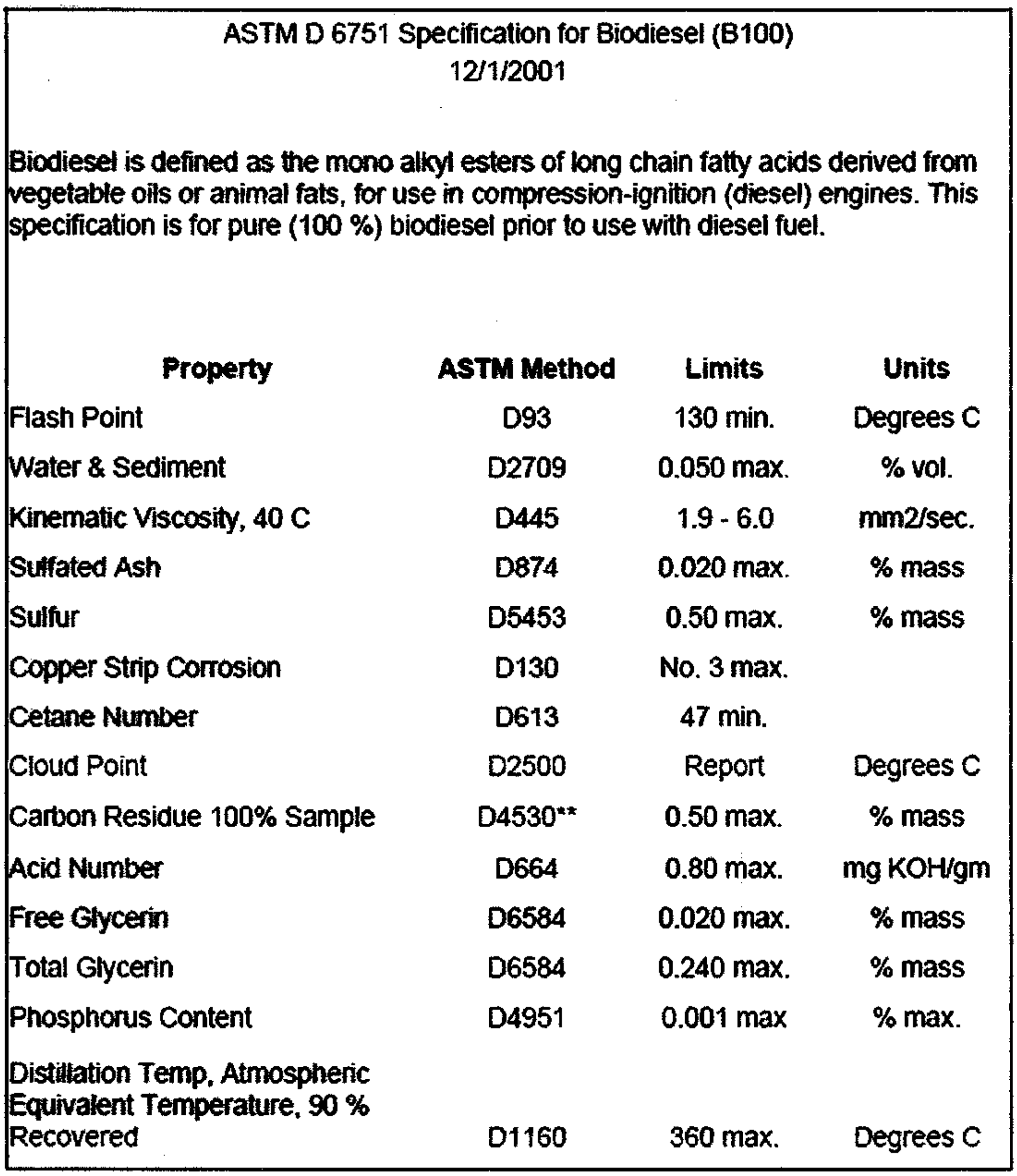


Figure 2: Triglyceride Chemical Structure.

Molecules having three fatty acid chains are referred to as triglycerides, while those with two fatty acid chains are diglycerides, and those with one fatty acid chain are monoglycerides.

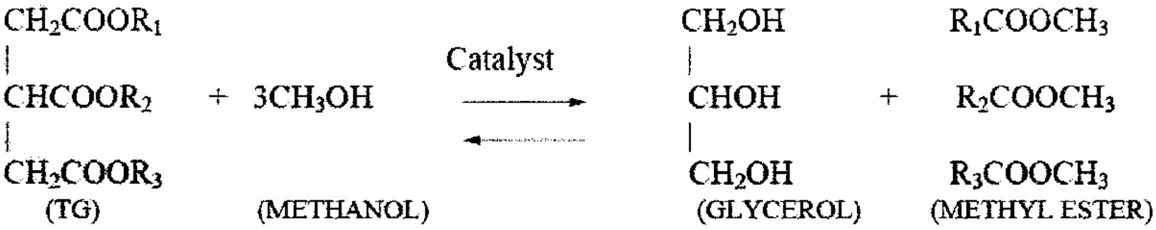


ASTM D 6751 Specification for Biodiesel (B100)
12/1/2001

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. This specification is for pure (100 %) biodiesel prior to use with diesel fuel.

Property	**ASTM Method**	**Limits**	**Units**
Flash Point	D93	130 min.	Degrees C
Water & Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40 C	D445	1.9 - 6.0	mm2/sec.
Sulfated Ash	D874	0.020 max.	% mass
Sulfur	D5453	0.50 max.	% mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane Number	D613	47 min.	
Cloud Point	D2500	Report	Degrees C
Carbon Residue 100% Sample	D4530**	0.50 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/gm
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus Content	D4951	0.001 max	% max.
Distillation Temp, Atmospheric Equivalent Temperature, 90 % Recovered	D1160	360 max.	Degrees C

Transesterification reaction



$$\begin{array}{lcl}\begin{array}{l} CH_2COOR_1 \\ | \\ CHCOOR_2 \\ | \\ CH_2COOR_3 \\ \text{(TG)} \end{array} + \underset{\text{(METHANOL)}}{3CH_3OH} & \overset{\text{Catalyst}}{\rightleftharpoons} & \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{(GLYCEROL)} \end{array} + \begin{array}{l} R_1COOCH_3 \\ \\ R_2COOCH_3 \\ \\ R_3COOCH_3 \\ \text{(METHYL ESTER)} \end{array}\end{array}$$

Transesterification process is a set of three consecutive chemical reactions between ester (TGs present in vegetable oils) and an alcohol in presence of a catalyst (homogeneous or heterogeneous). Alkyl esters in the carbon range C12-C20 result and are known as 'biodiesel' with glycerol as a byproduct. Transesterification reaction is sensitive to reaction parameters like, alcohol used, molar ratio of alcohol to oil (MR), temperature of the reaction (T), catalyst and catalyst amount (C% w/w of oil), and stirring rate (SR). The schematic of the overall transesterification reaction as shown above requires three moles of methanol to react with one mole of TGs. This overall reaction is reversible. To shift the equilibrium conversion in the forward direction (to get more yield of ME) either the molar ratio (methanol to oil) of the reaction should be increased or one of the products of the reaction should be separated and removed continuously.

CHAPTER 3

METHODOLOGY

3.1 Procedures

Palm Kernel oil, Canola Oil for experiment are purchased at Jusco, Ipoh, Malaysia. In UTP, Ethanol, Methanol, Sodium Hydroxide, Potassium Hydroxide are provided.

Equipments used for experiment are:

- Hot plate with magnetic stirrer.
- Clear glass container (1000ml).
- 500-cm3 three-necked glass flask with a water-cooled condenser.
- Stainless steel cutting blades.
- Scales.
- Translucent white plastic container with bung and screw-on cap.
- Funnels.
- PET bottles and thermometer

3.1.1 Transesterification of PKO with ethanol using NaOH catalyst

- 20.0 g of ethanol was measured and poured into a plastic container after which 1.0 g of NaOH was carefully added. The container was swirled round thoroughly for about 2 min repeatedly about six times for complete dissolution of NaOH in the ethanol to form sodium ethoxide.

- 100.0 g of PKO was measured out, pre-heated to 60□C in a beaker and poured into the blending beaker.

- Sodium ethoxide from the plastic container was carefully poured into the PKO, the blending beaker lid was secured tightly and swirling in the beaker was maintained for 90 min.

- The mixture was poured from the blender into a PET bottle for settling and the lid was screwed on tightly.

- The reaction mixture was allowed to stand overnight while phase separation occurred by gravity settling. The PKO biodiesel was carefully decanted into a PET bottle leaving the glycerol at the base.

- The biodiesel was washed with water adopting the method earlier reported. The procedure was replicated three times and average biodiesel yield as well as glycerol yield was measured on weight basis.

3.1.2 Transesterification of PKO with ethanol using KOH catalyst

- 20.0g of ethanol was measured and poured into a plastic container a funnel and the lid of the ethanol container was tightly replaced. 1.0g of KOH was carefully added to the plastic container via a second funnel. The bung and the screw on the cap were replaced tightly. The container was shook a few (about six) times by swirling round thoroughly for about 2 minutes until the KOH completely dissolved in the ethanol, forming potassium ethoxide.

- 100.0g of PKO was measured out in a beaker, pre-heated to the required temperature (60□C) and poured into the blender. With the blender still switched off, the prepared potassium ethoxide from the plastic container was carefully poured into the PKO. The blender lid was secured tightly and switch on. The mixture was left to blend for the 100minutes at moderate speed before the blender was switched off.

- The mixture was poured from the blender into a 2-litre PET bottle for settling and the lid was screwed on tightly. The reaction mixture was allowed to stand overnight while phase separation occured by gravity settling into (an expected) clear, golden / pale liquid biodiesel on the top with the light brown glycerol at the bottom of the bottle. The next day, the PKO biodiesel/ester at the top was carefully decanted into a PET bottle leaving the glycerol at the base.

3.1.3 Transesterification of canola oil with methanol/ethanol using KOH catalyst

- 20.0g of ethanol was measured and poured into a plastic container a funnel and the lid of the ethanol container was tightly replaced. 1.0g of KOH was carefully added to the plastic container via a second funnel. The bung and the screw on the cap were replaced tightly. The container was shook a few (about six) times by swirling round thoroughly for about 2 minutes until the KOH completely dissolved in the ethanol, forming potassium ethoxide.

- Commercial edible grade canola oil was obtained from a market. A 500-cm3 three-necked glass flask with a water-cooled condenser was charged with 50 g of canola oil, different volumes of anhydrous alcohol, and varied amounts of KOH catalysts. The mixture was refluxed at the required temperature for 9 h under stirring at 500 rpm.

- After the reaction, the solid catalyst was separated by filtration. The liquid was put into a separating funnel and was kept at ambient temperature for 24 h, after which 2 liquid phases appeared. The upper layer was biodiesel and the lower layer was glycerol. The conversion of canola oil was calculated from the quantity of total glycerol in the product. The procedure was carried out according to the AOCS Official Method Ca 14-56.

3.1.4 Transesterification of jatropha oil with methanol using NaOH catalyst

For this case, we prepare 14 samples as 14 treatments for jatropha oil with differents amount of catalysts or different reaction conditions in different reaction time. All treatments are shown in table 3. Preparation for catalyst and reactant are same to previous cases above. All procedures are also the same with transesterification of PKO with ethanol using NaOH catalyst.

Table 3: Transesterification preparations and reaction conditions for jatropha oil

Treatment	**Reaction Temp. (□C)**	**Reaction time (min)**	**Oil (g)**	**Methanol (g)**	**NaOH (g)**
TA1	60	120	100	***10***	1.0
TA2	60	120	100	***15***	1.0
TA3	60	120	100	***20***	1.0
TA4	60	120	100	***25***	1.0
TA5	60	120	100	20	***1.5***
TA6	60	120	100	20	***2.0***
TA7	60	120	100	20	[illegible]
TA8	60	***30***	100	20	1.0
TA9	60	***60***	100	20	1.0
TA10	60	***90***	100	20	1.0
TA11	60	***120***	100	20	1.0
TA12	***30***	120	100	20	1.0
TA13	***45***	120	100	20	1.0
TA14	***60***	120	100	20	1.0

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Transesterification of PKO with ethanol using NaOH catalyst

4.1.1 Transesterification process

The transesterification process yielded 95.8 g PKO biodiesel and 22.4 g glycerol, while 2.8 g of the total reacting masses could not be accounted for. These losses have been attributed to some unreacted alcohol, residual catalyst and emulsion removed during the washing stage of the production process. The results stated are averages of three different experimental runs. Detailed results for each of the experimental runs are as presented in Table 4. Economic considerations showed positive results as cost per kilogramme of the biodiesel was found to be less than that of fossil diesel. Besides, the major feedstocks are renewable agricultural products.

Table 4: Results for the transesterification experiment.

Experimental Conditions	**1st Run**	**2nd Run**	**3rd Run**	**Average**
Reaction temperature (approximated) (°C)	**60**	**60**	**60**	**60**
Reaction time (min.)	**90**	**90**	**90**	**90**
Palm kernel oil (PKO) quantity (g)	**100**	**100**	**100**	**100**
Ethanol quantity (g)	**20.0**	**20.0**	**20.0**	**20.0**
NaOH concentration (%) (in 100g PKO)	**1.0**	**1.0**	**1.0**	**1.0**
PKO biodiesel obtained (g)	**96.2**	**95.3**	**95.9**	**95.8**
Glycerol obtained (g)	**22.4**	**22.6**	**22.2**	**22.4**
Losses (g)	**2.4**	**3.1**	**2.9**	**2.8**
PKO biodiesel yield (%)	**96.2**	**95.3**	**95.9**	**95.8**

4.1.2 Fuel characterization

The laboratory scale PKO biodiesel produced and the commercial grade petroleum diesel were analyzed for basic fuel properties. Results obtained are presented in Table 5. With raw PKO having viscosity 32.40 mm2/s as earlier reported (Abigor et al., 2000; Alamu et al., 2007a; Alamu et al., 2008), the PKO biodiesel viscosity obtained showed 85.06% reduction.

This will enhance the biodiesel's fluidity in diesel engines. Higher specific gravity, pour point, and cloud point were obtained compared to that of petroleum diesel.

Table 5. Fuel characterization results for PKO biodiesel and petroleum diesel fuel.

Fuel Characteristics (Properties/Parameters)	(PKO biodiesel)	(Petroleum diesel)	EN14214 European biodiesel standard
Viscosity (mm^2/s @ 40□C)	4.752	2.847	3.50-5.00
Specific gravity (@ 60□F/60□F)	0.876	0.853	0.86-0.90
Pour point (□C)	2	-16	-
Cloud point (□C)	6	-12	-
Flash point (□C)	167	74	>120

At 15.56°C, specific gravity of PKO biodiesel was 1.033958 times that of fossil diesel. Comparison made revealed good agreement as evident from Table 3 for EN 14214 standard as well as rapeseed ethyl ester and canola ethyl ester biodiesel. The specific gravity obtained for the PKO biodiesel at 15oC falls within the limit specified by various international standards for biodiesel. EN14214 (Europe) standards specify specific gravity ranges (0.86 - 0.9) for biodiesel fuel. From this result, the specific gravity of 0.884 at 15oC obtained for the PKO biodiesel is in very good agreement with the above biodiesel standards.

4.1.3 Subconclusion

From the production and fuel characterization of PKO biodiesel carried out, the following conclusions can be drawn: The transesterification process carried out using 100 g PKO, 20.0 g ethanol, 1.0% NaOH (by weight of PKO) at 60°C reaction temperature and 90 min reaction time yielded 95.8 g PKO biodiesel. At 15.56°C, specific gravity of PKO biodiesel is 1.033958 times that of fossil diesel. At 40°C, the PKO biodiesel had 85.06% reduction of viscosity over its raw vegetable oil. Higher pour (2°C), cloud (6°C) and flash (167°C) points were obtained for the PKO biodiesel compared to -12, -16 and 74°C respectively obtained for commercial grade fossil diesel fuel. The limited fuel characterization carried out demonstrated that the PKO biodiesel produced can fuel a diesel engine.

4.2 Transesterification of PKO with ethanol using KOH catalyst

4.2.1 Transesterification process

The PKO biodiesel prepared using 30 min. reaction time yielded 87.40g PKO biodiesel and 32.40g glycerol, with 1.2g losses. These losses are obviously some un-reacted alcohol, residual catalyst and emulsion removed during the washing stage of the production process. Similar observation has been reported in the alkali-catalysed transesterification of Jatropha curcus oil (Chitra *et al.*, 2005). The results stated are averages of three different experimental runs. Detailed results for each of the experimental runs are presented in Table 6.

Table 6: Biodiesel production results for batch 1 experiment (reaction time = 30min)

Experimental Conditions	1st run	2nd run	3rd run	Average
Transesterification duration (min.)	30 minutes			
PKO biodiesel obtained (g)	88.20	87.50	86.50	87.40
Glycerol obtained (g)	32.40	32.30	32.50	32.40
Losses (g)	0.40	1.20	2.00	1.20
PKO biodiesel yield (%)	88.20	87.50	86.50	87.40

4.2.2 Optimal Transesterification Duration

With the reaction time increased to 60 min (batch 2 experiment), an improved biodiesel yield of 92.50% was obtained, with 27.2% glycerol and 1.3% losses as presented in Table 6. This trend continued with reaction time 90 min (batch 3 experiment) and 120 min (batch 4 experiment) with respective biodiesel yield of 96.0% and 96.0% (Table 7). This implies that within the temperature range 30 – 90 min., PKO biodiesel yield increased with reaction time; an observation earlier made by Chitra *et al.* (2005) for Jatropha curcus biodiesel and Yuan et al. (2004) for soybean biodiesel. Beyond 90 min reaction time however, there wasn't any significant change in the biodiesel yield. As evident from Table 7, PKO biodiesel yield neither increased nor decreased with reaction time between 90 min and 120 min. Hence, the minimum reaction time corresponding to the maximum process yield was 90 min.

Table 7: Three-run average results of biodiesel production for 4 batches of experiments (30-120min.)

	Batch			
	1	2	3	4
Transesterification duration (min.)	30	60	90	120
PKO biodiesel obtained (g)	87.4	92.5	96.0	96.0
Glycerol obtained (g)	32.4	27.2	23.4	22.0
Losses (g)	1.2	1.3	1.6	2.0
PKO biodiesel yield (%)	87.4	92.5	96.0	96.0

Once the maximum biodiesel yield has been achieved at 90 min reaction duration, it may no longer be cost effective for the transesterification reaction to be continued. Figure 3 reveals the situation at close to and slightly beyond the optimum reaction time; no biodiesel yield increase was evident. This shows that the effect of reaction time on KOH-catalysed transesterification of PKO with ethanol does not agree perfectly with earlier report on NaOH catalysed transesterification of Jatropha curcus oil with methanol beyond 90 min reaction time.

Possible explanation could be the different boiling points of the alcohols involved in each case. While methanol reported in Chitra *et al.* (2005) has a boiling point of 65□C, the boiling point of ethanol used in the present study is 13□C higher. Another possible explanation could be the inherent properties of the particular feedstock.

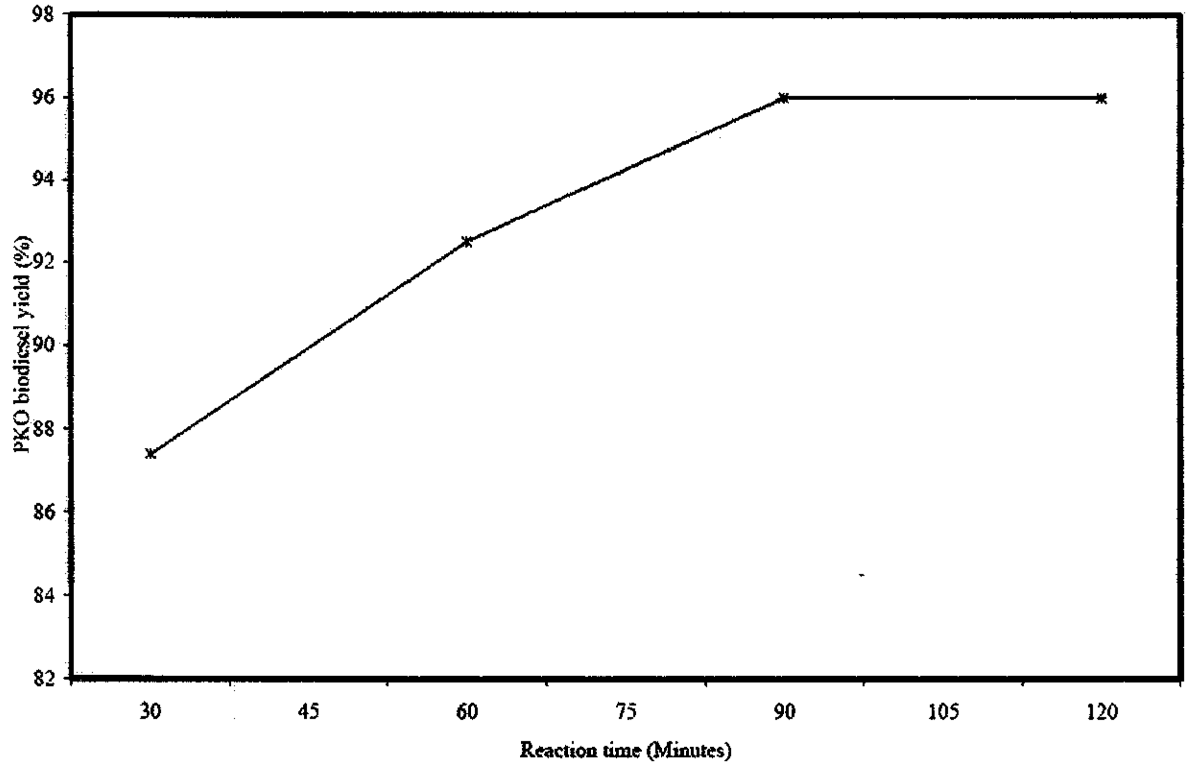


Figure 3: POK biodiesel yield vs. Reaction time

In characterizing the PKO biodiesel produced as alternative diesel fuel, The PKO biodiesel and the petroleum diesel, used as control, were analyzed for specific gravity at 60OF, viscosity at 40OC, pour point, cloud point and flash point. Results obtained are presented in Table 8.

Table 8. Fuel characterization results for PKO biodiesel and petroleum diesel fuel.

Fuel Characteristics (Properties/Parameters)	(PKO biodiesel)	(Petroleum diesel)
Viscosity (mm^2/s @ 40□C)	4.839	2.847
Specific gravity (@ 60□F/60□F)	0.883	0.853
Pour point (□C)	2	-16
Cloud point (□C)	6	-12
Flash point (□C)	167	74

4.2.3 Specific Gravity

Specific gravity has been described as one of the most basic and most important properties of fuel because some important performance indicators such as cetane number and heating values are correlated with it (Tat and Van Gerpen, 2000; Ajav and Akingbehin, 2002). It has also been reported to be connected with fuel storage and transportation (Yuan *et al.*, 2004). Results presented in Table 8 revealed that the specific gravity recorded for the PKO biodiesel is higher than the values obtained for the petroleum diesel. At the reference temperature (60°F = 15.56°C), where the specific gravity value obtained for PKO biodiesel and petroleum diesel are respectively 0.883 and 0.854 (Table 8), the specific gravity of PKO biodiesel is 1.033958 times that of petroleum diesel. The value of specific gravity obtained for PKO biodiesel (0.883) fall within the limit specified for biodiesel fuels (0.87 – 0.90) by the BIS Standard (Table 9). Specific gravity value for the control fuel sample (0.854) also fall within the range specified for diesel fuel (0.81 – 0.86) by the same Standard.

Table 9: Properties of Diesel and Biodiesel fuels

Properties	Diesel fuel	Biodiesel fuel
Specific gravity	0.81 – 0.86	0.87 – 0.90
Viscosity	2.0 – 5.0	3.5 – 5.0

At 15.56°C, the specific gravity obtained for the PKO biodiesel falls within the limit specified by various international standards. From Table 8, the specific gravity of 0.884 at 15.56°C obtained for the PKO biodiesel is in very good agreement with all the above standards as the value falls within the different ranges recommended.

4.2.4 Viscosity

Viscosity, the measurement of the internal flow resistance of a liquid, constitutes an intrinsic property of vegetable oils. It is of remarkable influence in the mechanism of atomization of the fuel spray. Results obtained for viscosity measurement fall within the range of values acceptable for alternative diesel fuel. These results also agree closely with a number of earlier works on other oil crops as well as series of Alcohol-Diesel blends.

From the result presented in Table 8, PKO biodiesel has higher viscosity than conventional diesel fuel. Viscosities for these biodiesel fuels were reported to be 1.3 to 2.1 that of low sulphur grade conventional diesel (No.2 Diesel).

The 40°C, used by Van Gerpen *et al.* (2004) as reference point for comparison of values of kinematic viscosity is the parameter required by biodiesel and petroleum diesel standards (Knothe and Seidley, 2005; Lebedevas and Vaicekauskas, 2006). At this temperature, the

PKO biodiesel has viscosity of 4.839 mm^2/s, which almost doubles the 2.847 mm^2/s obtained for the reference conventional petroleum diesel used (Table 8).

From the results obtained it can be seen that the esterification of PKO (a vegetable oil) produced a marked decrease in values of viscosity from the reported range of 30 to 50 mm^2/s for vegetable oils at 40°C (Brevad biodiesel.org, visited 2007) to 4.839 for PKO biodiesel at the same temperature. Abigor *et al.* (2000) specifically indicated that Nigerian palm kernel oil has a viscosity of 32.40 mm^2/s. With viscosity value of 4.839 mm^2/s obtained for the PKO biodiesel produced in this work, it implies that a reduction of 85.06% viscosity has been achieved in the PKO fuel. Also, the reduction in viscosity achieved in this study is 15.06% greater than that achieved by Abigor *et al.* (70%), where PKO was transesterified with ethanol using lipase catalyst. This appreciable reduction in viscosity, no doubt, will enhance the fluidity of this alkali catalysed ethyl ester alternative fuel in diesel engine.

It is also observed that the viscosity of PKO biodiesel (4.839 mm_2/s) fall within the range prescribed by ASTM D6751 standard (1.9 – 6.0) mm_2/s for biodiesel. Also, the viscosity of Petroleum diesel (2.847 mm_2/s) fall within the range prescribed by ASTM D975 (1.9-4.1) mm_2/s for conventional diesel fuel (Knothe and Steidly, 2005; Chitra *et al.*, 2005). Similar agreement is observed with the BIS standard in Table 9. This implies that the PKO biodiesel satisfies the fluidity requirement of an alternative biodiesel.

4.2.5 Pour Point

Pour point is the temperature at which wax becomes visible when the fuel is cooled. From Table 8, it is observed that the pour point obtained for the PKO biodiesel (2°C) is higher than that (-16°C) obtained for the conventional petroleum diesel.

Pour point has been described as an important parameter for low temperature operation of a fuel. It is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow.

4.2.6 Cloud Point

The cloud point is another important parameter for low temperature operation of a fuel. It is the temperature at which solidification of heavier components of the PKO biodiesel resulting in a cloud of crystals within the body of the biodiesel first appeared. The value obtained is within a comparable range with previous results.

It is observed from Table 8, that the cloud point obtained for the PKO biodiesel (6°C) is higher than that (-12°C) obtained for the conventional petroleum diesel. This agrees perfectly with the general report that biodiesel has higher cloud point than petroleum diesel (Alberta Research Council, 2006; Graboski and McCormic, 1998).

From Table 8, the cloud point obtained for the PKO biodiesel is 18°C higher than the cloud point for the petroleum diesel fuel.

4.2.7 Subconclusion

From the laboratory scale production and characterization of ethyl ester of PKO (biodiesel) studied, the following conclusions can be drawn: The transesterification process carried out using 100g PKO, 20.0g ethanol, 1.0% KOH (by weight of PKO) at 60°C reaction temperature and 100 minutes reaction time yielded 92g PKO biodiesel. At 60°F or 15.56°C reference temperature, specific gravity of PKO biodiesel is higher (1.033958 times) than that of fossil diesel. At 40°C (104°F) reference point, the PKO biodiesel had 85.06% reduction of viscosity over its raw vegetable oil, thus enhancing its fluidity in diesel engine. Higher pour point (2°C) was obtained for PKO biodiesel compared to conventional petroleum based diesel (-16°C). Cloud point obtained for PKO biodiesel (6°C) is higher than that (-12°C) obtained for petroleum diesel. The limited fuel characterization carried out demonstrated that the ethyl ester of PKO biodiesel produced can successfully fuel a diesel engine, through the level of agreement between the results obtained and previous works.

4.3 Transesterification of canola oil with methanol/ethanol using KOH catalyst

4.3.1 Transesterification process

The effects on biodiesel production of the methanol/canola oil molar ratio, type of alcohol, reaction temperature, and mass ratio of catalyst to oil were investigated. The transesterification process consists of a sequence of 3 consecutive reversible reactions in which the triglyceride is successively transformed into diglyceride, monoglyceride, and finally into glycerin and fatty acid methyl esters. The molar ratio of methanol to canola oil is an important factor that affects the conversion to methyl esters. Stoichiometrically, 3 moles of methanol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to drive the reaction towards completion and produce more methyl esters as products. Figure 4 reflects the effect of methanol/oil molar ratios on the conversion. As shown in this figure, with an increase in the methanol-loading amount, conversion was decreased. The highest conversion rate of 63.1% was achieved when the molar ratio was 6:1.

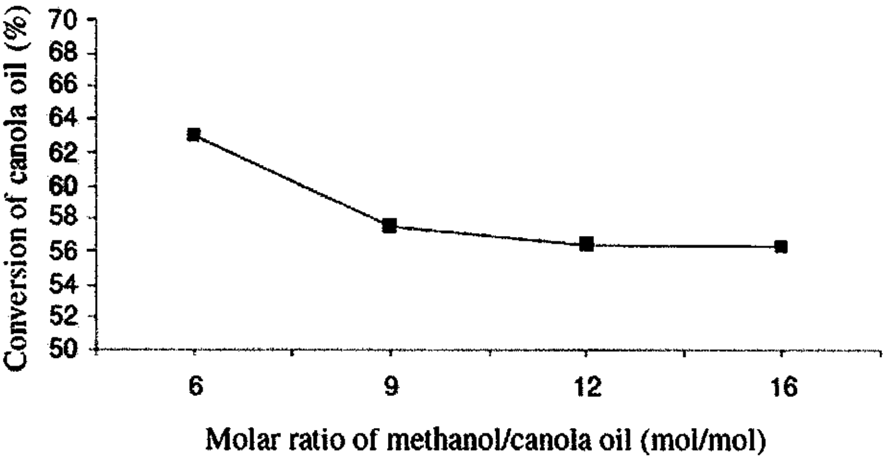


Figure 4: Conversion of canola oil as a function of the methanol/oil molar ratio. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; temperature: 60

The effect of the reaction temperature on the conversion of canola oil was studied. As shown in Figure 5, the transesterification reaction was not strongly dependent upon temperature. If the reaction temperature exceeds the boiling point of methanol, the methanol will vaporize and form a large number of bubbles, which inhibit the reaction on the 3-phase interface. The highest conversion rate of 63.1% was achieved when the reaction temperature was 60 □C.

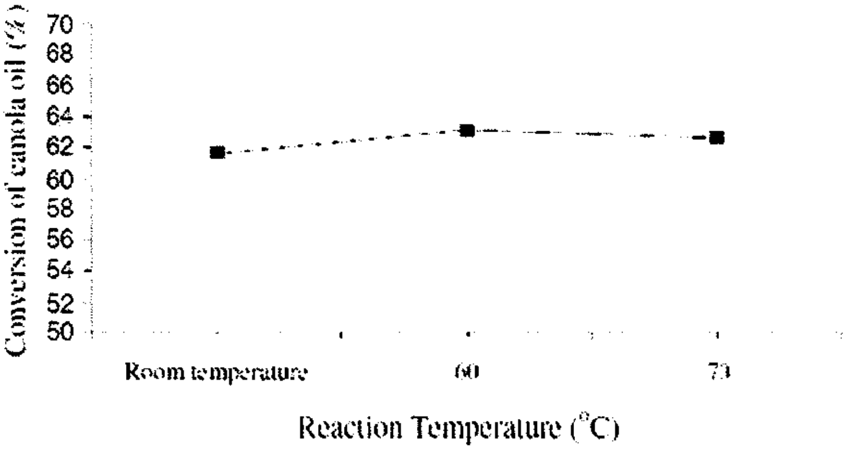


Figure 5. Conversion of canola oil as a function of reaction temperature. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; methanol/canola oil molar ratio: 6:1

The effect of the amount of catalyst on the conversion of canola oil was studied. The catalyst amounts tested were 3%, 6%, and 9%. These percentages were weight fractions of the oil supplied for these reactions.

As shown in Figure 6, the highest conversion of canola oil was observed when methanol was used in the transesterification reaction.

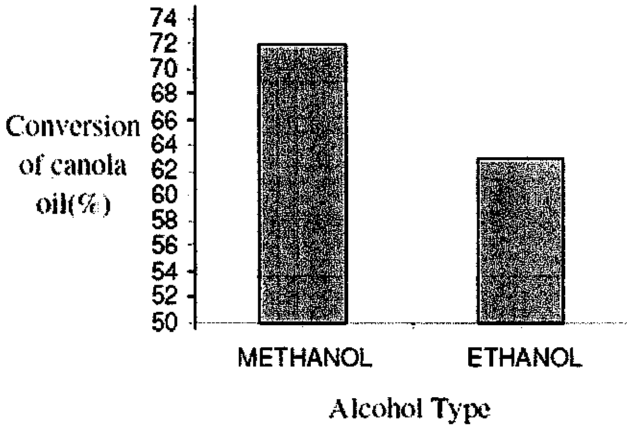


Figure 6. Conversion of canola oil as a function of alcohol type. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; alcohol/canola oil molar ratio: 6:1; temperature: 60□C

As shown in Figure 7, when the catalyst amount increased, the conversion of canola oil increased. Although the highest catalyst amount resulted in the highest conversion of canola oil, the cost of the catalyst has a crucial role in the economics of biodiesel.

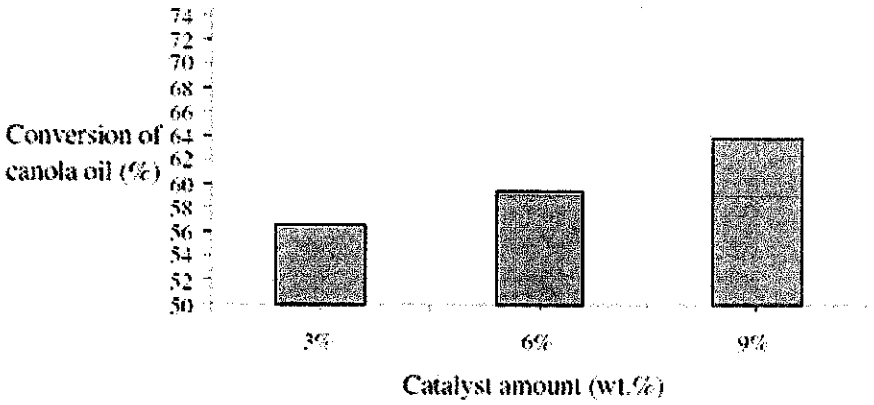


Figure 7. Conversion of canola oil as a function catalyst amount. Reaction conditions were as follows: Reaction time: 9 h; methanol/canola oil molar ratio: 12:1; temperature: 60□C

4.3.2 Subconclusion

In this study the transesterification of canola oil with methanol was studied in a system using KOH catalyst. The effects on biodiesel production of the ethanol/canola oil molar ratio, type of alcohol and co-solvent, reaction temperature, and mass ratio of catalyst to oil were investigated.

The results showed that methanol was the best alcohol for this reaction condition. The highest triglyceride conversion rate of 71.9% was achieved after 9 h of reaction at 60 ◦C, with a 6:1 molar ratio of methanol to canola oil and a 3 wt% catalyst.

4.4 Transesterification of jatropha oil with methanol using KOH catalyst

4.4.1 Transesterification process

The preliminary studies to determine the optimum quantity of methanol, catalyst NaOH, reaction temperature and reaction time required for the transesterification of Jatropha oil were conducted by varying the concentration of methanol from 10 to 25 %, NaOH concentration from 0.5 to 1.5 %, reaction temperature from 30 to 60°C and reaction time from 30 to 120 min.

Table 10: Average biodiesel yield in alkali-catalysed transesterification of Jatropha curcus oil under different treatments

#	Reaction Temp. (□C)	Reaction time (min)	Oil (g)	Methanol (g)	NaOH (g)	Biodiesel (g)	Glycerol (g)	Emulsion (g)	Loss (g)	Ester yield (%)
	60	120	100	***10***	1.0	29.17	69.83	9.50	2.5	**29.17**
	60	120	100	***15***	1.0	76.00	29.00	8.50	2.5	**76.00**
	60	120	100	***20***	1.0	98.00	16.17	3.83	3.0	**98.00**
	60	120	100	***25***	1.0	89.17	25.83	8.50	2.5	**89.17**
	60	120	100	20	***0.5***	92.17	18.67	7.17	2.5	**92.17**
	60	120	100	20	***1.0***	97.83	14.83	5.67	2.7	**97.83**
	60	120	100	20	***1.5***	75.17	37.33	7.50	1.8	**75.17**
	60	***30***	100	20	1.0	89.33	23.33	8.17	1.2	**89.33**
	60	***60***	100	20	1.0	94.50	17.67	7.50	1.7	**94.50**
	60	***90***	100	20	1.0	98.00	15.83	5.67	1.5	**98.00**
	60	***120***	100	20	1.0	97.83	15.17	6.33	1.3	**97.83**
	30	120	100	20	1.0	61.00	33.33	24.17	2.5	**61.00**
	45	120	100	20	1.0	79.33	24.67	14.83	2.2	**79.33**
	60	120	100	20	1.0	97.33	14.50	6.67	2.5	**97.33**

i. Effect of methanol quantity

The molar requirement of methanol was found to be 10.67 %. Hence, to optimize the amount of methanol required for the reaction, experiments were conducted with 10 %, 15 %, 20 % and 25 % methanol. The concentration of NaOH, reaction temperature and reaction time used with the methanol variations were constant at 1.0 %, 60°C and 120 min respectively. The average results of this study are presented in Table 1.

The results clearly indicate that the optimum concentration of methanol required for effective transesterification of Jatropha oil was 20 %. Moreover, it was found that when the concentration of methanol was increased above or decreased below the optimum, there was no significant increase in the biodiesel production, but the excess or shortfall in concentration of methanol only contributed to the increased formation of glycerol and emulsion.

The variation in methanol concentration versus ester yield percentage is shown in Figure 8. Figure 8 clearly shows that the maximum ester yield of 98 % was obtained using 20 % methanol.

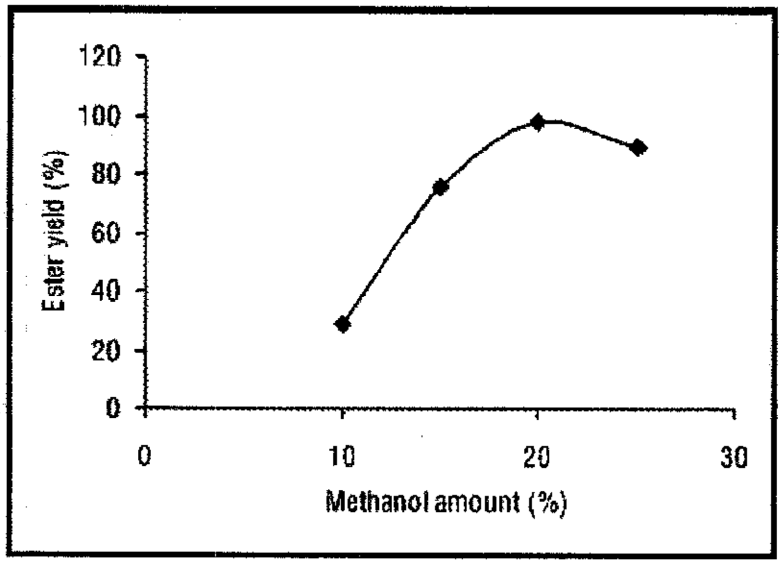


Figure 8: Variation in methanol amount vs. ester yield percentage in alkali transesterification

ii. Effect of NaOH concentration

The catalyst NaOH concentration variations adopted in this study were 0.5 %, 1.0 % and 1.5 %. The methanol concentration of 20 % that gave the best ester yield, constant reaction temperature and reaction time of 60°C and 120 min respectively were used with NaOH variations for the production of biodiesel from Jatropha oil. The average results of this study are presented in Table 10.

The results clearly indicate that the optimum concentration of NaOH required for effective transesterification was 1.0 %. It was observed that, if the NaOH concentration was decreased below or increased above the optimum, there was no significant increase in the biodiesel production, but there was increased formation of glycerol and emulsion.

The variation in NaOH concentration versus ester yield percentage is shown in Figure 3. It is seen clearly from Figure 9 that the maximum ester yield of 97.8 % was obtained using 1.0 % NaOH concentration.

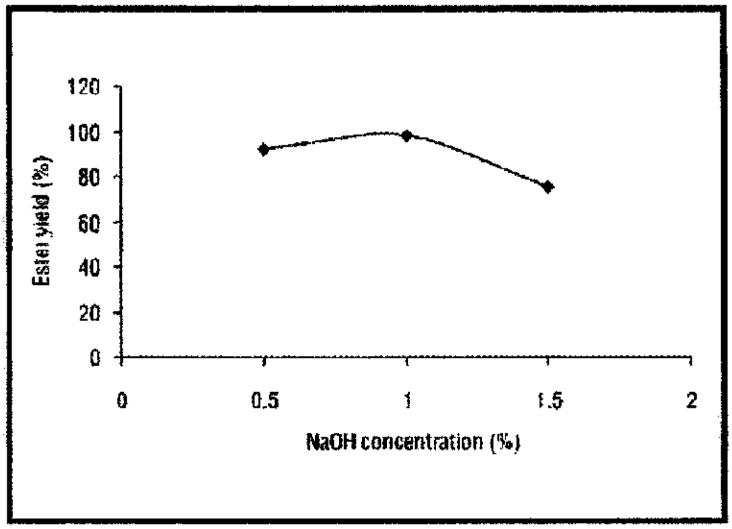


Figure 9: Variation in NaOH concentration vs. ester yield percentage in alkali transesterification

iii. Effect of reaction temperature

The temperature variations adopted in this study were 30, 45 and 60°C. The constant reaction time of 120 min and the constant methanol and NaOH concentrations of 20 % and 1.0 % respectively, which gave the best ester yield, were maintained with the temperature variations for the production of biodiesel from Jatropha oil. The average results of this study are presented in Table 10. The results clearly indicate that the maximum ester yield was obtained at 60°C temperature. The variation in reaction temperature versus ester yield percentage is shown in Figure 10. It clearly shows that the ester yield proportionately increased with the increase in reaction temperature. The reaction temperature should always be below the boiling point (65°C) of methanol and so the reaction temperature was fixed up to 60°C. The maximum ester yield of 97.3 % was obtained at 60°C as shown in Figure 10.

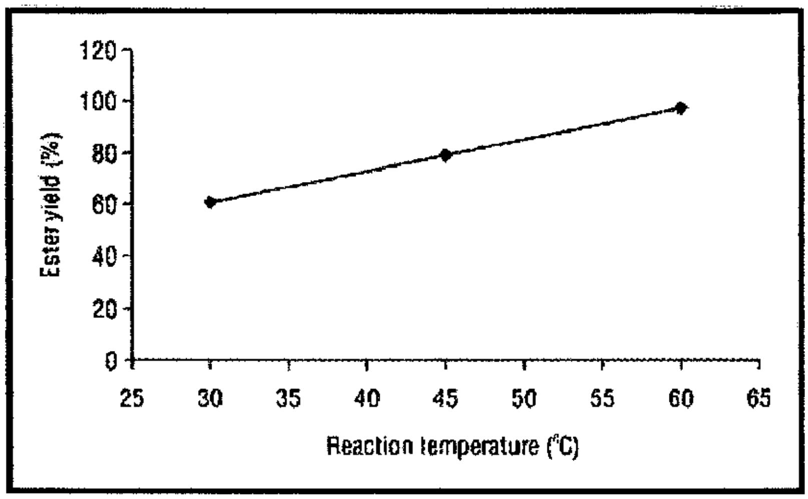


Figure 10: Variation in reaction temperature vs. ester yield percentage in alkali transesterification

iv. Effect of reaction time

In order to optimize the reaction time, the different reaction times selected for this study were 30, 60, 90 and 120 min. The constant methanol concentration of 20 %, constant NaOH concentration of 1.0 % and constant temperature of 60°C were maintained with reaction time variations. The average results of this study are given in Table 10.

The results clearly indicate that the biodiesel yield increased with the reaction time. The biodiesel yield was found to be more or less the same at 90 and 120 min of reaction time. The variation in reaction time versus ester yield percentage is shown in Figure 11 and it clearly shows that the maximum ester yield of 98 % was obtained at 90 min of reaction time.

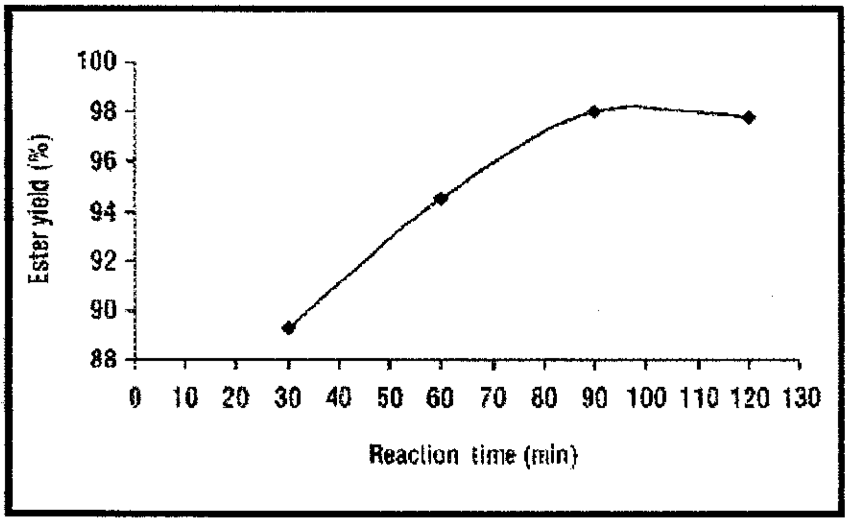


Figure 11: Variation in reaction time vs. ester yield percentage in alkali transesterification

The average biodiesel yield percentage in alkali-catalysed transesterification under different treatments for maximum ester yield is shown in Figure 12. The treatment TA10 with 20 % methanol concentration, 1.0 % NaOH concentration at 60°C with reaction time of 90 min yielded 98 % of biodiesel as shown in Table 10 and in Figure 12.

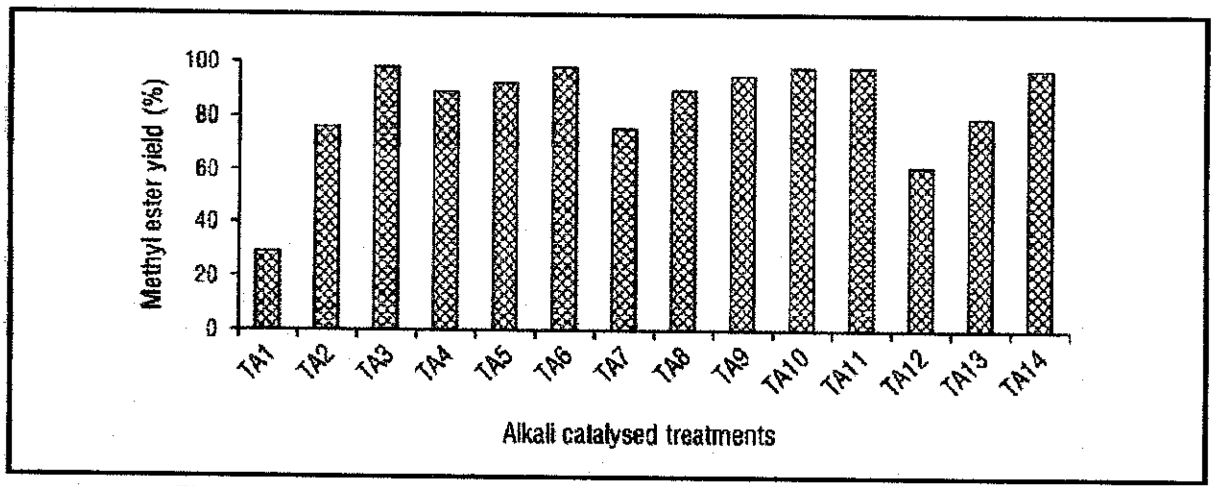


Figure 12: Methyl ester yield percentage vs. various alkali-catalysed treatments

v. Properties of fuel

The properties measured were compared with the BIS specifications and the results are presented in Table 11. All the properties of transesterified Jatropha oil were within the limits of BIS specifications as shown in Table 11. The decrease in kinematic viscosity from 29.36 to 4.78 cSt is the important fuel property of the transesterified Jatropha oil. This indicates that the raw Jatropha oil's ability to flow had been increased to a significant extent by transesterification. This increase in the fuel's ability to flow would induce complete burning of the fuel without any ignition delay. The specific gravity of biodiesel (0.8636) was also reduced to a significant extent when compared with the specific gravity of Jatropha oil (0.9136).

Table 11: Properties of *Jatropha* oil and pure biodiesel under optimized condition compared with BIS standards

Properties	***Jatropha* oil**	**Methyl ester (biodiesel)**	**BIS standard for diesel fuel**	**BIS standard for biodiesel fuel**
Kinematic viscosity (cSt)	29.36	4.78	2.0-5.0	3.5-5.0
Specific gravity	0.9136	0.8636	0.81-0.86	0.87-0.90

4.4.2 Subconclusion

Among all the treatment variations adopted, it was found that the maximum methyl ester yield of 98% was obtained using 20 % methanol and 1.0 % NaOH at 60°C reaction temperature. The minimum reaction time required for maximum ester yield was found to be 90 min. After optimizing the concentration of methanol and NaOH, reaction time and reaction temperature in alkali-catalysed transesterification of Jatropha curcus oil, experimental studies on large-scale production of biodiesel were also carried out. The kinematic viscosity of Jatropha oil at 40°C was found to be 8.4 times higher than that of diesel fuel and specific gravity was as high as 0.9136 compared to 0.81-0.86 for diesel fuel. The kinematic viscosity of Jatropha biodiesel at 40°C was determined to be 1/6 of the viscosity of raw oil and specific gravity at 40°C was observed to be 0.8636.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

CONCLUSION

After all the experiment from various sources of oil, with different transesterification method and different types of catalyst, we can come up with a conclusion that:

- Jatropha curcus is the best source oil for transesterification process using 20 % methanol and 1.0 % NaOH at 60°C reaction temperature. The minimum reaction time required for maximum ester yield was found to be 90 min. Thus, we can obtain up to 98% methyl ester yield. The kinematic viscosity of Jatropha curcus biodiesel product Jatropha biodiesel at 40°C was determined to be 1/6 of the viscosity of raw oil and specific gravity at 40°C was observed to be 0.8636. All of that values are in range of BIS specifications, so that this biodiesel is suitable for use.

- Palm kernel oil is also an alternative for the source oil of biodiesel, which also produce up with 20.0% ethanol, 1.0% NaOH (by weight of PKO) at 60°C reaction temperature and 90 min reaction time yielded 95.8% ethyl ester yield. In Malaysia, Palm Kernel Oil is one of the most common oil, so that the source for oil is easy to obtain, which has a big advantage for manufacturing.

- For canola oil, the highest triglyceride conversion rate of 71.9% was achieved after 9 h of reaction at 60□C, with a 6:1 molar ratio of methanol to canola oil and a 3 wt% catalyst. This is a low conversion, which may cause a big waste in source oil and also the conditions for reactions are more complicated than other sources of oil. So that, we do not take canola oil with this transesterification process conditions into account for industrial manufacturing.

RECOMMENDATION

- This project consists of many laboratory work but the equipment and chemicals in the laboratory are not always available, which caused a little inconveniece to work.

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APPENDIX : Photos of experiments


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Figure 13: Raw Palm Kernel Oil

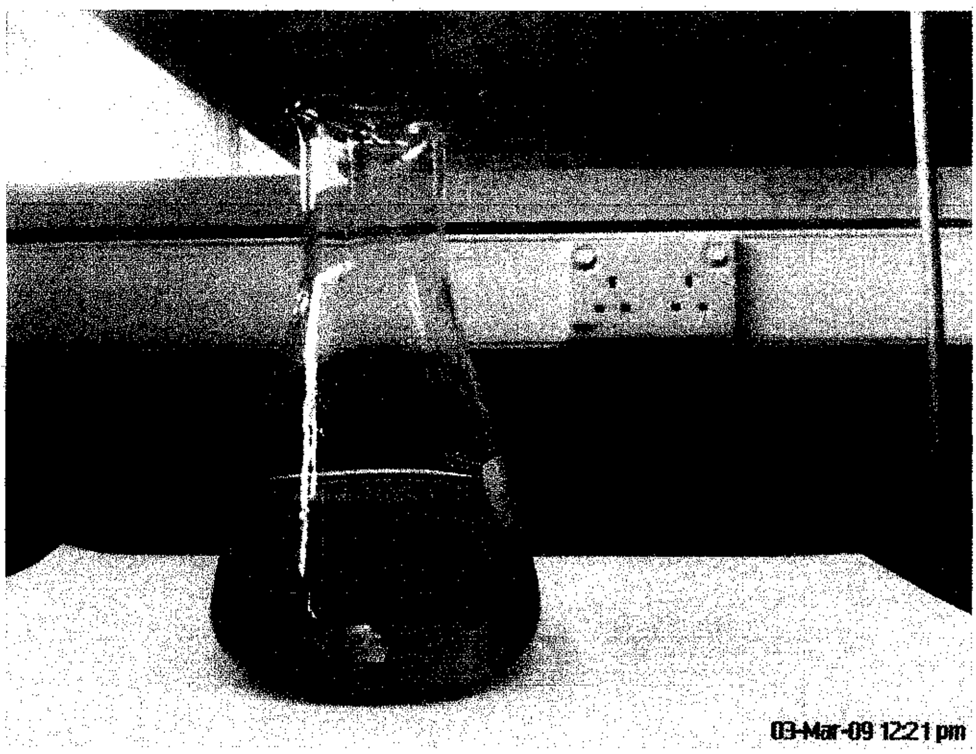
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Figure 14: Palm oil biodiesel

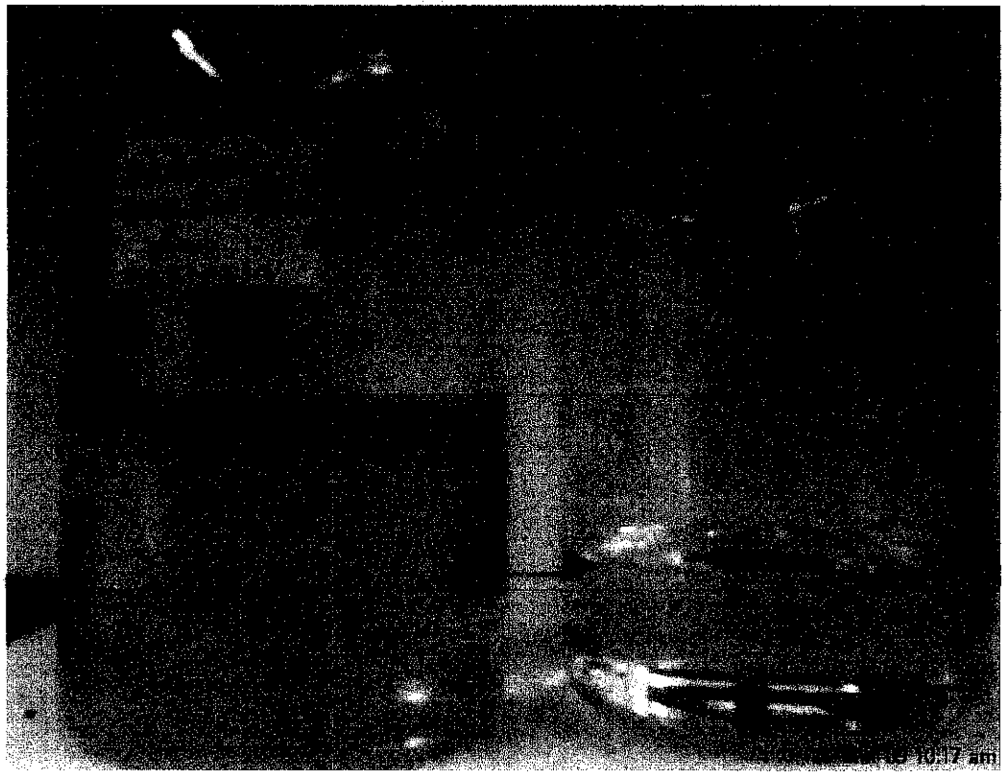

Figure 15: Canola biodiesel (left) and raw canola oil (right)

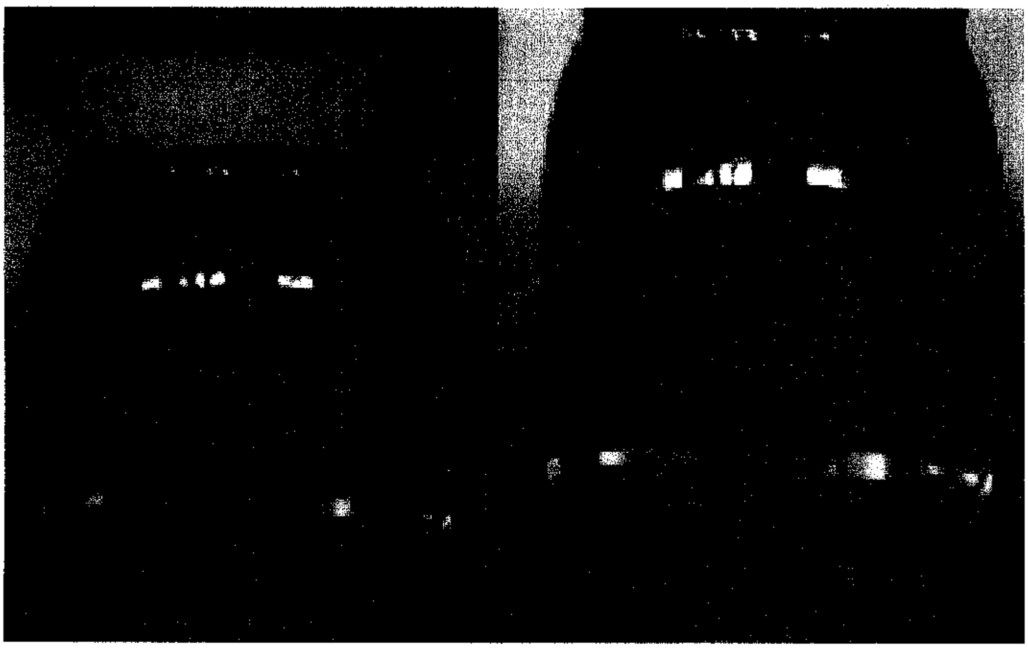

Figure 16: Jatropha biodiesel (left) and raw jatropha oil (right)