

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY KUMASI

COLLEGE OF SCIENCE

DEPARTMENT OF CHEMISTRY



**THE INFLUENCE OF PHYSICOCHEMICAL CHARACTERISTICS OF VEGETABLE OILS
ON THE QUALITY OF BIODIESEL PRODUCED FROM PALM OIL, PALM KERNEL OIL,
REFINED SOYABEAN OIL, UNREFINED SOYABEAN OIL AND *JATROPHA CURCAS* OIL.**

**A Thesis Submitted to the School of GRADUATE STUDIES, Kwame Nkrumah University
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Analytical Chemistry.**

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ABSTRACT

Biodiesel is a clean fuel, which is chemically produced from a variety of vegetable oils (VOs), animal tallows and waste cooking oils. This thesis examines the influence of physico-chemical characteristics of vegetable oils on the yield and quality of biodiesel. In this research, some physico-chemical characteristics of palm oil, palm kernel oil, soybean oil and *Jatropha curcas* oil such as acid value, iodine value, saponification value, viscosity, density, specific gravity and refractive index were determined. The following fuel properties of the biodiesel produced using the optimum conditions of the different oils were determined: viscosity, density, pour point, cloud point, water content, acid value, cetane index, ash content and sulphur content. The fuel properties of biodiesel for the various oils were compared with the latest American Standard for Testing Material (ASTM D 6751) and European standard for biodiesel. It was found that all the oils studied exhibited good fuel properties except palm oil biodiesel in which its viscosity, colour, carbon residue, acid values and other parameters fell outside the ASTM D 6751 (08) Limits. The results also revealed that, high acid value of VOs which denotes high FFA decreases the yield of biodiesel. Palm oil and palm kernel oil with high FFA values of 5.05 and 4.81 recorded less yields of 91.15% and 93.32% respectively, compared to 96.37% and 94.37% obtained from refined and unrefined soybean oils respectively, with low FFA values of 1.73 and 3.51. Again, it was found that, iodine value, density and viscosity of VOs have influence on the following quality parameters of the fuel; cetane index, cold point, pour point and kinematic viscosity, hence it was concluded that, the physico-chemical characteristics of the oils which depend on the type of oil, climate and the locality of plant have influence on the yield and quality of biodiesel produced from those oils.

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Ever since I was born, a vast array of people have stepped into my life and left prints of wonderful memories.

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Even though I have foot –of-clay as an imperfect human I have successfully come to the off this Thesis by the help of the above mentioned people.

DEDICATION.

The Thesis is dedicated to my parents Mr. and Mrs. Mensah for the support they have given me in all facets of life.

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LIST OF ABBREVIATIONS.

ASTM.....	American Standard for Testing Materials.
CFPP.....	Cold Filter Plugging Point
CN.....	Cetane Numbers
EN.....	European Norm
FAME.....	Fatty Acid Methyl Ester
FFA.....	Free Fatty Acid
IV.....	Iodine Values
JOD.....	<i>Jatropha curcas</i> Oil Diesel
KOH.....	Potassium Hydroxide
PKOD.....	Palm Kernel Oil Diesel
POD.....	Palm Oil Diesel
SBOD.....	Soybean Oil Diesel
RSBOD.....	Refined Soybean Oil Diesel
USBOD.....	Unrefined Soybean Oil Diesel
SV.....	Saponification Value
VOs.....	Vegetable Oils
CO.....	Carbon Monoxide

CHAPTER ONE

INTRODUCTION

1.1 Background

Nowadays, research on alternative fuels for internal combustion engines has been increasing due to an increase in the price of petroleum and increase in the environmental concerns (Marchetti *et al.*, 2007; Canakci, 2007). Another disadvantage of petroleum is that, they are finite and at their current usage rates, would be consumed shortly (Srivastava and Prasad, 2000). Diesel fuels have essential function in the industrial economy of a developing country such as Ghana and are used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector.

Higher fossil fuel demands in the industrialized world and the domestic sectors as well as their pollution problems make it necessary to develop renewable energy sources of limitless duration and smaller environmental impact than the traditional one. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. Vegetable oils have long been promoted as possible alternatives for fossil fuel, but it is only in recent years that systematic efforts have been made to utilize vegetable oil as fuels in engines. Fuel from these sources is technically feasible, environmentally acceptable, and readily available.

Vegetable oils are usually triglycerides, generally with a number of branched chains of different lengths and different degrees of saturation. These oils have about 10% lower heating value than fossil diesel due to the oxygen present in their molecules. The viscosity of vegetable oil is several times higher than that of mineral Diesel due to its large molecular mass and chemical structure. This can lead to unfavorable pumping and spray characteristics. The inefficient mixing

of vegetable oil with air contributes to incomplete combustion. The cloud point and pour point are higher, and the cetane number is comparable to that of fossil fuel (Srivastava and Prasad., 2000; Peterson and Auld 1991; Barnwal and Sharma, 2005).

The high flash point and lower volatility characteristics result in increased carbon deposit formation, injector coking, lubricating oil dilution and degradation. With vegetable oil as a fuel, short term engine performance results are comparable to those with fossil fuel, however, long term with vegetable oil or blends with fossil lead to severe engine deposits, piston ring sticking, and injector coking and thickening of the lube oil (Peterson *et al.*, 1983). Based on these problems, vegetable oils need to be modified to bring their combustion related properties closer to those of mineral Diesel (Ma and Hannah, 1990).

The fuel modification is mainly aimed at reducing the viscosity and increasing the volatility. Considerable efforts have been made to develop a vegetable oil derivative or biodiesel that approximates the properties and performance of the fossil fuels. The methods employed include preheating the oil, pyrolysis, micro emulsion, blending and transesterification (Krawczyk. 1996; Ma and Hanna, 1990).

The United State Standard Specification for Biodiesel (ASTM 6751), defines Biodiesel as a fuel comprising mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which can be used in diesel engines and heating systems (Mittelbach *et al.*, 1983; Staat and Vallet, 1994). Biodiesel has clear benefits in comparison with diesel fuel; it is a renewable fuel, non toxic, safer to handle, biodegradable, require no engine modifications and

reduces dependency on foreign oil imports (Gerpan JV, 2006; Carraretto *et al.*, 2004). It also has favorable combustion and emission profiles. For instance, emissions of Carbon monoxide (CO) and particulate matter decrease by 45%, Hydrocarbon (HC) 70% but NO_x emissions increases by 10% with 100% biodiesel (B100) as a fuel (Anon *et al.*, 2002). The carbon cycle, time for fixation of CO₂ from biodiesel is quite small compared to mineral Diesel thus contributing more to the reduction of greenhouse gas emissions compared to fossil diesel (Gerpan JV, 2006; Carraretto *et al.*, 2004; Agarwal *et al.*, 2003). Agarwal *et al.*, (2003), found that biodiesel provides good lubricating properties that can reduce component wear and enhance engine life. Hence, vegetable oil is a potential alternative for fossil fuel to harmonize agriculture, economic development and the environment.

1.2 STATEMENT OF PROBLEM

Vegetable oils have similar heating value to that of diesel fuel and can be used to make biodiesel fuels. However, the physico-chemical characteristics of the oils which depend on the type of oil, climate and the locality of plant have influence on the quality of biodiesel produced from those oils. This may affect the biodiesel yield, the stability and other properties of the biodiesel.

1.3 JUSTIFICATION

Several researchers have identified the most important variables that influence biodiesel production, namely, reaction temperature, type and amount of catalyst, quantity of alcohol, stirring rate and reaction time but the type of feedstock is one important parameter that needs great attention (Ma and Hanna, 1990; Freedman *et al.*, 1984; Dorado *et al.*, 2004; Encinar *et al.*, 2005; Dorodo *et al.*, 2002). Depending upon the climate and soil conditions, different nations are looking into different vegetable oils as potential diesel fuel replacement. Most of the western countries use soybean, sunflower, saffola, rapeseed, etc. for production of biodiesel and investigations on engines whilst in some of the Asian countries such as Malaysia palm oil is used (Korbitz, 1999; Dorado *et al.*, 2005; Bozbas, 2005). To extend the use of biodiesel, the main concern is economic viability of producing biodiesel. The price of feedstock (vegetable oil) is one of the most significant factors, which constitute approximately 75–88% of the total biodiesel production cost (Hass *et al.*, 2006). Another major limiting factor of biodiesel is the inverse relationship between its oxidation stability and its cold flow properties which depend on the physico-chemical characteristics of the oil. In Ghana, the use of biodiesel as an alternative source of energy is being considered but the type of feedstock and the effect of the physico-chemical characteristics of the oils on the quality of the biodiesel are yet to be fully investigated hence the need for this research.

1.4 MAIN OBJECTIVE

This research is intended to determine the influence of physico-chemical characteristics of vegetable oils on the quality of biodiesel obtained from palm oil, palm kernel oil, soybean oil and *Jatropha curcas* oil.

1.5 SPECIFIC OBJECTIVES

The specific objectives are to:

1. To determine the physicochemical properties of palm oil, palm kernel oil, soybean oil and *Jatropha curcas* oil.
2. To produce biodiesel from palm oil, palm kernel oil, soybean oil and *Jatropha curcas* oil.
3. To determine the fuel properties of Biodiesel obtained from the different oils and compare the values with standard.
4. To determine how the physico-chemical properties affect the quality of the biodiesel.
5. Give appropriate recommendation(s) based on the findings.

1.6 SCOPE OF STUDY.

In this research, the following physico-chemical characteristics of palm oil, palm kernel oil, soybean oil and *Jatropha curcas* oil were determined: acid value, iodine value, saponification value, viscosity, density, specific gravity and refractive index.

The different oils were transesterified to produce biodiesel using KOH as catalyst. The various factors that affect transesterification of oil to biodiesel such as reaction temperature, ratio of alcohol to vegetable oil and amount of catalyst were varied for the various oils to obtain the optimum conditions for the oils.

The following fuel properties of the biodiesel produced using the optimum conditions of the different oils were determined: viscosity, density, pour point, cloud point, water content, acid value, cetane index, ash content and sulphur content. The fuel properties of biodiesel for the various oils were compared with the latest American Standard for Testing Material (ASTM D 6751) and European standard for biodiesel.

From the experimental results, the influence of the physico-chemical properties of vegetable oils on yield and quality of biodiesel obtained from the different oils were concluded.

CHAPTER TWO

LITERATURE REVIEW

2.1 Historical development of Biodiesel

The idea to use vegetable oils as fuels is more than a hundred years old. Rudolf Diesel conducted an engine tests on plant oils at the World's Exhibition in Paris in 1900 (Shay, 1993). The idea for this test had apparently stemmed from the French government, who was searching for a means of domestic fuel production in their African colonies. Several other European countries took up the idea after the Exhibition, which resulted in a number of articles in different European Countries. Consequently, Petroleum-based fuels soon became available in large quantities at comparatively low cost and interest in plant oils diminished. In the early 1970s, however, world-wide oil crises and growing ecological awareness led to the rediscovery of plant oils as possible alternatives to hydrocarbon-based fuels but with some challenges.

Plant oils typically show viscosities ten to twenty times higher than the viscosity of fossil diesel fuel. This quality leads to poor fuel atomization in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves (Mathot, 1921). Higher flash points of vegetable oils and their tendency for thermal or oxidative polymerization lead to the formation of deposits on the injector nozzles, a gradual dilution and degradation of the lubricating oil and the sticking of piston rings. Hence, long term operation with "neat" plants oils or mixtures with fossil diesel fuel could result in engine break down, (Srivastava and Prasad, 2000). These problems can be solved by either adapting the engine to the fuel or by adapting the fuel to the engine. The former led to the development of plant oil engines, while the latter led to modification of plant oils by various technologies to produce fuels which approximate the

properties and performance of fossil fuel (Schwab *et al.*, 1987). The three most widely used technologies are *Pyrolysis*, *Microemulsification* and *Transesterification*

2.2 Methods of producing Biodiesel

2.2.1 Pyrolysis

Pyrolysis strictly defined as the conversion of one substance into another by means of heat or with the aid of catalyst (Sonntag, 1979). It involves heating in the absence of air or oxygen (Sonntag, 1979) and cleavage of chemical bonds yield small molecules (Weisz *et al.*, 1979). The pyrolysed material can be vegetable oils, animal fat, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years especially in those areas of the world that lack deposit of petroleum (Sonntag, 1997). The first pyrolysis of vegetable oil was conducted in an attempt to synthesized petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oil to obtain products suitable for fuel. The cetane number of plant oils was found to increase by pyrolysis, and the concentration of sulphur, water and sediment for the resulting products were acceptable. In modern standards, viscosity of the pyrolysed oil is considered too high, ash and carbon residue far exceed the values for fossil fuel, and the cold flow properties are poor (Schwab *et al.*, 1983). Moreover, removal of oxygen during thermal decomposition eliminates one of the main ecological benefits of oxygenated fuels, thus complete combustion due to oxygen availability in the combustion chamber (Ma and Hanna, 1999).

2.2.2. *Micro – emulsification*

According to Schwab *et al* (1987), micro-emulsion is a colloidal equilibrium dispersion of optically isotropic fluid which has micro structures with dimensions generally in the 1 – 50nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non ionic amphiphiles. It can improve spray characteristics by explosive vaporization of low boiling constituents in the micelles (Pryde, 1984). Studies of Goering *et al.* (1982) on short term performance of both ionic and non ionic microemulsions of aqueous ethanol in the soybean oil was nearly as good as that of No.2 diesel, in spite of the lower cetane number and energy content but their durabilities were not determined. Another studies by Ziejewski *et al.*, (1984) using an emulsion of 53% (vol) alkali – refined and winterized sunflower oil, 13.3% (vol) 190 – proof ethanol and 33.4% (vol) 1- butanol found that the non ionic emulsion had a viscosity of 6.31 cSt at 40°C, a cetane number of 25 and an ash content of less than 0.01%, therefore concluded that microemulsions of vegetable oils with alcohols could not be recommended for long – term use in diesel engines. The fuels produced through micro-emulsion leads to incomplete combustion, the formation of carbon deposits, and an increase in the viscosity of the lubricating oil.

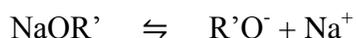
Microemulsions display considerably lower volumetric heating values as compared to hydrocarbon – based diesel fuel due to their high alcohol contents (Srivastava and Prasad, 2000) and have been assessed insufficient in terms of cetane number and cold temperature behaviours (Maurer, 1998).

2.2.3. Transesterification

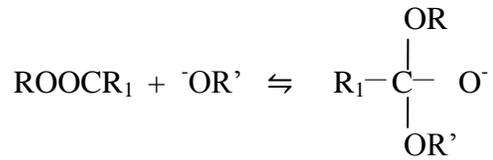
Transesterification is the reaction between triglycerides and lower alcohols to produce free glycerol and the fatty acid ester. This has turned out to be an ideal modification, for biodiesel'' production. Henriques (1898) achieved almost complete conversion by reacting vegetable oils with methanol in the presence of potassium hydroxide as a catalyst. In the 1930s and 1940s this reaction was frequently applied in the fat and soap industry. Bradshaw's patent application from 1941, which still serves as a model for many biodiesel production plants all over the world, was based on transesterification (Bradshaw, 1941). The Belgian patent 42287 on the production of palm oil ethyl esters acid – catalyzed transesterification describe the first use of fuel which will now to be known as "biodiesel" (Chavanne, 1942). Only a year later, a bus fuelled with palm oil ethyl esters ran between Brussels and Louvain (van de Abeele, 1943).

The pioneering efforts in utilizing transesterified vegetable oils seem to have petered out afterwards. The idea was taken up after a break in fatty acid alkyl esters fuels studies in the early 1980s. The first patent applications on the use of vegetable oil methyl esters as diesel fuel substitutes were filed in 1980 (Hartman, 1980 Tanaka *et al*, 1980).

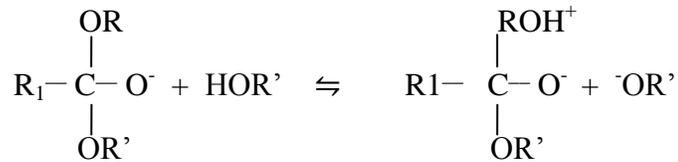
Chemically, in transesterification or alcoholysis reactions one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid alkyl esters. The process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol.



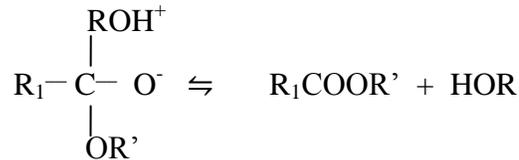
Step 1:



Step 2:



Step 3:



In each step one mole of alcohol is consumed and one mole of ester is liberated. In order to shift the equilibrium to the right, methanol is added in an excess over the stoichiometric amount in most commercial biodiesel production plants.

Another advantage of methanolysis as compared to transesterification with higher alcohols is the fact that the two main products, glycerol and fatty acid methyl esters (FAME), are hardly miscible thus form separate phases – an upper ester phase and lower glycerol phase. This process removes glycerol from the reaction mixture and enables high conversion. Finally regardless of the type of alcohol used, some form of catalyst has to be present to achieve high ester yields under comparatively mild reaction conditions.

2.3. Feed stocks for biodiesel production

2.3.1 Fats and Oil

2.3.1.1 Traditional raw materials

As shown in Figure 2.1, four crops clearly dominate the oil feedstock used for global biodiesel production. With a share of nearly 85%, rapeseed oil is by far leading the field, followed by sunflower seed oil, soybean oil and palm oil. The section denoted “others” is distributed between linseed oil; beef tallow and recycled frying oil (Korbitz, 1998).

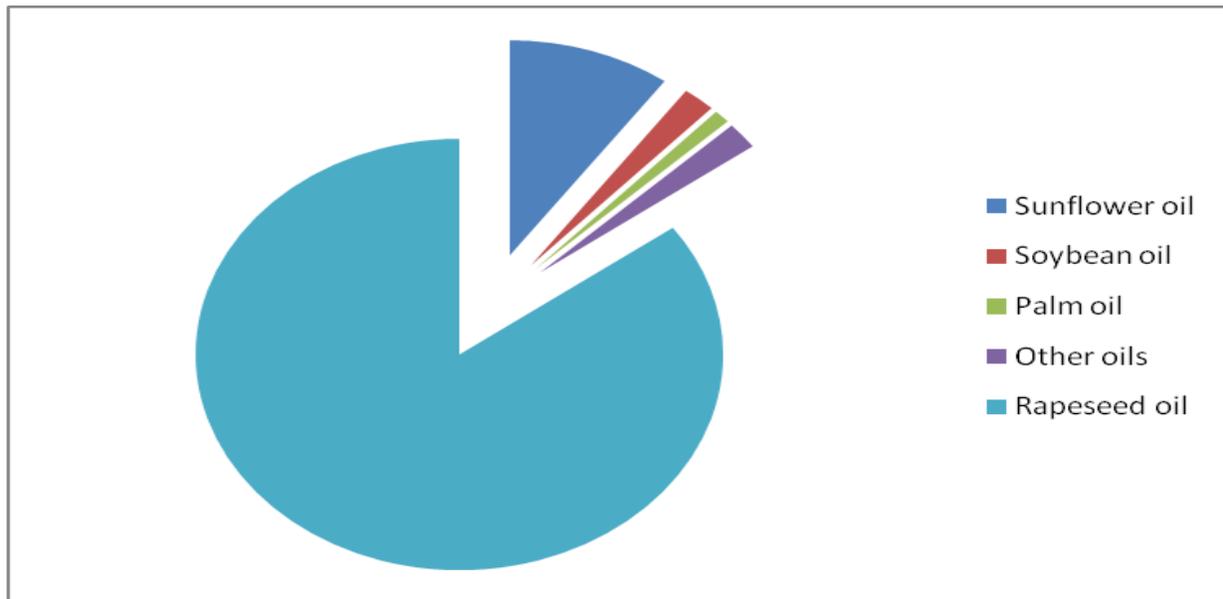


Figure 2.1 Feedstocks for world-wide biodiesel. (adapted from *Korbitz, 1998*)

Table 2.1: shows that rapeseed oil, sunflower oil, soybean oil and oil palms also constitute the four major oil crops cultivated for human consumption and various industrial applications, albeit in a different order.

Table 2.1 : World-wide production of Eight major vegetable oils.

Vegetable oils	Estimated production [million metric tons]	Vegetable oils	Estimated production [million metric tons]
Soybean	31.83	Peanut	4.81
Palm	28.13	Cottenseed	3.90
Rapeseed	12.57	Palm kernel	3.50
Sunflower	9.45	Coconut	3.33

Source: Gunstone, 2003.

Finally, information on fatty acid composition and typical hectare yields for the four traditional raw materials for the production of biodiesel are provided in Table 2.2.

Table 2.2:Fatty acid composition of the four traditional oil sources used for biodiesel production.

	12:0 (% wt)	14:0 (% wt)	16:0 (% wt)	18:0 (% wt)	18:1 (% wt)	18:2 (% wt)	18:3 (% wt)	Litres oil/ha	References
Palm oil	0.5	1-2	40-48	4-5	37-46	9-11	0.3	5950	<i>Crabbe et al., (2001)</i>
Rapeseed oil	-	-	3-5	1-2	55-65	20-26	8-10	1190	<i>Ma et al., (1999)</i>
Soybean oil	-	-	11-12	3-5	23-25	52-56	6-8	446	<i>Canakci et al., (2001)</i>
Sunflower oil	-	-	4	4	78	13	-	952	<i>DaSilva et al., (2003)</i>

2.3.1.1.1 Rapeseed Oil

Rapeseed oil (*Brassica napus* L. ssp. *Oleifera*) was originally chosen for transesterification experiments by biodiesel pioneers because of its low price compared to other readily available vegetable oils (Mittlebach, 1989). However, it soon became apparent that with its high content of monounsaturated oleic acid and the low levels of both saturated and polyunsaturated acids, the oil is practically the ideal raw material regarding combustion characteristics, oxidative stability and cold temperature behavior. Due to its favourable properties, rapeseed oil still is the feedstock of choice in most European countries, including the world's largest biofuel producers, Germany and France.

Rapeseed oil used to be characterized by high levels of erucic acid (~50%), which causes serious damage to heart and liver in experimental animals (Roth and Kormann, 2000). Moreover, the presence of glucosinolates in the oil meal significantly reduced its value as animal fodder. Therefore, from the 1960s onwards, plant breeders developed cultivars with reduced levels of erucic acid and glucosinolates, which are now known as "Canola" due to the outstanding achievements of Canadian biologists in this field. Today most rapeseed grown belongs to these so-called "double zero" (00) varieties, yielding oil with less than 2% erucic acid and meal with glucosinolate levels below 30 $\mu\text{mol/g}$. Nevertheless, for some technical applications high-erucic rapeseed is still cultivated (Gunstone, 2001).

2.3.1.1.2 Sunflower Seed Oil

Sunflower seed oil (*Helianthus annuus*) comes second in the list of vegetable oil sources for biodiesel production in Europe. It is a recognized valuable oil source for human consumption. The high contents of linoleic acid limit the use of sunflower seed oil for fuel production. According to the European biodiesel standard (EN 14214), pure sunflower oil methyl esters cannot be used as a fuel for diesel engines, as it exceeds the limit for iodine value set at ≤ 120 g I₂/100g. Moreover, unadditivated sunflower oil fuels also give poor ratings for oxidative stability. To solve these problems, cultivars enriched in oleic acid have been bred (Da Silva et al., 2003).

2.3.1.1.3 Soya Bean

Soya bean oil (*Glycine max*) is the most popular biodiesel feedstock in the United State of America, and by far the most frequently produced vegetable oil globally due to the utilization of soybean meal as a protein fodder. Similar to sunflower oil, soybean oil displays iodine values of 121-143g /100g. Therefore, EN 14214 excludes pure soybean oil methyl esters from serving as a fuel, although this regulation is highly disputed by many experts.

2.3.1.1.4 Palm Oil

The palm oil (*Elaeis guineensis*) plays an important role for biofuel production in South Asia. Various parts of the palm fruits can be utilized for oil production for human consumption and industrial applications. The mesocarp of the fruit yields palm oil, which is characterized by high amounts of medium- chain saturated (palmitic acid) and monounsaturated (oleic acid) fatty, acid. Palm oil contains tocopherols in concentrations of 600 to 1000 ppm and carotenoid levels of 500

to 700 ppm. The latter give the oil its typical red colour (Demirbas, 2003). As these minor components serve various industrial purposes i.e. as food additives, recovery strategies from palm oil used for biodiesel production are very promising.

Palm oil can be separated into two fractions- solid palm stearin and liquid palm olein. So far palm oil itself and palm stearin fractions have mainly attracted attention as raw materials for biodiesel production. The main advantages of palm oil are high hectare yield and moderate world- prices compared to other edible vegetables oils. If biodiesel fuels are to be economically competitive with fossil diesel, even in the absence of tax concession programs, production cost have to be kept low. This poses considerable difficulty with most other highly refined vegetable oils, which could also be utilized for food purposes.

The oil palm, however, is a low- value commodity crop (Murphy, 2003), hence, production of biodiesel from palm oil makes economic sense. Nevertheless, its high contents of saturated fatty acids, leading to unacceptably high values for cold filter plugging point (+11°C) and cloud point (+13°C) prevents winter operation on neat palm oil methyl esters in temperate climates. Moreover high contents of free fatty acids in the feedstock cause problems in traditional alkali-catalyzed biodiesel production and thus necessitate deacidification or acid- catalyzed pre-esterification steps.

2.3.1.2 Alternative edible oils

Apart from the “great four” on biodiesel production- rapeseed, sunflower seed, soybean and palm oils, other edible plants oils have successfully been transesterified to produce biofuels. The choice of raw material in a specific region mainly depends on the respective climatic conditions.

As the Mediterranean climate is not ideally suited to the cultivation of rapeseed, several alternative crops have been tested in Southern European countries, including sunflower seed oil, Ethiopian mustard and cardoon oil. Ethiopian mustard (*Brassica carinata*) is closely related to rapeseed. Native to the Ethiopian highlands, however, the crop is highly adaptive to low rainfall and high temperature and thus enables far higher seed yields than *Brassica napus* (Cardone *et al.*, 2003).

Limitations to the use of *Brassica carinata* seed oil for biodiesel production have so far been its high contents of erucic and linolenic acid and the correspondingly high iodine value of about 130g I₂/100g. Low erucic acid Cultivars, which have recently been developed, may enhance the value of Ethiopian mustard seed meal as a fodder, but do not display improved properties regarding iodine value. Cardoon (*cynara cardunculus*) is a plant belonging to the Asteracea family and is thus related to sunflower and safflower. It is native to the Mediterranean region, where it grows wild or is cultivated as a fodder (Encinar *et al.*, 1999). Very similar to soybean oil in its fatty acid composition, however, problems with meeting iodine value limits are to be expected.

Alternative edible oils utilized in South Asian countries include palm kernel oil (*Elaeis guineensis*) and coconut oil (*cocos nucifera*). Palm fruit kernels yield oil which significantly differs from palm oil in its chemical composition, displaying a high content of saturated short-chain fatty- acid, such as lauric and myristic acid. Palm kernel oil typically contains 600 to 1000 ppm of tocopherol and tocotienol, but only traces of carotenoids, so that it is yellowish in colour (Dembars, 2003). Both coconut oil and palm kernel oil are used in a wide arrange of dietary and

industrial applications. They serve as cooking fats and starting materials for the production of margarines, shortenings and edible fats coatings.

Palm kernel oil is additionally utilized as an inexpensive substitute for cocoa butter, whereas coconut oil is used for production of detergents and cosmetics. Recently these two lauric oils have also entered the focus of attention as raw materials for biodiesel production (Abigor et al., 2000). Whereas their nearly 90% share of saturated acids within their fatty acid pattern has positive effects on cetane number, it proves detrimental for cold- temperature properties so that neat biodiesel fuels based on lauric acid oils cannot be used in temperate climates .

2.3.1.3 Non-edible oils

One way of reducing the production cost for biodiesel fuels is the use of non-edible oil, which tend to be considerably cheaper than edible vegetable oils (Srivastava and Prasad, 2000).

A number of plant oils contain substances which make them unsuitable for consumption. Among non-edible oils already used for biodiesel production, castor oil, physic nut oil and various oils which are produced in India deserve special attention.

Caster (*Ricinus communis*) is known as a house plant, although the seed contains ricin, a highly toxic lectin. During oil recovery, ricin remains within the pressed cake. Nevertheless, the recovered oil is not fit for nutritional purposes due to its laxative effect (Roth and Kormann, 2000). This property is ascribed to the fact that castor oil contains up to 90% of linoleic acid.

2.4.1 The influence of operating variables of transesterification on Biodiesel yield

2.4.1.1 Free fatty acid and moisture

Free fatty acids and moisture content are key parameters for determining the viability of the vegetable oil in the transesterification process. To carry the base catalyzed reaction to completion; a free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil, the smaller is the conversion efficiency and vice versa (Dorado et al, 2002). Ma et al (1998), studied transesterification of beef tallow catalyzed by the NaOH in the presence of free fatty acids and water. Without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest. When 0.6% of FFA was added, the apparent yield of BTME reached its lowest, less than 5%, with any level of water added. When 0.9% of water was added, without addition of FFA, the apparent yield was about 17%. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids. Conversely, the acid catalyzed process can also be used for esterification of these free fatty acids.

The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all materials should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gels that interfere in the reaction as well as with separation of glycerol (Freedman *et al*, 1984). When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide.

Most biodiesels are currently made from edible oils by using methanol and an alkaline catalyst. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feed stocks. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction (Canakci and Gerpen, 2001).

2.4.1.2 Catalyst type and concentration

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective (Ma and Hanna, 1998). If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids to be used can be sulphuric acid, phosphoric acid, hydrochloric acid or organic sulphonic acid. Methanolysis of beef tallow was studied with the catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe (Ma et al, 1998). The catalysts NaOH and NaOMe reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively.

Sodium methoxide causes formation of several by-products mainly sodium salts, which are to be treated as waste. In addition, high quality oil is required with this catalyst (Ahn E et al, 1995). As a catalyst in the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil. Refined and crude

oils with 1% either sodium hydroxide or potassium hydroxide catalyst resulted in successful conversion. Attempts have been made to use basic alkaline-earth metal compounds in the transesterification of rapeseed oil for production of fatty acid methyl esters. The reaction proceeds if methoxide ions are present in the reaction medium (Gryglewicz,1999). Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is low, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water requires treatment, and free fatty acid and water interfere with the reaction.

Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems, which can overcome the problems mentioned above (Fuduka *et al.*, 2001). In particular, the by-products, glycerol can be easily removed without any complex process, and the free fatty acids contained in the waste oils and fats can be completely converted to alkyl esters. In general, the production cost of a lipase catalyst is significantly greater than that of an alkaline one.

2.4.1.3 Molar ratio of alcohol to oil and type of alcohol

One of the most important variables affecting the yield of the ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of

6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters (Tomasevic and Marinkovic, 1999). However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium back to the left, lowering the yield of esters.

The transesterification of Cynara oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield increased as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the separation of glycerin is difficult and the apparent yield of esters decreased because part of the glycerol remains in the biodiesel phase. Therefore, molar ratio 9:1 seems to be the most appropriate (Enciner *et al.*, 2002).

The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer.

In ethanolysis, the emulsions are more stable and severely complicate the separation and purification of esters (Zhou *et al.*, 2003). The emulsions are caused in part by formation of the intermediates, monoglycerides and diglycerides, which have both polar hydroxyl groups and

non-polar hydrocarbon chains. These intermediates are strong surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react.

2.4.1.4 Effect of reaction time and temperature

The conversion rate increases with reaction time. Freedman *et al.* (1984), transesterified peanut, cotton-seed, sunflower and soybean oil under the condition of methanol–oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60 °C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93–98%). Ma *et al.* (1999), studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeded very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min.

Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied with three different temperatures (Freedman *et al.*, 1984). After 0.1 h, ester yields were 94, 87 and 64% for 60°C, 45°C and 32 °C, respectively. After 1 h, ester formation was identical for 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters (Ma and Hanna, 1999).

2.5.1 Fuel properties and specification of biodiesel

Since biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. Austria was the first country in the world to define and approve the standards for rapeseed oil methyl esters as diesel fuel. As standardization is a prerequisite for successful market introduction and penetration of biodiesel, standards or guidelines for the quality of biodiesel have also been defined in other countries like Germany, Italy, France, the Czech Republic and in the United States.

The parameters, which define the quality of biodiesel, can be divided into two groups. One group contains general parameters, which are also used for mineral oil based fuel, and the other group especially describes the chemical composition and purity of fatty acid alkyl esters.

Table 2.3 : International quality standards on neat biodiesel fuels.

Parameters	Austria (ON)	Czech (CSN)	France	Germany(DIN)	Italy (UNI)	USA (ASTM)
Density at 15 °C g/cm ³	0.85–0.89	0.87–0.89	0.87–0.89	0.875–0.89	0.86–0.90	-
Viscosity at 37.8 mm ² /s	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	1.9-6.0
Flash point (°C)	100	110	100	110	100	130
CFPP (°C)	0/-5	-5	-	0–10/-20	-	-
Pour point (°C)	-	-	-10	-	0/-5	-
Cetane	≥49	≥48	≥49	≥49	-	≥47

Conradson	0.05	0.05	-	0.05	-	0.05
Carbon residue (%)						
Iodine number	≤120	-	≤115	≤115	-	-
Acid value (mgKOH/g)	≤0.8	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5

Source: (Meher *et al.*, 2006)

2.5.1.1 Viscosity

Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specifications proposed are nearly same as that of the diesel fuel.

2.5.1.2 Flash point

Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose.

2.5.1.3 Cold filter plugging point

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature, fuel may thicken and might not flow properly thus affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petrodiesel. Normally either pour point or CFFP are specified. Pour point is the lowest temperature at which the oil specimen

can still be moved. French and Italian biodiesel specifications specify pour point where as others specify CFPP.

2.5.1.4 Cetane number

Cetane number is indicative of its ignition characteristics. The cetane number the measures how easily ignition occurs and the smoothness of combustion. The higher the cetane number the better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and HC. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency.

2.5.1.5 Carbon residue

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel.

Carbon Residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. The presence of high level of alcohol in biodiesel causes accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content is required.

Biodiesel fuel mainly consists of fatty acid alkyl esters and its quantities are specified according to the specifications of various countries. The presence of mono- di- and triglycerides cause engine problems like fuel filter plugging affecting the fuel properties and are specified in most of the biodiesel standards

CHAPTER THREE

EXPERIMENTAL MATERIALS AND METHODS

3.1 Experimental Samples

Refined Soybean oil and Unrefined Soybean oil were purchased from Wa in the Upper West region of Ghana. Palm oil and Palm kernel oil were obtained at Juaben Oil Mills and a local market in Ayigya, Kumasi, respectively; whilst *Jatropha curcus* oil was purchased from Accra. All the oils were used without purification.

3.2 Chemicals Used

Methanol (99.5%), Analytical Reagent, BDH)

Wij's reagent

Carbon tetrachloride

Hydrochloric acid (95%), Analytical Reagent, BDH)

Sodium thiosulphate (99%), Analytical Reagent, HARRIS)

Potassium hydroxide (90%), Analytical Reagent, HARRIS)

3.3 Material and Equipment Used

Abbey Refractometer

25ml density bottle

Burette

Pipette

Viscometer

Crucible

Electric muffle furnace

Meeker gas burner

Mechanical shaker

Hydrometer

Lovibond Tintometer

Reflux condenser

3.2.0 METHODOLOGY

3.2.1 Characterization of the Vegetable Oils

3.2.1.1 Determination of the Saponification Value

An American Standard for Testing Material (ASTM) method- (D 5558-95) was used for the determination of the Saponification Values of the vegetable oils. 2-5g of the oil was weighed into the Erlenmeyer flask or conical flask. 25ml of 0.5M ethanolic KOH was added and the resulting mixture was refluxed for 60 minutes. The resulting solution was subsequently titrated against 0.5M HCl with phenolphthalein as indicator. The resulting end point was obtained when the pink colour changed into colourless. The same procedure was used for the blank. The Saponification value (SV) was then calculated using the expression;

$$\text{Saponification value (S.V.)} = \frac{56.1 (B-S) \times M \text{ of HCl}^{(f)}}{\text{Weight of sample}}$$

(Source ^(f) : ASTM-D 5558 (95))

Where;

B – ml of HCl required by blank

S – ml of HCl required by sample

N – Molarity of HCl

56.1– Molar mass of KOH

3.2.1.2 Determination of acid value

Acid values of the various vegetable oils were also determined by ASTM method (ASTM – D 974(00)). 0.2 – 0.5g of sample were weighed into 250ml conical flask. 50ml of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was titrated against 0.1M KOH using phenolphthalein as indicator. The acid value was determined after which the free fatty acid was calculated respectively as follows;

$$\text{Acid Value} = \frac{A \times M \times 56.1^{(f)}}{W}$$

(Source ^(f) : ASTM-D 974 (00))

Where,

A = ml of 0.1M KOH consumed by sample

M = Molarity of KOH

W = weight in grams of the sample

Then

$$\text{Free fatty acid} = \frac{\text{Acid Value}}{2}$$

3.2.1.3 Determination of Iodine Value

0.5g of oils was weighed into conical flask and 20ml of carbon tetrachloride was added to dissolve the oil. 25ml of Wij's reagent was added to the flask using a measuring cylinder in a fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled.

The flask was then placed in the dark for 35minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 100ml of water were added using a measuring cylinder. The content was titrated with 0.1M sodium thiosulphate solution. Few drops of 1% starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorously shaking. The same procedure was used for the blank test.

The Iodine Value (I.V) is given by the expression

$$\text{Iodine Value (I.V)} = \frac{12.69C (V_1 - V_2)}{M}$$

Where

C = concentration of sodium thiosulphate

V₁ = volume of sodium thiosulphate used for blank

V₂ = volume of sodium thiosulphate used for determination

M = mass of sample

12.69= Constant.

3.2.1.4 Determination of refractive index

Abbey refractometer was used in this determination. A drop of the sample was transferred into a glass slide of the refractometer. Water at 30°C was circulated round the glass slide to keep its temperature uniform. Through the eye piece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated and the mean value noted and recorded as the refractive index

3.2.1.5 Determination of density

The densities of the oils were determined by ASTM method D – 1298 – (99)

The sample was brought to a specified temperature and a test portion was transferred to a hydrometer cylinder that had been brought to approximately the same temperature. The appropriate hydrometer, also at a similar temperature, was lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale reading and the temperature of the test portion were taken. The observed hydrometer reading was reduced to the reference temperature by means of a petroleum measurement table. Any hydrometer correction was applied to the observed reading and the corrected hydrometer scale reading recorded to the nearest 0.1kg/m^3 as density

3.3.1. Production of Biodiesel

In the study, refined soybean, unrefined soybean, palm, palm kernel, and *Jatropha curcas* oils were converted to their monoalkyl esters by transesterification.

3.3.1.1 General procedure.

The mixture was heated and stirred by a combination of hot plate and magnetic stirrer. Previously prepared alcohol-catalyst solution was added to the oil in 250ml conical flask at the required temperature while stirring at about 1000 rpm. This stirring speed was kept constant for all experiments.

The alcohol-catalyst solution was added while the oil was being stirred because of the fact that the reaction is very slow at the beginning of the reaction due to mixing and dispersion of alcohol into feedstock. Hence, the mixing of the reactants enhances the reaction rate and increases the ester conversion.

After the reaction was complete, the mixture was poured into the separating funnel and allowed to settle overnight. The product mixture was separated into two liquid layers after settling: crude ester layer on top and glycerol layer at the bottom. (The density of glycerol is much higher than that of ester, and it is insoluble in the ester phase.)



Fig. 3.1: Setup showing crude ester layer on top and glycerol layer at the bottom.

Glycerol was flowed out by means of a separating funnel, and the remaining ester layer was washed four times with distilled warm water to remove soap, residual alcohol, catalyst, and unreacted tri, di-, and monoglycerides. The number of washing processes was not increased because increasing the washing beyond four times does not have further benefit.



Fig. 3.2: Washing of Biodiesel.



Fig. 3.3: Refined Biodiesel Samples.

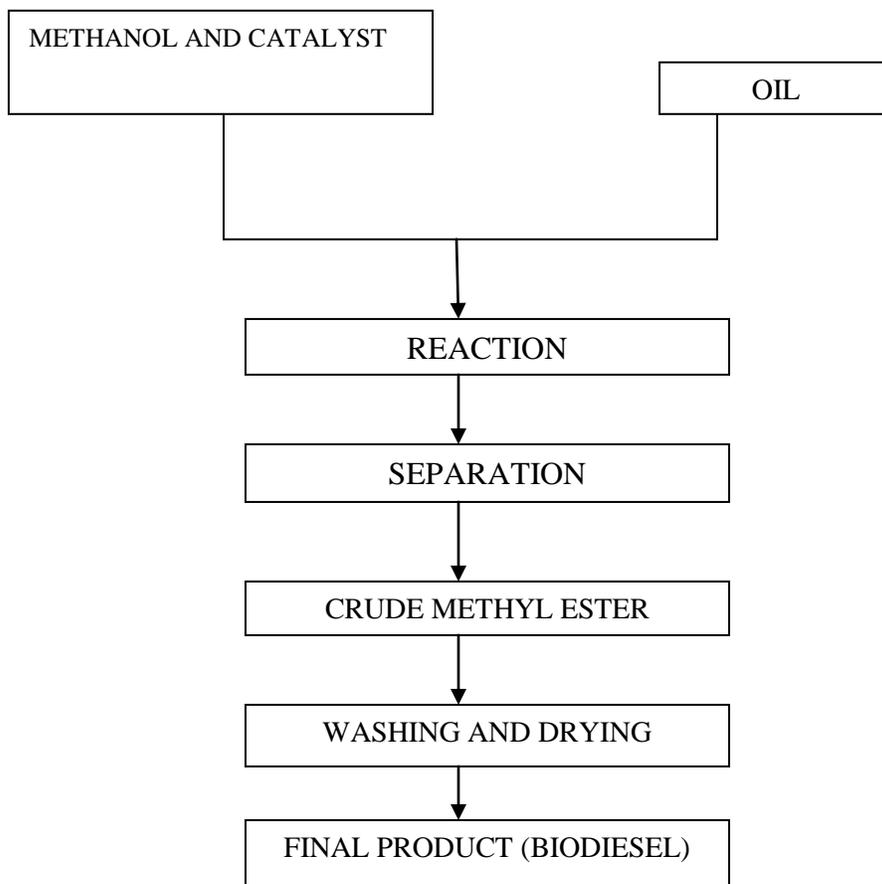


Fig. 3.4: Flow diagram of biodiesel production.

3.3.1.2 Effects of oil –to-methanol ratio

49 cm³ of each of the oils was preheated in 250cm³conical flask to 60⁰C on a heating plate. (1%^{w/w} of oil) of KOH catalyst was dissolved in 6.0cm³methanol (1:3) and the resulting solution was added to the oil in the flask.

The reaction was timed as soon as the catalyst/methanol solution was added to the reactor and mechanically stirred continuously for 20 minutes to ensure the completion of the conversion of the fatty acid into fatty acid methyl esters (FAMES). The mixture was transferred into a separating funnel, allowing glycerol to separate by gravity for 1hr. After removing the glycerol

layer, the methyl ester layer was washed with two volumes of water to remove methanol and the catalyst and glycerol residues. The volume of each of the purified biodiesel produced was measured and the biodiesel yield (vol. %), was calculated.

The procedure was repeated for 4:1, 5:1, 6:1, 7:1, 8:1, 9:1 and 10:1 methanol/oil ratio of each of the oils to obtain the optimal methanol/oil ratio for the various oils.

3.3.1.3 Effect of catalyst concentration

The optimal methanol/oil ratios of the various oils were used and at constant temperature of 65°C, a catalyst concentration of 0.25% was dissolved in optimum volume of 99.8% methanol required for each oil and the resulting solution was added to optimum volume of oil in the flask. The reaction was timed as soon as the catalyst/methanol solution was added to the reactor and mechanically stirred continuously for 20 minutes to ensure the completion of the conversion of the fatty acid into fatty acid methyl esters (FAMES).

The mixture was transferred into a separating funnel, allowing glycerol to separate by gravity for 1hr. After removing the glycerol layer, the methyl ester layer was washed with two volumes of water to remove methanol and the catalyst and glycerol residues. The volume of the purified biodiesel produced was measured and the biodiesel yield (wt. %), calculated. The procedure was repeated for all the oils, but this time varying the amount of catalyst from (0.5-2.0%) until their optimum catalytic concentrations were achieved.

3.3.1.4 Effect of reaction temperature.

The optimum methanol-to-oil ratio and the optimum catalyst concentration of the various oils were kept constant and the temperature of the oils was varied ;(30,40,50,60 ,65 and 70°C). The volume of the purified biodiesel produced was measured and the biodiesel yield (wt. %), relative to the amount of each oil was calculated from the methyl ester.

3.4.1. Determination of Fuel Properties of Biodiesel

3.4.1.1 Colour of the Biodiesel

The visual determination of the colour of the biodiesel was done using ASTM D – 1500 (98). The readings of the colour were made with Lovibond Tintometer. Prior to this, a sample container filled to a depth of 50mm with distilled water was placed in the compartment of the colorimeter with the standard glasses to facilitate colour adjustment. The Biodiesel sample was then placed in its container in the middle of the compartment. The containers were covered to exclude all exterior light. The light source was switched on and the colour of the sample compared with the standard glasses ranging from 0.5 to 4.5. When an exact colour match was not found and the sample colour was between two standard colours, the higher of the two colours was reported.

3.4.1.2 Determination of pour point

The pour point was determined by ASTM method (ASTM D – 97).

The sample was poured into the test jar to the level mark. The test jar was closed with the cork carrying the high – pour thermometer. The position of the cork and the thermometer were adjusted for the cork to fit tightly, the thermometer and the jar were coaxial and the thermometer

bulb was immersed 3mm below the surface of the sample. After this, the test jar was placed into the cooling medium.

The sample was cooled at a specified rate and examined at interval of 3°C for flow characteristics until a point was reached at which the sample showed no movement when the test jar was held in a horizontal position for 5seconds. The observed reading of the thermometer was recorded. 3°C was added to the recorded temperature and the result was recorded as the pour point.

3.4.1.3 Determination of Conradson carbon residue

The mass of each clean Sample Vial used in the sample analysis was determined and was recorded to the nearest 0.1µg. Appropriate mass of the sample was transferred by using syringe into a tarred sample vial and the weight of the sample and the vial taken and recorded to the nearest 0.1µg. The loaded sample vials were placed into vial the holder and the position of each sample noted. The weighed quantity of the sample was placed in a glass vial and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for about 3 hours. The sample undergoes coking reactions and the volatiles formed were swept away by the nitrogen. The carbonaceous type residue remaining was reported as a percentage of the original sample as carbon residue (micro). The mass percentage carbon residue in the original sample was calculated as follows;

$$\% \text{Carbon residue} = \frac{A \times 100}{W}$$

A = carbon residue

W = sample used (g)

3.4.1.4 Determination of water by distillation

The material to be tested was heated under reflux with water and immiscible solvent such as toluene which co-distills with water in the sample. Condensed solvent and the water were continuously separated in a trap, the water settled in the graduated section of the trap and the solvent returned to the still. The water in the sample was calculated as weight or volume percent as follows:

$$\% \text{ Water (v/v)} = \frac{\text{vol in water trap, ml} - \text{water in solvent, blank, ml}}{\text{Vol in test sample, ml}}$$

$$\% \text{ Water (v/m)} = \frac{\text{vol in water trap, ml} - \text{water in solvent, blank, ml}}{\text{Mass of test sample, g}}$$

3.4.1.5 Determination of ash content

The evaporating dish or crucible that is to be used for the test was heated at 700°C to 800°C for a minimum of 10 minutes and was cooled to room temperature in a suitable container. The weight of the crucible was taken to the nearest 0.1 μg. Mass of 20 – 25g of the sample were weighed into the dish and the mass of the sample noted. The crucible with the sample was heated with a Meaker burner until the contents were ignited by the flame. The temperature of the crucible was maintained for the sample to burn at a uniform and moderate rate until only carbonaceous residues were left in the crucible. The residue was heated in the muffle furnace at 775 ± 25°C until all carbonaceous material disappeared. The dish was cooled to room temperature in a suitable container (desiccators) and its weight was taken to the nearest 0.1 μg. The ash content of the biodiesel was calculated as follows:

Calculation:

The mass of the ash was calculated as a percentage of the original sample as follows

$$\text{Ash mass \%} = (w/W) \times 100$$

Where

w = mass of Ash (g)

W = mass of sample (g)

3.4.1.6 Determination of kinematic viscosity

The temperature of the viscometer bath was adjusted to 38.9°C. A calibrated thermometer was held in upright position and inserted into the bath by a holder. A clean dry calibrated viscometer was selected and carefully flushed with a dry nitrogen gas to remove the moist room air.

A sample of the biodiesel was drawn up into the working capillary of the viscometer and the timing bulb was then allowed to drain back as an additional safeguard against moisture condensing or freezing on the walls. The charged viscometer was inserted into the bath at a depth such that at no time during the measurement of the flow time, was any portion of the sample in the viscometer less than 20mm below the surface of the bath.

The viscometer together with its content, was allowed to remain in the bath for 30minutes to reach the test temperature (38.9°C). A suction bulb was used to adjust the head level of the biodiesel to a position in the capillary arm of the viscometer about 7mm above the first timing mark. The biodiesel was then allowed to freely flow and the time required for the meniscus to pass from the first to the second timing marks was noted with a stop watch. The procedure was

repeated to make a second measurement of flow time and the average of these determinations was used to calculate the kinematic viscosity. The viscometer was thoroughly cleaned with sample solvent and dried by vacuum. The procedure was repeated for the other samples of the biodiesel (ASTM D 445-97)

Calculation:

$$v = C \times t$$

Where

v = kinematic viscosity, mm²/s

C = calibration constant of the viscosity, (mm²/s)/s

t = mean flow time, s

3.4.1.7 Determination of basic sediment and water

50ml of the biodiesel and 50ml of toluene were mixed in a 100ml centrifuge tube with the tube tip having graduation of 0.01ml over the range of 0 to 0.2ml. The tube and its content were stoppered and allowed to attain the laboratory temperature (28°C). The tube was placed in a trunnion cup opposite another filled tube to establish a balanced condition of a mechanical shaker. The samples were whirled for agitation at a speed of 1800rpm for 10 minutes to ensure homogeneity. The combined water and sediment at the bottom of the tube was reported to the nearest 0.005ml (ASTM D2709 – 96).

3.4.1.8 Determination of total acid number

25.0g of the biodiesel was weighed into a clean titration beaker. A magnetic stirrer was carefully placed into the beaker to prevent splashing of sample. 100ml of isopropyl alcohol was poured into the beaker and 0.1ml of P-naphtholbenzene indicator solution was added. The titration beaker was assembled with purging stopper previously connected with a rotameter and nitrogen purge gas. The burette tip was inserted into the beaker 10mm above the surface of the solution through the hole in the stopper.

The purge gas was opened and allowed to flow through the beaker at a rate of 10L/h for 30seconds. The stirring rate to mix the solution efficiently was adjusted to prevent splashing or mixing the purge gas into the solution. The sample was titrated with the standardized 0.01M KOH titrant at 28°C. The end point was noted when the orange colour of the indicator changed to a stable green colour. The titration was conducted using the same procedure but this time omitting the sample (blank titration). (ASTM D-3339-95)

Calculation

Calculate the acid number of the sample as follows:

$$\text{Acid number} = \text{mg KOH/g} \frac{56.10 M (A - B)}{W}$$

Where: A = millilitres of titrant required for titration of the sample

B = millilitres of titrant required for titration of the blank

M = molarity of the titrant and

W = grams of sample used

CHAPTER FOUR

RESULTS AND DISCUSSION.

4.1 Physicochemical Properties of the Oils.

Results of the physical and chemical properties of the five studied oils (Palm Oil, Palm kernel Oil, Refined Soybean Oil, Unrefined Soybean Oil and *Jatropha curcas*) are presented in Table 4.1. At room temperature (30°C), all the oils were liquids. Colours of the various oils were, however, different. Palm Kernel oil, unrefined oil soybean oils and *Jatropha curcas* oil were golden yellow while Palm oil and refined soybean were red and light yellow respectively (Table 4.1). Again, the analyses revealed that, there were variations in the densities, specific gravities, refractive indices, viscosities, saponification values, iodine values and acid values of the five studied oils. Interestingly, unrefined soybean oil was found to be the densest and at the same time having the highest specific gravity of 0.939 with palm kernel oil, least dense and having the lowest specific gravity of 0.916.

Acid value of the oils ranged from 3.45 to 10.10 with the least value corresponding to refined soybean oil and the highest to palm oil. Levels of unsaturation in refined soybean oil and unrefined soybean oil are similar since they registered approximately equal iodine values at relatively high side of 121.0 and 124.3 respectively. Beside these two oils, iodine values of the rest are less than 100 with palm kernel oil having the least of 13.5.

The saponification values were in the range of 192 to 247.0 with the highest corresponding to palm kernel oil and refined soybean oil having the least value.

Table 4.1: Physicochemical properties of the five oils Studied.

Parameter	Palm oil	Palm kernel oil	Refined Soybean oil	Unrefined Soybean oil	Jatropha curcas oil
Physical state @ 30°C	Liquid	Liquid	Liquid	Liquid	Liquid
Colour	Red	GoldenYellow	Light Yellow	GoldenYellow	GoldenYellow
Density/ g/cm ³	0.903	0.897	0.919	0.920	0.918
Specific gravity @ 30°C	0.922	0.916	0.938	0.939	0.937
Refractive index @ 30°C	1.464	1.456	1.474	1.473	1.465
Viscosity (cSt) @ 37.8°C	39.6	35.5	32.6	33.2	34.2
Acid Value /mgKOH/g	10.10	9.62	3.45	7.01	9.52
Free fatty acids (as oleic acid)	5.05	4.81	1.73	3.51	4.76
Iodine value (I ₂ g 100g ⁻¹ of oil)	59.3	13.5	121.0	124.3	93.0
Saponification value (mg/KOH/g)	201	247	192	197	202.6

4.1.1 The physicochemical characteristics of palm oil and palm kernel oil.

The table below shows the physicochemical properties of the Ghana's palm oil and palm kernel oil from Ghana compared to palm kernel oil from Thailand.

Table 4.2: Physicochemical properties of palm kernel oil from Ghana and palm Kernel oil

From Thailand.

Parameter	Ghana's Palm oil	Ghana's Palm kernel oil	Thailand's palm kernel oil ^b
Physical state @ 30°C	Liquid	Liquid	Liquid
Colour	Red	GoldenYellow	GoldenYellow
Density/ g/cm ³	0.903	0.897	-----

Specific gravity @ 30°C	0.922	0.916	0.918
Refractive index @ 30°C	1.464	1.456	1.452
Viscosity (cSt) @ 37.8°C	39.6	35.5	28.65
Acid Value /mgKOH/g	10.10	9.62	3.18
Free fatty acids (as oleic acid)	5.05	4.81	1.59
Iodine value (I ₂ g 100g ⁻¹ of oil)	59.3	13.5	18.1
Saponification value (mg/KOH/g)	201	247	255

Source^b: Lalita A. *et al.*, (2008).

The iodine value of the palm kernel oil from Ghana was 13.5 (mg/g) which is lower than the one from Thailand and far lower than the value for palm oil which was 59.3 (mg/g). The high iodine value of palm oil showed that the oil upholds the good qualities of plant oil and (Eromosele *et al.* 1997). The acid value and free fatty acid content of the oils are low in general. The saponification value of Ghana's palm kernel oil (247 mg/g) was lower compared to the Thailand's palm kernel oil (255 mg/g).

The colour of both the Ghana's palm kernel oil and the Thailand's palm kernel oil was Golden yellow at room temperature. The viscosity of the Ghana's palm kernel oil was 35.5cSt which is higher than that of the Thailand's palm kernel oil (28.65 cSt).

The differences in the physicochemical characteristics of palm kernel oil from the two countries may be due to the differences in their fatty acid composition which depends on locality and climate conditions.

4.1.2 The physicochemical characteristics of soybean oil.

The table below shows the physicochemical properties of the Ghana soybean oil compared to the Nigeria oil.

Table 4.3: Physicochemical properties of Ghana's soybean oil and Nigeria's soybean oil.

Parameter	Ghana refined Soybean oil	Ghana unrefined Soybean oil	Nigeria soybean oil^c
Physical state @ 30°C	Liquid	Liquid	-----
Colour	Light Yellow	GoldenYellow	-----
Density/ g/cm ³	0.919	0.920	0.922
Specific gravity @ 30°C	0.938	0.939	-----
Refractive index @ 30°C	1.474	1.473	1.425
Viscosity (cSt) @ 37.8°C	32.6	33.2	38.9
Acid Value /mgKOH/g	3.45	7.01	2.8
Free fatty acids (as oleic acid)	1.73	3.51	1.4
Iodine value (I ₂ g 100g ⁻¹ of oil)	121.0	124.3	138
Saponification value (mg/KOH/g)	192	197	-----

Source^c: Asba E.H and Ibanga E.J., (2008).

The iodine value of the Ghana soybean oil was 121 and 124.3 (mg/g) for refined and unrefined soybean oils respectively, these values are lower than the Nigeria soybean oil (138 mg/g). Higher

iodine value indicates higher unsaturation of fats and oils. The acid value and free fatty acid content of the Ghana's soybean oil are higher than that of the Nigeria soybean oil.

The viscosities of Ghana soybean oil were 32.6cSt and 33.2cSt for refined and unrefined soybean oils respectively and are lower than that of Nigeria soybean oil (38.9 cSt).

4.1.3 The physicochemical characteristics of *Jatropha curcas* oil.

Table 4.4: Physicochemical properties of Ghana's *Jatropha curcas* oil, Nigeria's *Jatropha curcas* oil and Malaysia's *Jatropha curcas* oil.

Parameter	Ghana <i>Jatropha curcas</i> oil	Malaysia <i>Jatropha curcas</i> oil ^d	Nigeria <i>Jatropha curcas</i> oil ^f
Physical state @ 30°C	Liquid	-----	-----
Colour	GoldenYellow	GoldenYellow	Light Yellow
Density/ g/cm ³	0.918	-----	-----
Specific gravity @ 30°C	0.937	-----	-----
Refractive index @ 30°C	1.465	1.467	1.468
Viscosity (cSt) @ 37.8°C	34.2	36.00	17.52
Acid Value /mgKOH/g	9.52	1.50	3.50
Free fatty acids (as oleic acid)	4.76	1.03	1.76
Iodine value (I ₂ g 100g ⁻¹ of oil)	93.0	135.85	105.20
Saponification value (mg/KOH/g)	202.6	208.50	198.85

Source ^d : Jumat S. and Rozani A. 2008 ;

^f : Akintayo 2004

The iodine value of the Ghana *J. curcas* seed oil was 202.6 (mg/g) which is lower than the Malaysian *J. curcas* seed oil but higher than the Nigeria *J. Curcas* seed oil. The oil shows a high iodine value which indicates high content of unsaturated fatty acids. The acid value and free fatty acid content of the *Jatropha* oil are low in general. The saponification value of the Ghana *J. Curcas* seed oil (202.6 mg/g) was higher compared to the Nigerian *J. curcas* seed oil (198.85 mg/g). The Ghana *J. curcas* oil was golden-yellow in colour at room temperature, whereas the Nigerian *J. Curcas* seed oil was light yellow. The viscosity and refractive index of the Ghana *J. curcas* seed oil were 34.2cSt and 1.465 respectively.

4.2 The effect of physicochemical characteristics on biodiesel yield and quality.

4.2.1 Acid value.

The acid value of oil is used as a measure of quality. The acid value of the oil must not be too high, as this denotes an excessively high content of free fatty acids (FFA). FFA can be determined from the acid value. As shown in Figure 4.1, high FFA, affect the yield of the biodiesel. This is in accordance with literature. The acid value of the vegetable oil should be less than one for a base catalyzed transesterification process. Dorodo *et al* (2002), also reported that transesterification would not occur if the oils have FFA content more than 3%, while Van Gerpan (2006), reported that the reaction can be catalyzed with an alkali catalyst up to about 5% FFA content of the vegetable oil. It is known that oils with FFA content higher than 5% decrease the transesterification yield, inhibiting the formation of methoxides by neutralization of part of the catalyst present and producing soaps within the reaction medium. Soap formation would

exacerbate the problem of phase separation at the stage of product recovery and as a result, it has low yield of biodiesel product. The acid-catalyzed esterification of the oil is an alternative method (Crabbe *et al.*, 2001), but it is much slower than the base-catalyzed transesterification reaction. Therefore, an alternative process such as a two-step process has been investigated for feedstock having the high FFA content (Veljkovic' *et al.*, 2006).

From Table 4.1, an acid value of 21.58 was recorded for Palm oil which corresponds to high level of free fatty acids of 10.78% compared to 4.81%, 1.73%, 3.51% and 5.05% for Palm kernel oil, refined soybean oil, unrefined soybean oil and Jatropha curcas oil respectively.

In this study, the FFA content of the oils was found to be within the acceptable limit (3–5%) for base catalyzed transesterification.

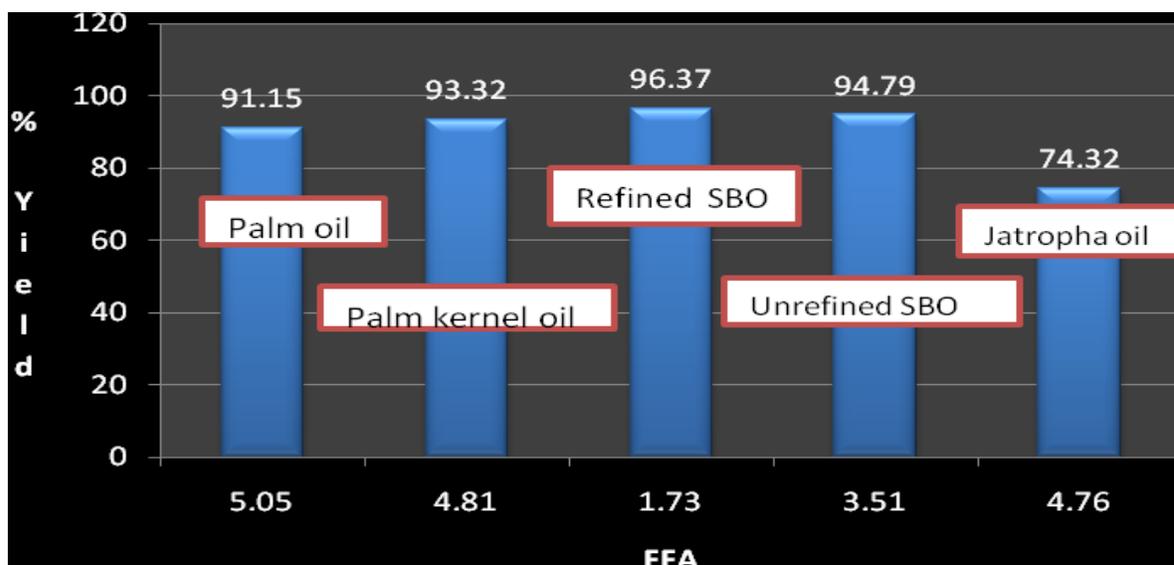


Fig. 4.1: Effect of FFA on FAME Yield.

4.2.2 Saponification Value

The saponification value indicates the ability of the oil to make soap. High saponification value indicates that oils are normal triglycerides and very useful in production of liquid soap and

shampoo industries. The saponification values (SV) of the oils analysed are in the range of 192.0 to 247. Those with high saponification values such as palm kernel oil (247.0 mg/KOH/g), *Jatropha curcas* oil (202.6 mg/KOH/g) and palm oil (201.0 mg/KOH/g) indicate an index of high average molecular weight of triacylglycerols in the oils. Therefore those oils may be a good raw material for soap making.

4.2.3 Iodine value.

The iodine value (IV) is a measurement of the unsaturation of fats and oils. High iodine value indicates high unsaturation of fats and oils (Knothe, 2002; Kyriakidis and Katsiloulis, 2000).

From Table 4.1, the iodine values for palm kernel oil, palm oil and *Jatropha curcas* oil are below 100 ± 1 g of 100g^{-1} oil. However, that of refined soybean oil and unrefined soybean oil was recorded at 121 g of 100g^{-1} oil and 124.3 g of 100g^{-1} oil respectively.

Low-IV oils are more saturated with fewer double-bonds (palm kernel oil, palm oil and *Jatropha curcas* oil). High-IV oils are more unsaturated with more double-bonds (Soybean oil). The results generally show decrease in the average degree of unsaturation of the oil, compared to the possibility that some oils can absorb 200g iodine and beyond. The generally low IVs imply that they are all non-drying oils. Also it suggests that the oil contains mostly saturated triglyceride molecules with the exception of soybean oil which has comparatively high iodine value.

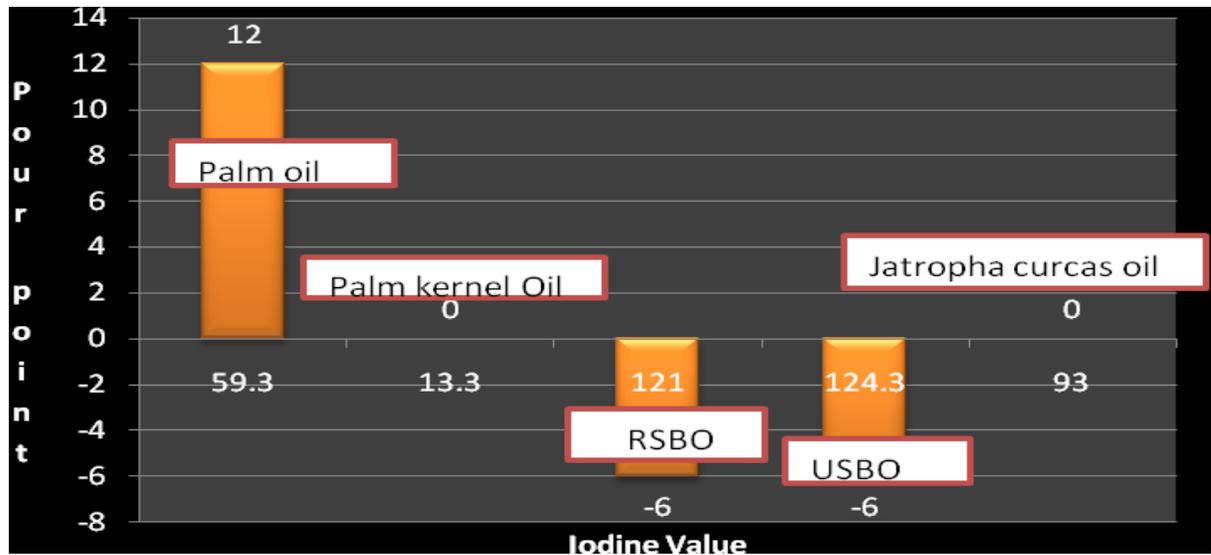


Fig.4.2: The effect of Iodine value of VO's on Pour point of Biodiesel produced from them.

Low-IV oils have higher cetane values and are more efficient fuels than high-IV oils, but they also have higher melting points and are usually solid at room-temperature. Biodiesel made from low-IV oils also has a higher melting point and might only be suitable for use as summer fuel. High-IV oils have lower melting points and make better cold-weather biodiesel, but with high-IV oils there is more risk of the biodiesel oxidising and polymerising (drying) into a tough, insoluble plastic-like solid. This can lead to the formation of deposits or to deterioration of the lubricating engine (Mittelbach, 1996).

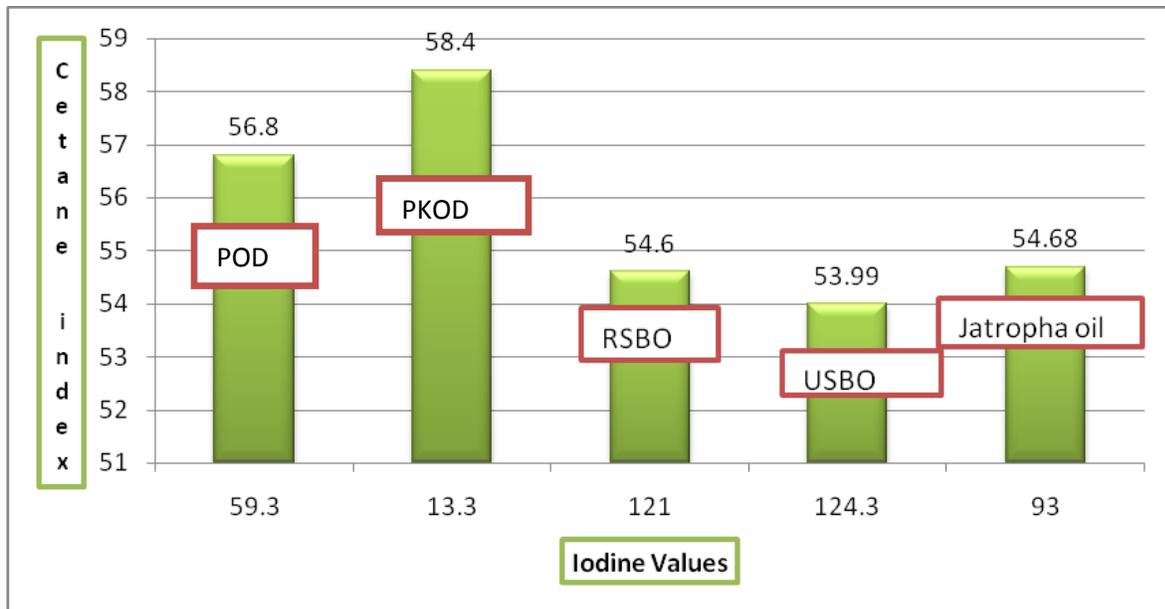


Fig.4.3: The effect of Iodine value of VOs on Cetane number of Biodiesel produced from them

Fuels with this characteristic (e.g soybean oil) are also likely to produce thick sludges in the sump of the engine, when fuel seeps down the sides of the cylinder into crankcase (Gunstone, 2004). Biodiesel made from high-IV oils should be stored carefully and used quickly.

4.2.4 Density.

The density of material is defined as the measurement of its mass per unit volume (e.g. in g/ml). The density of vegetable oil is lower than that of water and the differences between vegetable oils are quite small, particularly among the common vegetable oils. Generally, the density of oil decreases with molecular weight, but increase with unsaturation level (Gunstone, 2004).

This implies that vegetable oils with high density result would polymerise and leads to formation of deposits in car engine.

4.2.5 Specific gravity

Specific gravity is the heaviness of a substance compared to that of water, and it is expressed without units. The specific gravity obtained for all oil samples are less than 1 when measured at 30°C. The common physical properties of such oils are that they float on water but are not soluble in it; they are greasy to touch, and have lubricating properties; they are not readily volatile and may be burned without leaving any residue.

4.2.6 Viscosity.

Viscosity is defined as the resistance of liquid to flow. Viscosity increases with molecular weight but decreases with increasing unsaturated level and temperature (Nouredini *et al.*, 1992). At temperature of 37.8°C, kinematic viscosity of the palm oil and palm kernel oil were detected as 39.6cSt and 35.5cSt respectively. The kinematic viscosity of the refined soybean oil, unrefined soybean oil and *Jatropha curcas* oil were recorded as 32.6, 33.2 and 34.2cSt, respectively.

The viscosity of oils must be reduced for biodiesel application since the kinematic viscosity of biodiesel is very low compared to vegetable oils. The high viscosity of the *jatropha curcas* seed oil is not suitable if its used directly as engine fuel, since it often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubricating oil as a result of contamination by the vegetable oils. Different methods such as preheating, blending, ultrasonically assisted methanol transesterification and supercritical methanol transesterification can be used to reduce the viscosity and make them suitable for engine applications (Pramanik, 2003; Banapurmath, 2008).

4.3 Influence of operating variables on biodiesel yield

4.3.1 Effects of Methanol / Oil on ratio Esther yield.

One of the most important parameters affecting the yield of the ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3 mol of ester and 1 mol of glycerol, but from literature it is found that excess alcohol is required to drive the reaction close to completion. The presence of slight excess amount of alcohol during the transesterification reaction is essential to break the glycerine- fatty acid linkages. But too much excess of methanol should be avoided. Increasing the molar ratio of methanol/oil beyond 6:1 neither increases the product yield nor the ester content, but rather makes the ester recovery process complicated which raises cost. Leung and Guo (2006), suggested that methanol has polar hydroxyl group which can act as an emulsifier causing emulsification. Thus separation of the ester layer from the water layer becomes difficult. In this research, methanol was used. The effect of methanol in the range of 3:1 to 10:1 (molar ratio) was investigated, keeping other process parameters fixed. The reaction temperature was kept constant at 65 ± 1 °C, and reaction was performed for 2 hours. The reaction was performed with constant concentrations of KOH. Analyses of the five oils (Palm oil, Palm kernel oil Refined soybean oil, Unrefined soybean oil and Jatropha curcas oil) revealed that, increase in methanol/oil ratio produces a corresponding increase in the yield till the optimum yield is achieved (Table 4.5).

Table 4.5 : Effect of Methanol/oil ratio on Ester Yield.

Methanol/oil	Refined Soybean oil Biodiesel	Unrefined Soybean oil Biodiesel	Palm oil Biodiesel	Palm kernel oil Biodiesel	Jatropha oil Biodiesel
3:1	79.59	80.27	0.00	0.00	42.18
4:1	85.03	86.39	70.06	74.83	62.59
5:1	94.56	89.11	71.43	85.03	76.87
6:1	92.51	93.19	85.03	93.88	87.75
7:1	91.15	91.16	87.07	92.52	84.35
8:1	89.80	80.95	90.47	90.84	80.30
9:1	88.44	78.23	72.79	88.43	79.60
10:1	84.35	74.83	66.66	84.35	73.46

The yields of methyl esters versus methanol/oil ratio of the five oils are shown in Figure. 4.1. As shown in Figure 4.3, maximum ester yield was obtained at a methanol/oil ratio of 5:1 for Refined Soybean oil; 6:1 for Unrefined Soybean oil, Palm kernel oil and Jatropha curcas oil. However, the maximum ester yield obtained at a methanolysis of Palm oil was at methanol/oil ratio of 8:1. It was found that the ester yield increases with increase in molar ratio of methanol to vegetable oil, and for low values of molar ratio, the ester yield was sensitive to the concentration of KOH. This is because higher mass ratio of reactant increases the contact between the methanol and oil molecules so the methyl ester concentration increases with increasing mass ratio of methanol to oil. But the production yield decreases with increased mass ratio of reactant. These results agree with those obtained by J. M. Encinar *et al.* (2005), who indicated that an excess of alcohol will increase the ester conversion by shifting the equilibrium to the right, but higher amount of alcohol interferes with the separation of glycerin because there is an increase in solubility.

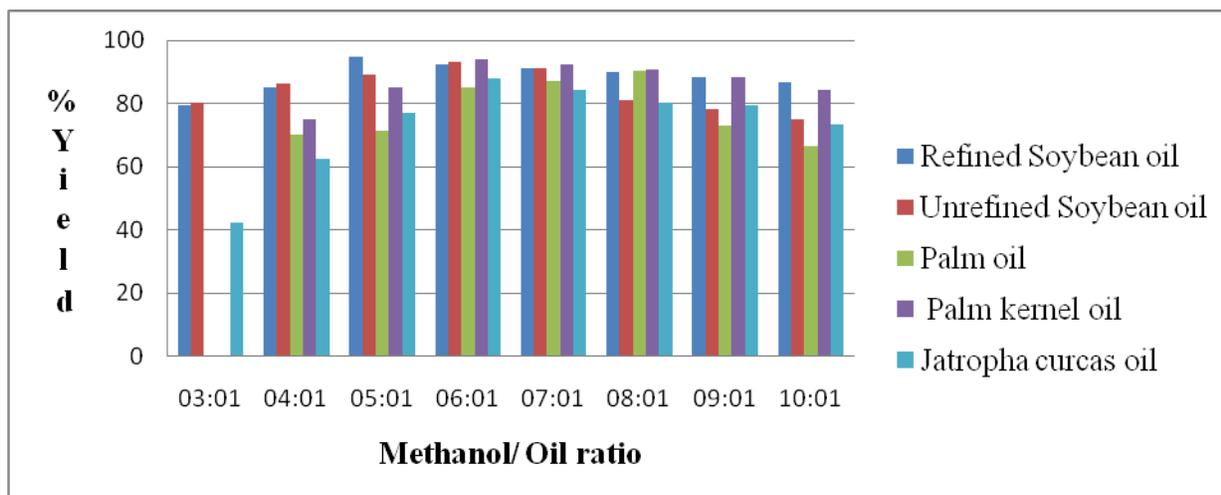


Fig 4.4: The effect of Methanol/Oil ratio on Ester Yield.

4.3.2 Effects of catalyst concentration on ester yield.

KOH catalyzed transesterification of Refined Soybean Oil, Unrefined Soybean Oil, Palm Oil, Palm kernel Oil and *Jatropha curcas* Oil were investigated by changing KOH to oil ratios (%w/w) as shown in Table 4.6.

Table 4.6 : The effect of Catalyst Concentration on Ester Yield

Catalyst concentration	Refined Soybean oil Biodiesel	Unrefined Soybean oil Biodiesel	Palm oil Biodiesel	Palm kernel oil Biodiesel	Jatropha oil Biodiesel
0.25%	82.52	0.00	0.00	0.00	0.00
0.50%	89.12	51.70	0.00	0.00	17.51
0.75%	92.52	61.22	0.00	91.16	18.79
1.0%	96.60	92.52	92.51	94.56	22.02
1.25%	93.88	90.47	95.42	89.12	36.45
1.50%	92.52	79.59	82.67	87.08	72.33

1.75%	88.02	78.04	83.67	82.56	74.02
2.0%	86.57	72.36	88.44	79.32	76.43
2.25%	83.67	70.06	82.37	77.80	71.59
2.50%	82.56	68.48	79.80	76.20	62.17

The results for the effect of catalyst concentration on Ester Yield for the five studied oil at their optimum molar ratios of methanol to oil are shown in Figure 4.4. It was found that the ester yield increases as the amount of catalyst increased from 0.25% to 1.0% for refined soybean oil, unrefined soybean oil and Palm kernel oil. However for Palm oil and Jatropha curcas oil, the ester yield increases from 0.25% to 1.25% and 0.25% to 2.0% respectively.

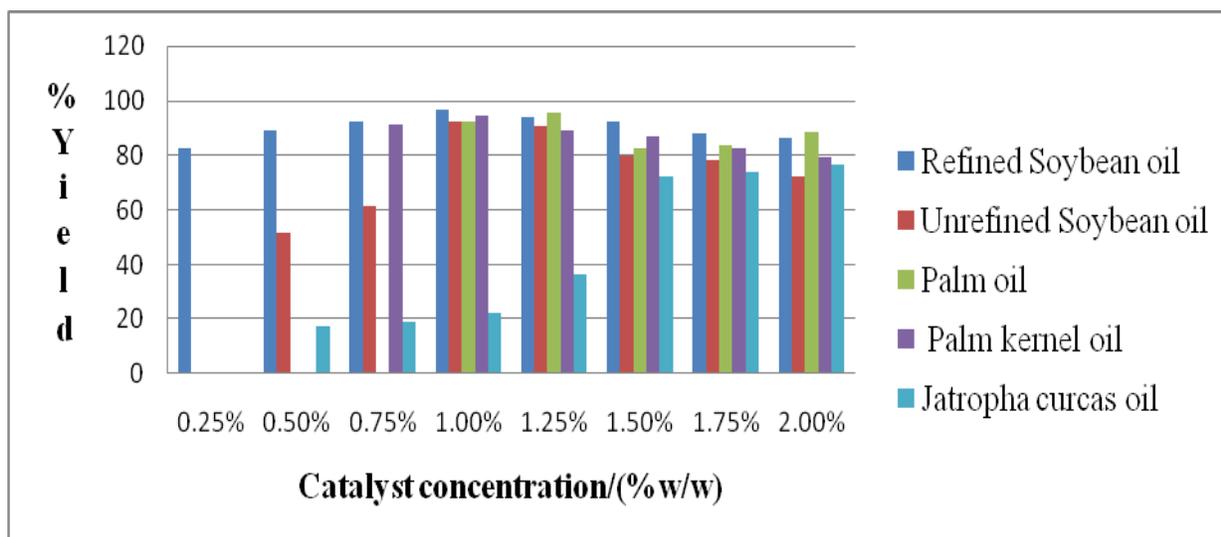


Fig 4.5: The effect of Catalyst Concentration on Ester Yield.

From Figure 4.4, it is revealed that, Ester yield decreases drastically as the KOH concentration increases beyond the optimum catalyst concentration. This lesser yield at high KOH concentration may possibly be due to high soap formation. Therefore, excess KOH reduces the

yield and also leads to undesirable extra processing cost because it is necessary to remove it from the reaction products at the end.

Again, the analyses of the results show that, high conversion was obtained with 1.0% of KOH to oil ratio and 6:1 of methanol to oil ratio, and under these conditions, the FAME yield was 96.60% for Refined Soybean Oil, 92.52% for Unrefined Soybean Oil and 92.51% for Palm kernel oil. The results of Palm oil and *Jatropha curcas* oil indicate that the optimum conditions of KOH catalyzed transesterification required more catalyst. The optimum KOH to oil ratio at their optimum methanol to oil ratio were 1.25% w/w for Palm oil and 2.0%(w/w) for *Jatropha curcas* oil. The high KOH concentration needed for the transesterification of palm oil and *Jatropha curcas* oil as compared to that of soybean oil and palm kernel oil may be due to differences in FFA. KOH catalyzed reaction is reported to be very sensitive to the purity of the reactant.

FFA content should not exceed a certain limit. The efficiency of the reaction is affected to some extent when FFA content is high (Freedman *et al.*, 1986).

4.3.3 The effect of temperature on ester yield.

For studying the effect of temperature on the transesterification reaction, the reaction temperature was varied as 30, 40, 50, 60, 65, 70 and 75 °C, while the other parameters such as reaction time (2 hrs) and their optimum molar ratios and catalyst concentrations previously determined were kept constant. The results are shown below in Table 4.7.

Table 4.7 : The effect of Temperature on Ester Yield

Temperature /°C	Refined Soybean oil Biodiesel	Unrefined Soybean oil Biodiesel	Palm oil Biodiesel	Palm kernel oil Biodiesel	Jatropha oil Biodiesel
30	89.12	88.43	0.00	85.71	34.69
40	93.20	92.56	0.00	89.08	57.14
50	97.96	93.20	64.62	91.16	68.02
60	89.12	91.16	85.03	95.23	73.47
65	93.20	95.92	88.44	97.27	70.07
70	90.48	89.12	84.35	92.52	61.22
75	87.08	84.35	80.95	86.39	52.38

Analysis of the results show that for all the five oils studied, biodiesel yield increases as the temperature increases, only up to a threshold value. Beyond this point, no further increase in biodiesel yield is observed. For Refined Soybean oil, the highest Biodiesel yield of 97.96% was obtained at a temperature of 50°C. A value of 65°C was the optimum temperature for Unrefined Soybean, Palm Kernel Oil and Palm oil. However, for the Jatropha curcas oil, the highest Biodiesel yield of 73.47% was recorded at 60°C, (Figure 4.5).

This observation that temperature increase influences the reaction in a positive manner had also been affirmed by other researchers (Srivastava A and Prasad R, 2000; Ma F and Hanna MA, 1990; Freedman B *et al.*, 1984 and Canakci M and Van Gerpen G, 1999).

Also, for all the five oils studied, it is found that ester yield decreases as the reaction temperature increases above 65°C. The boiling point of methanol is 65°C and temperature higher than this will burn the alcohol and result in much lesser yield. The lesser methyl ester yield may also probably be due to a negative interaction between the temperature and catalyst concentration due to the side reaction of saponification. This is because solubility of reactant at higher temperature

reduced the separation between methyl ester and glycerol phase leading to decrease in production yield.

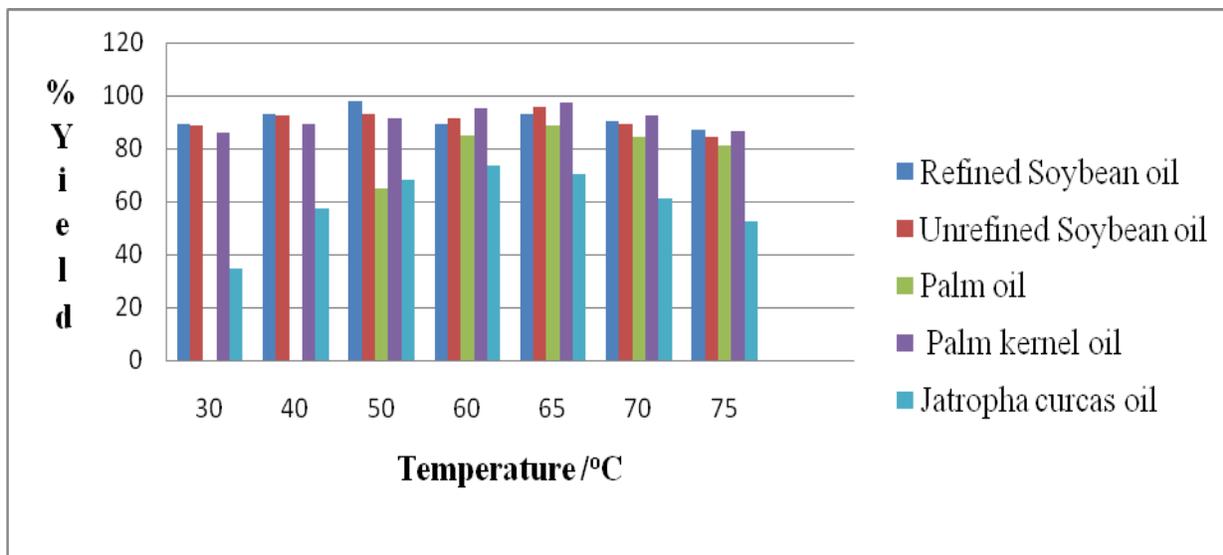


Fig 4.6 : The effect of Temperature on Ester Yield.

4.3.4 Process Parameter Selection.

The optimum parameters affecting transesterification for each of the five oils were selected. The results are presented in Table 4.8.

Table 4.8 : The optimum reaction conditions for the five oils

Feedstock type	Optimum methanol/oil ratio	Optimum catalyst conc. (%w/w)	Optimum temperature/°C	Reaction time/Hrs	% Yield.
Refined soybean oil	5:1	1.0%	50 °C	2hrs	96.37%
Unrefined soybean oil	6:1	1.0%	65 °C	2hrs	93.32%
Palm kernel oil	6:1	1.0%	65 °C	2hrs	94.79%
Palm oil	8:1	1.25%	70 °C	2hrs	91.15%
Jatropha curcas oil	6:1	2.0%	60 °C	2hrs	74.32%

The analyses of the results revealed that, for the transesterification of the refined soybean oil, optimum reaction conditions were found to be 50°C reaction temperature, 5:1 molar ratio of methanol to oil, 1.0% catalyst (w/w) and 2hrs reaction time. These conditions gave an ester (soybean oil methyl ester) yield of 96.37% by weight, and the ester viscosity was found to be 5.49 cSt at 37.8°C. The optimum reaction conditions for unrefined soybean oil were found to be 65 °C reaction temperature, 6:1 molar ratio of methanol to oil, 1.0% catalyst (w/w) and reaction time of 2hrs. These conditions gave an ester (soybean oil methyl ester) yield of 94.79% by weight, and the ester viscosity was found to be 5.92 cSt at 37.8°C.

For the transesterification of palm kernel oil, to achieve an ester yield of 93.32%, a 65 °C reaction temperature, 6:1 molar ratio of methanol to oil, 1.0% catalyst (w/w) and reaction time of 2hrs were used. The ester viscosity was found to be 4.14cSt at 37.8°C. However, the transesterification of palm oil gave a different result. A reaction temperature of 70°C, methanol to oil ratio of 8:1, a catalyst concentration of 1.25% and a reaction time of 2hrs are required to obtain an ester yield of 91.15% and the viscosity of the ester was found to be 6.20 cSt at 37.8°C.

As is shown in Table 4.8, the optimum reaction conditions for *Jatropha curcas* oil were found to be 60 °C reaction temperature, 6:1 molar ratio of methanol to oil, 2.0% catalyst (w/w) and reaction time of 2hrs. These conditions gave the least ester yield of 74.32% by weight, and the ester viscosity was found to be 7.16 cSt at 37.8°C.

The results of the percentage yield of ester at their optimum conditions for the five oils are shown in figure 4.6.

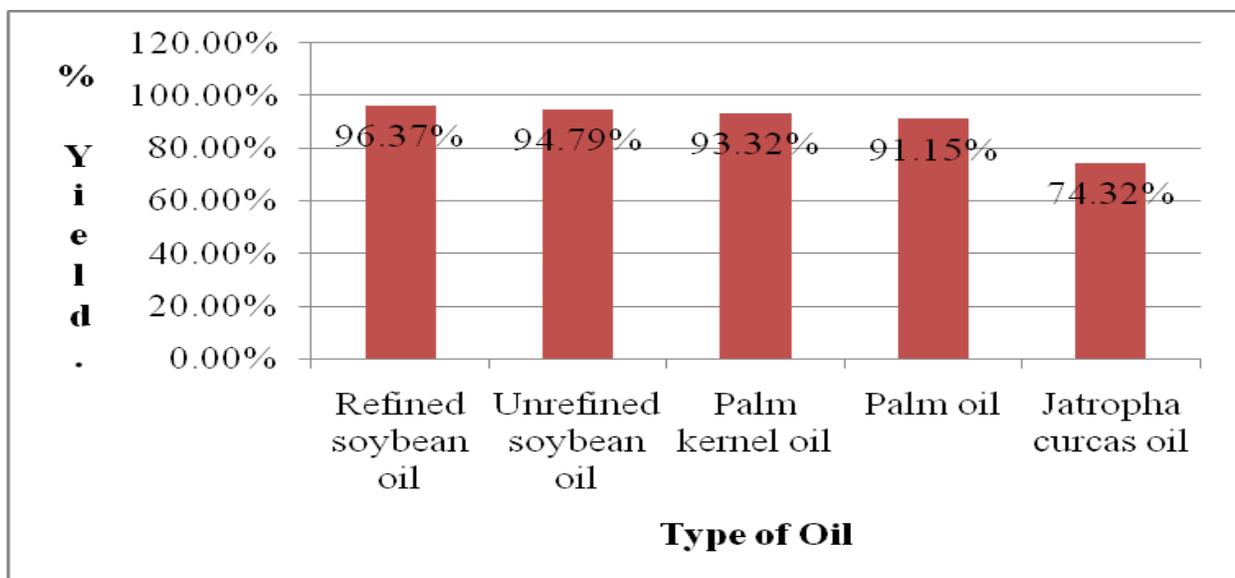


Fig. 4.7 : Percentage yield of ester at their optimum conditions for the different oils.

4.4 Fuel properties of the Biodiesel obtained for the five studied oils.

The table below shows the quality of Biodiesel obtained from refined soybean oil, unrefined soybean oil, palm oil, palm kernel oil and jatropha curcas oil in comparism with American standard (ASTM) and European standard (EN). Their qualities were determined in order to determine whether the methyl esters from the five oils have adequate values as biodiesel fuel candidate in agreement with ASTM D 6751 (08) and EN 14214 (03).

Table 4.9 : Comparison of fuel properties of biodiesels produced from the different oils.

TEST	POD	PKOD	SBOD (RE)	SBOD (UNRE)	JOD	STANDARD	TEST METHOD
DENSITY@15 ⁰ C /Kg/m ³	877.6	878.4	889.6	891.0	885.2	830-900	ASTM D-1298 ASTM D-4052
COLOUR	3.5	0.5	0.5	1.0	0.5	3.0max	ASTM D-1500
KINEMATIC VISCOSITY @ 37.8 ⁰ C / cSt	6.20	4.14	5.49	5.92	7.16	1.6-6.5	ASTM D-445
CONRADSON CARBON RESIDUE /(% wt.)	0.25	0.06	0.09	0.13	0.15	0.20max	ASTM D-4530
TOTAL ACID NUMBER /(mgKOH/g)	0.16	0.37	0.35	0.26	0.14	0.8 max	ASTM D-974
ASH CONTENT (% wt.)	0.006	0.001	0.002	0.005	0.001	0.02 max	ASTM D-482
CETANE INDEX	56.80	58.40	54.60	53.99	54.68	42 min	ASTM D-130
WATER BY DISTILLATION.(% vol)	<0.05	<0.05	<0.05	<0.05	<0.05	0.05max	ASTM D-95
BASIC WATER AND SEDIMENT /(% vol)	<0.05	<0.05	<0.05	<0.05	<0.05	0.10max	ASTM D-2706
POUR POINT /(⁰ C)	+12	-6	-6	-6	0	+15max	ASTM D-97
CALCIUM AND MAGNESIUM, COMBINED/(ppm).	5.18	0.025	<0.01	4.48	<0.01	5 max	EN 14538
SODIUM AND POTASium COMBINED/(ppm).	14.20	1.942	1.033	3.820	1.125	5 max	EN 14538
TOTAL SULPHUR CONTENT /(%wt).	0.017	0.008	0.005	0.009	0.010	0.5max	ASTM D-2622

4.4.1 Density.

The standard for biodiesel states that the fuel should have a density between 0.830 and 0.900 g/cm³. This property is important mainly in airless combustion systems because it influences the

efficiency of atomization of the fuel (Ryan et al., 1984). The results obtained showed that for all the five oils studied, the biodiesels produced had a density in the range of 0.864–0.900 g/cm³.

Different density values for FAME of the various oils may be due to their different fatty acids composition as well as their purity. Density increases with decreasing chain length and increasing number of double bonds (Worgetter *et al.*, 1998). This explains the high values for fuels rich in unsaturated compounds such as soybean oil methyl ester (889.6 and 891.0 Kg/m³) for refined and unrefined soybean oil or Jatropha oil methyl ester (885.2 Kg/m³), (Mittelbach *et a.*, 2004).

As is shown in Table 4.1 and Table 4.9, the densities of the individual oils is smaller than their corresponding FAMEs. This is in agreement with literature because density is decreased by the presence of low-density contaminants, such as methanol and since methanol was used in the transesterifying the various oils to their respective methyl esters, the densities of the neat oils will be reduced.

4.4.2 Kinematic viscosity at 37.8 °C

According to ASTM D 6751(08) and EN 14214(03), for biodiesel to be used in diesel engines, the kinematic viscosity must be between 1.9 and 6.5 mm²/s and 3.50 and 5.0 mm²/s respectively. The kinematic viscosities of the biodiesels produced from the five oils ranged from 4.14 to 7.16 mm²/s. Viscosity is closely related to the fatty acids composition of a given biodiesel sample. It increases with increasing length of fatty acid chain (Knothe, 2002). On the other hand, viscosity is inversely related to the number of double bonds. This explains the high viscosity ratings for biodiesel obtained from saturated materials such as palm oil (6.20mm²/s) and palm kernel oil (5.92mm²/s) and low readings for highly unsaturated compounds such as soybean methyl ester

(4.14mm²/s and 4.52mm²/s). The unexpected high viscosity value of methyl ester derived from *Jatropha curcas* oil (7.16mm²/s) may be attributed to high fuel ageing during storage since viscosity increases would be caused by polymerization induced by oxidative degradation (Canakci *et al.*, 1999). From figure 4.7, it can be observed that, the kinematic viscosities of the neat oils are lower than their corresponding methyl esters. This is in agreement with literature as it has been shown that through transesterification, the kinematic viscosity of the vegetable oil is lowered.

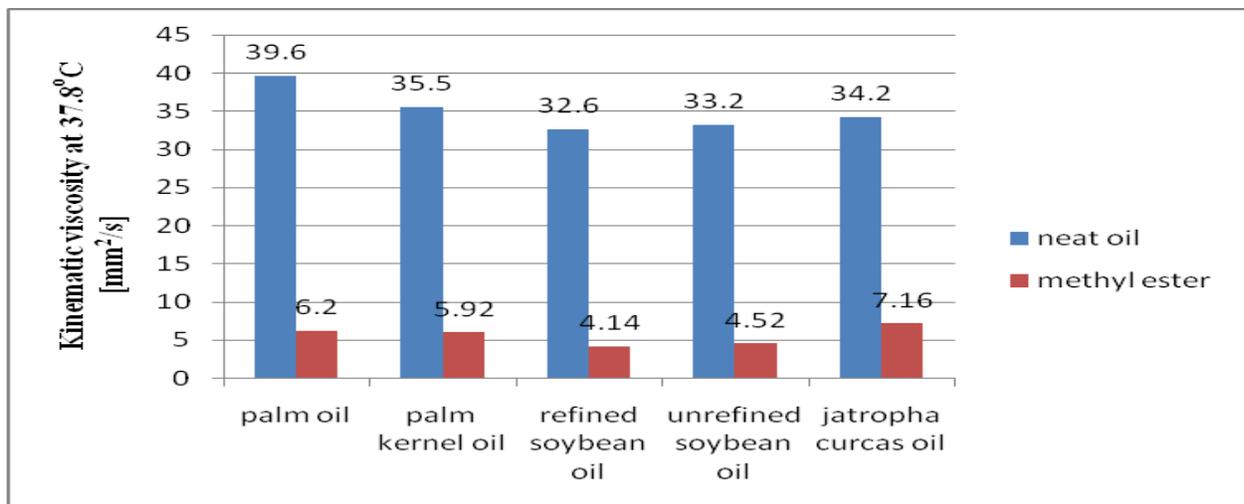


Fig. 4.8 : Viscosities of the five studied oils and their respective methyl esters.

4.4.3 Cetane number

This parameter serves as a measure of the ignition quality of diesel fuel. High cetane numbers signify only short delays between fuel injection and ignition, and thus ensure good cold start behavior and a smooth run of the engine. Fuels with low cetane numbers tend to cause diesel knocking and show increased gaseous and particulate exhaust emissions due to incomplete combustion (Srivastava and prasad, 2000). The results show that palm oil methyl ester and palm kernel oil methyl ester registered high values of 56.80 and 58.40, respectively. However, cetane number of unrefined soybean oil methyl ester, refined soybean oil methyl esters and jatropha

curcas oil methyl ester recorded comparatively low values of 53.99, 54.60 and 54.68 respectively. Analyses of the results revealed that, the cetane number of methyl esters of all the five oils studied were above the minimum value of 47 set by ASTM D 6751 (03) and also exceeded 51 which is the minimum value established by EN 41214 (03).

4.4.4 Acid value

The acid value measures the content of free fatty acids in biodiesel. Considering that the presence of free fatty acids influences fuel aging due to hydrolytic cleavage of ester bond, the European and American Standards specify a maximum values of 0.5 mg of KOH/g and 0.8 mg of KOH/g of sample respectively.

Analyses of the results revealed that, the acid values of methyl esters of all the oils studied were within specifications with palm kernel oil methyl ester and refined soybean oil methyl ester registering high values of 0.37 and 0.36. However, that of jatropha curcas oil methyl ester, palm oil methyl ester and unrefined soybean oil methyl ester were recorded as 0.14, 0.16 and 0.26 respectively. Acid value is influenced by the type of feedstock used for fuel production and its respective degree of refinement (Cvengros, 1998). The unexpectedly high acid value for refined soybean oil methyl ester as compared to Biodiesel derived from crude oils may be attributed to fuel ageing during storage, as it gradually increases due to hydrolytic cleavage of the ester bond.

4.4.5 Sodium and Potassium content

Because the presence of high amounts of sodium and potassium in biodiesel induces metal corrosion as well as saponification of the methyl esters phase, EN 14214 (2003) and ASTM 6751 (2003) specify a maximum value of 5 mg/kg. It is well known that the content of sodium and

potassium in biodiesel is mainly determined by the efficiency of the washing step. The sodium and potassium contents of biodiesels derived from four oils were in the range of 1.03–3.82 mg/kg of fuel and it was that of palm oil only, that was out of the specification. These results indicate that the washing procedure used was efficient in sodium and potassium removal for the four oils except palm oil.

4.3.6 Water content

Fuel contaminated with water can cause engine corrosion or react with the glycerides to produce soaps and glycerine. Therefore, EN 14214 (2003) and ASTM 6751 (2003) impose a maximum content of 0.05% of water in fuels. Analyses of the results revealed that, for all the five oils studied, the water content was within the specifications.

4.3.7 Sulphated ash

Ash content describes the amount of inorganic contaminants, such as abrasive solids and catalyst residues and the concentration of soluble metal soaps contained in a fuel sample. These compounds are oxidized during the combustion process to form ash, which is connected with engine deposits.

EN 14214 (2003) and ASTM 6751 (2003) had established a maximum value of 0.02% for sulphated ash. This property is important since high values are generally associated with coking of injectors and clogging of fuel filters. The values obtained for the five studied oils were between 0.001% and 0.006%, meeting the fuel specifications.

4.3.8 Pour point

Pour point is a measure of the fuel gelling temperature, at which point the fuel can no longer be pumped. The values of pour point for the biodiesel produced in this study were +12°C for palm oil, 0°C for *Jatropha curcas* oil and - 6°C for refined soybean oil, unrefined soybean oil and palm kernel oil. According to ASTM standard D 6751, no limit is specified for Pour point. The reason is that the climate conditions in the world vary considerably, thus affecting the needs of biodiesel users in a specific region (Anwar and Rashid, 2008).

CHAPTER FIVE.

CONCLUSIONS AND RECOMMENDATIONS.

From the results of the study, the following conclusions and recommendations were made.

- All the five studied oils exhibited good physicochemical properties and could be useful as biodiesel feedstock.
- The optimum reaction conditions for transesterification of the refined soybean oil were found to be 50°C reaction temperature, 5:1 molar ratio of methanol to oil, 1.0% catalyst (w/w) at 2hrs reaction time. These conditions gave an ester (soybean oil methyl ester) yield of 96.37% by weight, and the ester viscosity was found to be 5.49 cSt at 37.8°C.
- The optimum reaction conditions for unrefined soybean oil were found to be 65 °C reaction temperature, 6:1 molar ratio of methanol to oil, 1.0% catalyst (w/w) and a reaction time of 2hrs. These conditions gave an ester (soybean oil methyl ester) yield of 93.32% by weight, and the ester viscosity was found to be 5.92 cSt at 37.8°C.
- For the transesterification of palm kernel oil, to achieve an ester yield of 94.79%, a 65 °C reaction temperature, 6:1 molar ratio of methanol to oil, 1.0% catalyst (w/w) and reaction time of 2hrs were used. The ester viscosity was found to be 4.14cSt at 37.8°C. However, the transesterification of palm oil gave a different result. A reaction temperature of 70°C, methanol to oil ratio of 8:1, a catalyst concentration of 1.25% and a reaction time of 2hrs are required to obtain an ester yield of 91.15% and the viscosity of the ester was found to be 6.20 cSt at 37.8°C.

- The optimum reaction conditions for *Jatropha curcas* oil were found to be 60 °C reaction temperature, 6:1 molar ratio of methanol to oil, 2.0% catalyst (w/w) and reaction time of 2hrs. These conditions gave the least ester yield of 74.32% by weight, and the ester viscosity was found to be 7.16 cSt at 37.8°C.
- All the oils studied exhibited good fuel properties except palm oil Biodiesel in which its viscosity, colour, carbon residue, acid values and other parameters fell outside the ASTM D 6751 (08) Limits.
- The physico-chemical characteristics of the Feedstock affect the yield and quality of Biodiesel. Low Iodine values which implies higher composition of saturated fatty acids in feedstock will increase the cetane number of biodiesel but will lower its cloud and pour points. Whereas, higher Iodine values which means higher composition of unsaturated fatty acids will enhance the cloud point and pour point of biodiesel it will have poor cetane number. Hence, a balance has to be maintained between the ratio of saturated and unsaturated components of the oil to be used as a feedstock for biodiesel production.

5.2 RECOMMENDATION:

1. The physicochemical properties of other oils on the yield and quality of biodiesel need to be investigated.
2. Other factors affecting the transesterification process such as mixing intensity and reaction time should be investigated further to obtain the optimized conditions of the various oils.

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APPENDIX

Table 1A : Effect of Methanol/oil ratio on Ester yield for Refined Soybean Biodiesel.

Methanol/oil ratio	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
3:1	6	49	38	40	39	77.55	81.63	79.59	79.59
4:1	8	49	42	42	41	85.71	85.71	83.67	85.03
5:1	10	49	46	47	46	93.88	95.92	93.88	94.56
6:1	12	49	46	45	45	93.88	91.83	91.83	92.51
7:1	14	49	45	44	45	91.83	89.80	91.83	91.15
8:1	16	49	44	44	44	89.80	89.80	89.80	89.80
9:1	18	49	44	43	43	89.80	87.76	87.76	88.44
10:1	20	49	41	42	41	83.67	85.71	83.67	84.35

Table 2A : Effect of Methanol/oil ratio on Ester Yield for Unrefined Soybean Biodiesel.

Methanol/oil ratio	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
3:1	6	49	39	39	40	79.59	79.59	81.63	80.27
4:1	8	49	43	42	42	87.75	85.71	85.71	86.39
5:1	10	49	44	44	43	89.79	89.79	87.75	89.11
6:1	12	49	46	45	46	93.87	91.84	93.87	93.19
7:1	14	49	45	45	44	91.84	91.84	89.79	91.16
8:1	16	49	40	39	40	81.63	79.59	81.63	80.95
9:1	18	49	39	37	39	79.59	75.51	79.59	78.23
10:1	20	49	37	36	37	75.51	73.47	75.51	74.83

Table 3A : Effect of Methanol/oil ratio on Ester Yield for Palm kernel Biodiesel

Methanol/oil ratio	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
3:1	6	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4:1	8	49	38	36	36	77.55	73.47	73.47	74.83
5:1	10	49	42	42	41	85.71	85.71	83.67	85.03
6:1	12	49	46	47	45	93.88	95.92	91.84	93.88
7:1	14	49	45	45	46	91.84	91.84	93.88	92.52
8:1	16	49	44	44	45	89.80	89.80	91.84	90.84
9:1	18	49	42	43	45	85.71	87.75	91.83	88.43
10:1	20	49	41	41	42	83.67	83.67	85.71	84.35

Table 4A : Effect of Methanol/oil ratio on Ester Yield for Palm oil Biodiesel

Methanol/oil ratio	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
3:1	6	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4:1	8	49	36	34	33	73.47	69.38	67.43	70.06
5:1	10	49	34	36	35	69.38	73.47	71.43	71.43
6:1	12	49	41	42	42	83.67	85.71	85.71	85.03
7:1	14	49	43	41	44	87.76	83.67	89.79	87.07
8:1	16	49	44	45	44	89.79	91.84	89.79	90.47
9:1	18	49	36	35	36	73.47	71.43	73.47	72.79
10:1	20	49	33	34	31	67.34	69.39	63.26	66.66

Table 5A : Effect of Methanol/oil ratio on Ester Yield for Jatropha oil Biodiesel.

Methanol/oil ratio	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
3:1	6	49	22	20	20	44.89	40.82	40.82	42.18
4:1	8	49	31	30	31	63.27	61.22	63.27	62.59
5:1	10	49	38	38	37	77.55	77.55	75.51	76.87
6:1	12	49	43	44	42	87.75	89.79	85.71	87.75
7:1	14	49	41	40	43	83.67	81.63	87.75	84.35
8:1	16	49	40	40	38	81.67	81.67	77.55	80.30
9:1	18	49	38	39	40	77.55	79.59	81.67	79.60
10:1	20	49	36	37	35	73.46	75.51	71.42	73.46

Table 6A : The effect of catalyst concentration on ester yield for Soybean (refined) Oil Biodiesel

Catalyst conc. (%w/w)	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
0.25	10	49	46	45	45	93.88	91.84	91.84	92.52
0.50	10	49	43	44	44	87.76	89.80	89.80	89.12
0.75	10	49	45	45	46	91.84	91.84	93.88	92.52
1.0	10	49	47	48	47	95.92	97.96	95.92	96.60
1.25	10	49	46	45	47	93.88	91.84	95.92	93.88
1.50	10	49	45	45	46	91.84	91.84	93.88	92.52
1.75	10	49	43	43	42	87.76	87.76	85.71	87.08
2.00	10	49	42	41	40	85.71	83.67	81.63	83.67
2.25	10	49	40	39	41	81.63	79.59	83.67	81.63
2.50	10	49	36	35	37	73.46	71.42	75.51	73.46

Table 7A: The effect of catalyst concentration on ester yield for soybean (unrefined) Oil Biodiesel.

Catalyst conc. (%w/w)	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
0.25	12	49	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.50	12	49	26	25	25	53.05	51.02	51.02	51.70
0.75	12	49	30	30	30	61.22	61.22	61.22	61.22
1.0	12	49	46	45	45	93.88	91.84	91.84	92.52
1.25	12	49	45	44	44	91.84	89.79	89.79	90.47
1.50	12	49	39	38	40	79.59	77.55	81.63	79.59
1.75	12	49	38	39	39	77.55	79.59	79.59	78.91
2.00	12	49	35	36	34	71.43	73.46	69.38	71.42
2.25	12	49	34	33	33	69.38	67.34	67.34	68.02
2.50	12	49	33	33	32	67.34	67.34	65.30	66.66

Table 8A : The effect of catalyst concentration on ester yield for Palm kernel Biodiesel

Catalyst conc. (%w/w)	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
0.25	12	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	12	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.75	12	49	44	45	45	89.80	91.84	91.84	91.16
1.0	12	49	46	46	47	93.88	93.88	95.92	94.56
1.25	12	49	44	44	43	89.80	89.80	87.76	89.12
1.50	12	49	43	42	43	87.76	85.71	87.76	87.08
1.75	12	49	40	39	42	81.63	79.59	85.71	82.31
2.00	12	49	38	39	37	77.55	79.59	75.51	77.55
2.25	12	49	37	36	36	75.51	73.49	73.49	74.16

2.50	12	49	34	35	33	69.38	71.43	67.35	69.39
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Table 9A : The effect of catalyst concentration on ester yield for Palm oil Biodiesel

Catalyst conc. (%w/w)	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
0.25	16	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	16	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.75	16	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0	16	49	46	45	45	93.88	91.83	91.83	92.51
1.25	16	49	47	47	46	95.92	95.92	93.88	95.42
1.50	16	49	43	40	39	87.76	81.63	79.59	82.67
1.75	16	49	42	40	41	85.71	81.63	83.67	83.67
2.00	16	49	44	43	43	89.79	87.76	87.76	88.44
2.25	16	49	40	41	40	81.63	83.67	81.63	82.31
2.50	16	49	39	39	40	79.59	79.59	81.63	80.27

Table 10A: The effect of catalyst concentration on ester yield for Jatropha oil Biodiesel

Catalyst conc. (%w/w)	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
0.25	12	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	12	49	9.0	8.0	9.0	18.36	16.32	18.36	17.68
0.75	12	49	10.0	10.0	9.0	20.40	18.36	20.40	19.72
1.0	12	49	11.0	10.0	12.0	22.44	20.40	24.49	22.44
1.25	12	49	17	18	17	34.69	36.73	34.69	35.37
1.50	12	49	35	34	35	71.43	69.39	71.43	70.75
1.75	12	49	36	35	35	73.47	71.43	71.43	72.11
2.00	12	49	37	38	38	75.51	77.55	77.55	76.87

2.25	12	49	35	35	34	71.43	71.43	69.38	70.75
2.50	12	49	30	31	31	61.22	63.27	63.27	62.59

Table 11A : The effect of temperature on ester yield for soybean (refined) Oil Biodiesel.

Temperature/°C	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
30	10	49	43	44	44	87.76	89.80	89.80	89.12
40	10	49	46	46	45	93.88	93.88	91.84	93.20
50	10	49	48	48	48	97.96	97.96	97.96	97.96
60	10	49	43	44	44	87.76	89.80	89.80	89.12
65	10	49	45	46	46	91.84	93.88	93.88	93.20
70	10	49	44	44	45	89.80	89.80	91.84	90.48
75	10	49	43	42	43	87.76	85.71	87.76	87.08

Table 12A : The effect of temperature on ester yield for soybean (unrefined) Oil Biodiesel.

Temperature/°C	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
30	12	49	43	43	44	87.76	87.76	89.79	88.43
40	12	49	47	46	46	95.92	93.88	93.88	92.56
50	12	49	46	45	46	93.88	91.84	93.88	93.20
60	12	49	45	44	45	91.84	89.80	91.84	91.16
65	12	49	47	48	46	95.92	97.96	93.88	95.92
70	12	49	44	43	44	89.80	87.76	89.80	89.12
75	12	49	42	41	41	85.71	83.67	83.76	84.35

Table 13A : The effect of temperature on ester yield for Palm kernel Oil Biodiesel.

Temperature/°C	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
30	12	49	42	41	43	85.71	83.67	87.76	85.71
40	12	49	43	44	44	87.76	89.79	89.79	89.08
50	12	49	45	45	44	91.84	91.84	89.79	91.16
60	12	49	48	46	46	97.95	93.87	93.87	95.23
65	12	49	48	48	47	97.95	97.95	95.91	97.27
70	12	49	45	46	45	91.84	93.87	91.84	92.52
75	12	49	43	43	41	87.76	87.76	83.67	86.39

Table 14A: The effect of temperature on ester yield for Palm Oil Biodiesel.

Temperature /°C	Volume of methanol/ml	Volume of oil/ml	Yield/ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
30	16	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	16	49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	16	49	32	32	31	65.30	65.30	63.26	64.62
60	16	49	42	41	42	85.71	83.67	85.71	85.03
65	16	49	44	43	43	89.79	87.76	87.76	88.44
70	16	49	42	41	41	85.71	83.67	83.67	84.35
75	16	49	39	40	40	79.59	81.63	81.63	80.95

Table 15A: The effect of catalyst concentration on ester yield for soybean *Jatropha curcas* Oil Biodiesel.

Temperature/ °C	Volume of methanol/ ml	Volume of oil/ ml	Yield/ ml			% Yield (v/v)			Average % Yield
			1 st	2 nd	3 rd	1 st	2 nd	3 rd	
30	12	49	16	18	17	32.65	36.73	34.69	34.69
40	12	49	29	28	27	59.18	57.14	55.10	57.14
50	12	49	33	34	33	67.34	69.39	67.34	68.02
60	12	49	37	35	36	75.51	71.43	73.47	73.47
65	12	49	35	34	34	71.42	69.39	69.39	70.07
70	12	49	30	31	29	61.22	63.26	59.18	61.22
75	12	49	25	26	26	51.02	53.06	53.06	52.38