

**PREPARATION AND STUDIES OF BIODIESELS FROM *THEVETIA PERUVIANA*
(YELLOW OLEANDER) SEED OIL AND *SUS DOMESTICUS* (PIG) LARD**

BY

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AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA.**

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BY

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ZARIA, NIGERIA.

DECEMBER, 2015

Declaration

I declare that the work in this Thesis entitled “**Preparation and Studies of Biodiesels from *Thevetia peruviana* (Yellow Oleander) Seed Oil and *Sus domesticus* (Pig) Lard**”, has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

Yakubu Ali DALLATU

Name of Student

Signature

Date

Dedication

This research work is dedicated to my wife, Mrs. Rhoda Y. Dallatu and our children, Unomliyi, Alionom and Apemu for their patience, support and encouragement.

Certification

This thesis, entitled “PREPARATION AND STUDIES OF BIODIESELS FROM *THEVETIA PERUVIANA* (YELLOW OLEANDER) SEED OIL AND *SUS DOMESTICUS* (PIG) LARD” by Yakubu Ali DALLATU meets the regulations governing the award of the degree of Doctor of Philosophy (Ph.D.) Analytical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Abstract

Studies of biodiesels from *Thevetia peruviana* (yellow oleander) seeds oil (YO) and *Sus domesticus* (pig lard) (PL) were carried out. Oil was extracted from YO and PL rendered from pig fat, which yielded 64.7% and 85.4% oil respectively. Some physicochemical parameters: flash points of 192°C and 165°C, calorific values of 13.79MJ/Kg and 12.02MJ/kg were obtained for YO and PL respectively. The FTIR analyses of the YO, PL and biodiesel showed the carbonyl functional group at 1739 cm^{-1} to 1745 cm^{-1} as the most intense and prominent bands. The carbonyl (-C=O vibration) group of esters showed strong absorption bands at 1740 cm^{-1} in the IR spectra of the biodiesels, indicating the presence of fatty acid methyl esters. The GC-MS analysis of the oils and biodiesels showed about 80% saturated/ monounsaturated fatty acids in both YO and PL, signifying high potential for biodiesel production. Biodiesels were prepared from the YO and PL using the base- catalyzed transesterification method. Biodiesel yields increased with increase in temperature and reaction time with minimal effect of catalyst concentration. The condition adjudged to be optimal for transesterification of YO and PL was at a temperature of 60°C, reaction time of 60 min and catalyst concentration of 1% w/w. Under this condition biodiesel yields were found to be 97.41% for yellow oleander methyl ester (YOME) and 95.12% for pig lard methyl ester (PLME) respectively. There was similarity in fatty acid composition in both YOME and PLME, with high oleic acid (57.84%), palmitic acid (15.56% to 18.07%), stearic acid was in the range of 15.98% to 15.65%, which placed them as better substitutes for fossil diesel. Fuel properties of blends (B10 to B50) of YOME and PLME with fossil diesel (FD) agreed with the ASTM specifications for biodiesels. The Kinematic viscosities of PLME-blends (from 3.76 mm^2/s in B10 to 4.84 mm^2/s in B90) fall within the allowable limits of 3.5 - 5.0 mm^2/s specified by ASTM D6751. The kinematic viscosities of YOME blends B60

(5.04 mm²/s) and B90 (6.53 mm²/s) were above the ASTM limit. The specific gravity of the blended fuels of PLME-FD was not affected by the increasing biodiesel portion in the blend. All the blends show low cloud points above the ASTM limit of 4°C (except for B10 and B20 blends of YOME which are 3°C and 4°C respectively). At elevated temperatures of 100°C - 250°C specific gravities of all blends decreased while kinematic viscosity decreased with increase in treatment temperature. Long time storage of biodiesel fuels showed a steady increase in flash point, density, kinematic viscosity and acid value, with a decrease in peroxide and calorific value over the storage period of 120 days. As fraction of B100 increase in blends, the calorific value decreased by 1.10% in B20, 2.43% in B40 and 2.63% in B80 in YOME blends. Rate of decrease in calorific values also gets higher with storage time. Biodiesels from mixtures of YO and PL (ratio of 1:1, 1:2, and 2:1) gave high cloud point and low cetane numbers, however, their flash points, specific gravity and viscosity were all within the ASTM limits for biodiesel. Flash points of PL:YO (1:1) FAME and PL:YO (1:2) FAME were higher than that of FD (88°C). Biodiesel from yellow oleander seed oil was found to be a better substitute for conventional diesel than biodiesel from pig lard.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations:

AGO	Automotive Gasoline Oil
ASTM	American Society for Testing and Materials
ASTM-P	ASTM colour of pig lard methyl ester blends
ASTM-Y	ASTM colour of yellow oleander oil methyl ester blends
AV	Acid value
B10	10 % biodiesel +90 % diesel
B20	20 % biodiesel +80 % diesel
B30	30 % biodiesel +70 % diesel
B40	40 % biodiesel +60 % diesel
B50	50 % biodiesel +50 % diesel
B60	60 % biodiesel +40 % diesel
B70	70 % biodiesel +30 % diesel
B80	80 % biodiesel +20 % diesel
B90	90 % biodiesel +10 % diesel
B100	100 % biodiesel
CFPP	Cold flow properties
CN-P	Cetane number of pig lard methyl ester blends
CN-Y	Cetane number of yellow oleander oil methyl ester blends
CP-P	Cloud point of pig lard methyl ester blends
CP-Y	Cloud point of yellow oleander oil methyl ester blends

CV-P	Calorific value of pig lard methyl ester blends
CV-Y	Calorific value of yellow oleander oil methyl ester blends
DI-P	Diesel index of pig lard methyl ester blends
DI-Y	Diesel index of yellow oleander oil methyl ester blends
EN	European Nations
FAME	Fatty acid methyl ester
FD	Fossil diesel
FFA	Free fatty acid
FP-P	Flash point of pig lard methyl ester blends
FP-Y	Flash point of yellow oleander oil methyl ester blends
GC-MS	Gas chromatography - mass spectrometry
IV	Iodine value
KV	Kinematic viscosity
KV-P	Kinematic viscosity of pig lard methyl ester blends
KV-Y	Kinematic viscosity of yellow oleander oil methyl ester blends
MTBE	methyl tert-butyl ether
PL	Pig lard
PLME	Pig lard methyl ester
PV	Peroxide value
SV	Saponification value
SVO	Straight vegetable oil
S-P	Sulphur (%) in pig lard methyl ester blends
SPG-P	Specific gravity of pig lard methyl ester blends

SPG-Y	Specific gravity of yellow oleander oil methyl ester blends
S-Y	Sulphur (%) in yellow oleander oil methyl ester blends
TBO	Tree bearing oil
THF	tetrahydrofuran
UAE	Ultrasonic-assisted extraction
YO	Yellow oleander seed oil
YOME	Yellow oleander oil methyl ester

CHAPTER ONE

1.0 INTRODUCTION

The world's population has relied heavily on fossil fuels for energy generation and transportation for over two centuries (Devanesan *et al.*, 2007). The rapid growth of the world's population over the past one hundred years and rapid industrialisation among nations have resulted in high energy demand in the industries as well as in the domestic sector. This has led to increase in the depletion of petroleum products and pollution problems due to the widespread use of fossil fuels. Hence, the world's reserves of fossil fuels are continually being depleted and new discoveries are smaller with lower quality (Munack *et al.*, 2001; Agbo and Oparaku, 2006).

Energy demand is growing and has been projected to increase by more than 50% in 2025 (Adams, 2002), with much of this increase in demand emerging from several rapidly developing nations like Nigeria. Fossil fuels are non-renewable and once consumed cannot be replenished. This is pointing to the fact that the supply may well run out one day. The depletion of world petroleum reserves and increased environmental concerns have led to increase in energy insecurity and hence stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand.

Going by the present rate of global fossil fuel consumption, crude oil reserves could be depleted in less than the next 50 years (Devanesan *et al.*, 2007). It has been widely reported that not less than ten major oil fields from the 20 largest world oil producers are already experiencing decline in oil reserves (Alamu *et al.*, 2007a). According to the U.S. Energy Information Administration, the global supply of crude oil, other liquid hydrocarbons, and biodiesels are expected to be adequate to meet the world's demand for liquid fuels for at least the next 25 years.

There is substantial uncertainty about the levels of future fossil fuels supply and demand, a clear indication that in some few years to come these oil reserves will be expended (EIA, 2014). This has stimulated interest in alternative sources for fossil fuels. An alternative fuel must be technically feasible, sustainable, economically acceptable and readily available (Meher *et al.*, 2006). Biodiesel is therefore gaining attention worldwide as an alternative automobile fuel.

An important factor in the search for alternative sources of fuel is the concern over greenhouse gas emission from fossil fuels. Fossil fuels such as petroleum, coal and natural gas, which have been used to meet the energy needs of man, are associated with negative environmental impacts such as global warming resulting from green house gases (Munack *et al.*, 2001; Saravanan *et al.*, 2007). These emissions such as CO₂, CO, NO₂, NO, SO₂ and SO₃ are responsible for some of the major environmental problems of urban and industrial areas and their surroundings by depleting the ozone layer and causing global warming (Turner, 2005). Also, the environmental concerns regarding greenhouse gas emissions and commitment of the International Community to significantly reduce emissions as formalised by the Kyoto Protocol (UNFCCC, 1998) adopted in December, 1997 triggered the need to find more sustainable alternatives to fossil fuels.

1.1 Renewable Energy

Biodiesel consists of the simple alkyl esters of fatty acids and is oxygenated, sulphur free, biodegradable, non-toxic and environmentally friendly alternative automotive fuel. It can be produced from renewable sources such as vegetable oils, animal fats, restaurant waste oil and frying oil. Its use does not require any major modification in the existing diesel engine. Biodiesel has been reported (Batidzirai *et al.*, 2012) to be a promising long-term renewable energy source which has potential to address both environmental impacts and security concerns posed by

current dependence on fossil fuels. The advantages of bio-fuel over the conventional diesel fuel include low smoke and particulates, low carbon monoxide and hydrocarbon emissions; improved biodegradability, reduced toxicity and higher cetane number which can improve engine performance and clean emission (Encinar *et al.*, 2007). A typical biodiesel produces about 65% less net carbon monoxide, 78% less carbon dioxide, 90% less sulphur dioxide and 50% less unburnt hydrocarbon emission (Knothe and Steidley, 2005).

The major constraint in the wide spread use of biodiesel is the production cost which includes the costs of raw materials and the process operation. The feedstocks for biodiesels are also used for food, making their prices high and may even get higher in future (USDA, 2008), hence the main hurdle to its commercialization. The cost of raw materials represents approximately 60- 75% of the total cost of biodiesel production (Jeong *et al.*, 2009; Ma and Hanna, 1999). As a future prospective, biodiesel has to compete economically with petroleum diesel fuels. One way of reducing the biodiesel production cost is to use the less expensive/low cost feed stock containing fatty acids such as animal fats, inedible oils, restaurant waste oil, frying oil, products of refining of vegetable oil instead of edible vegetable oil which could lead to food crisis (Veljkovic *et al.*, 2006; Cankci *et al.*, 2001; Mittelbatch *et al.*, 1992). These low cost feed stocks are more challenging to process because they contain high amount of free fatty acids (FFA) but could be overcome by improving on the production process through the use of two stage transesterification processes at optimum reaction conditions for maximum biodiesel yield (Kombe *et al.* 2013).

1.2 Statement of the Problem

Fossil fuel is non-biodegradable; therefore, its usage for energy generation has attracted global concern in recent times, because of its high emission of green house gases during

combustion. These emissions are the principal causes of environmental degradation, global warming and green house effects (Bells and Davis, 2006), ozone layer depletion and some incurable diseases across the globe (UCS, 2002). The fossil fuels take million of years to form and are depleting without an immediate replacement (IEA, 2009).

The ever-increasing competing demand for energy sources, coupled with the fact that fossil fuel is non-renewable, has led to the prediction that world's reserves of fossil fuel would be expended before the end of the 21st century (Shahriar and Erkan, 2009). Petroleum crises, which includes uncertainties concerning petroleum fuels availability, environment issues due to increase in Green House Gas (GHG) emission, ozone layer depletion and increasing concern over global warming pose a great risk. Also the high production cost of biodiesel emanating mainly from the feed stock and the use of edible oils could lead to food crisis. All these contending issues are worldwide concerns and have led to the global shift in reliance on fossil fuel to more environmentally friendly and sustainable source of energy in order to fulfill an increasing energy demand.

It has become also imperative to direct focus on mitigating the production cost which is primarily due to the cost of raw material by the use of low cost feed stock (animal fat) and determination of the optimum reaction conditions at which increase in the yield of the methyl ester (biodiesel) could be achieved in order to supplement the conventional petrol diesel. Research in this area has been centred on discovering and improving feedstock for biodiesel production. Several articles have been published with the aim of improving on the yield and fuel properties of biodiesel produced from different vegetable oils (Odeigah *et al.*, 2012; Knothe *et al.*, 2009; Knothe, 2008; Voca *et al.*, 2008).

1.3 Justification of the Research

Nigeria depends on imports for its supply in fossil fuels and for the past few years it has faced a crisis of oil supply and unpredictable prices. Use of fossil fuels leads to increase in greenhouse gases (SO₂, NO₂, CO₂ etc.) that lead to destruction of ozone layer and contribute to climate change. These problems provide adequate reasons and incentives to focus on renewable energy alternatives to fossil fuels. Nigeria ought to diversify its energy supply sources by developing alternative renewable sources of energy from non-edible oils to mitigate the impact of fossil fuel on its economy and the environment.

Biodiesel, among the alternative sources of energy, appears to offer the best opportunities. Biodiesel production from conventional sources such as soybean, rapeseed, sunflower and palm oil, has increasingly placed strain on food production, price and availability. High cost of edible vegetable oils is a major challenge for economic viability of biodiesel industries and can hardly be afforded by poor and underdeveloped countries. It is therefore inevitable to look for non-edible but economically viable feedstocks as an alternative to edible vegetable oils.

Several feedstocks such as karanja (*Pongamia glabra*) (Raheman and Phadatare, 2004, Sarma *et al.*, 2005), field pennycress (*Thlaspi arvense* L.) (Moser *et al.*, 2009), rubber (*Hevea brasiliensis*) (Ramadhas *et al.*, 2005), *Jatropha curcas* (Shah *et al.*, 2004; Prueksakorn and Gheewala, 2008), microalgae (*Chlorella vulgaris*) (Scragg *et al.*, 2003), terminalia (*Terminalia belerica* Robx.) (Chakraborty *et al.*, 2009), mahua (*Madhuca indica*) (Puhan *et al.*, 2005 and Raheman and Ghadge, 2007) and others are already under consideration by the world community. In Nigeria, the preferred oils for biodiesel production are the non-edible oils in appreciable quantity. Some recent studies show the utilization of non-edible oils for biodiesel

production from *Jatropha curcas* L. (Liu *et al.*, 2012) and neem seed oils (Aransiola *et al.*, 2012). Oluwaniyi and Ibiyemi (2007) reported the high oil yield of *Thevetia peruviana* seed, which could be an excellent feedstock for the biodiesel industry.

Lard is prohibited by dietary law that forbids the consumption of pork, such as ‘*kashrut*’ and ‘*halal*’. Some religions like Islam, Judaism and Hinduism do not allow their followers to consume any foods containing lard in its formulation (Regenstein *et al.*, 2003). Where the pig flesh is being processed and isolated for commercial purpose, the fatty tissues are less valued and can be obtained from the butchers at a give away price. The diminishing use of lard as food in northern Nigeria has rendered it available as feedstock for production of biodiesel in Nigeria.

The utilisation of *Thevetia peruviana* (yellow oleander) seed oil and *Sus domesticus* (pig) lard as renewable raw materials for biodiesel production in Nigeria will not affect food security. It will reduce biodiesel production cost and ensure its sustainability and availability. It will also give rise to availability of alternative fuel that meets ASTM standard which is renewable, environmentally friendly and affordable, hence mitigating green house effect and redeeming our climate.

1.4 Research Aim and Objectives

1.4.1 Aim

The aim of this work is to continue the search for sustainable renewable feedstock in biodiesel production in Nigeria by assessing the viability of using a less popular non-edible seed oil- *Thevetia peruviana* and animal fat- *Sus domesticus* for biodiesel production and to evaluate their quality as compared to ASTM standards.

1.4.2 Objectives :

- i. To determine the oil content of *Thevetia peruviana* (yellow oleander seeds) and *Sus domesticus* (pig lard);
- ii. To determine the physicochemical and fuel properties of yellow oleander seed oil and pig lard;
- iii. To determine the fatty acid composition of the yellow oleander (*Thevetia peruviana*) seed oil and the pig (*Sus domesticus*) lard and of their methyl esters;
- iv. To determine the functional groups in the yellow oleander (*Thevetia peruviana*) seed oil and the pig (*Sus domesticus*) lard and in their methyl esters (YOME and PLME);
- v. To study the effect of process variables (such as reaction temperature, time and KOH catalyst loading) in the transesterification process for biodiesel production of yellow oleander methyl ester and pig lard methyl ester using methanol and the production of biodiesel from the mixtures of the oils at optimum conditions;
- vi. To determine the physicochemical and fuel properties of the YOME, PLME, their blends and biodiesels of the mixed oils at room temperature and compare with ASTM standards;
- vii. To investigate the effect of high temperature and storage period on the stability and shelf-life of YOME, PLME and their blends.

CHAPTER TWO

2.0 LITERATURE REVIEW

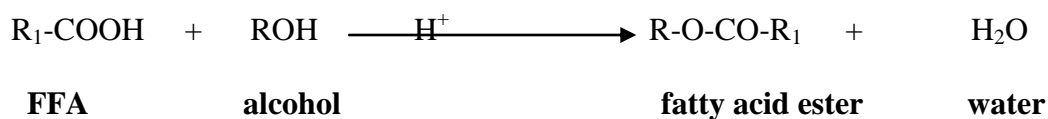
2.1 Triglycerides

Chemically, vegetable oils and animal fats are composed of triglycerides molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule (O'Brien, 2009). Different fatty acids have different physical and chemical properties, thus the fatty acid profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat. Considerable research has been done on vegetable oils as diesel fuel, some included palm oil, soybean oil, sunflower oil, coconut oil and rapeseed oil (Ajiwe, 2004; Ezeanyanaso, 2010).

The first diesel engines did not run on “diesel” fuel, but on vegetable oil (Knothe, 2001). A sample molecule of which is about three times larger than normal diesel molecules. Up to three fatty acids can be attached to the glycerin molecule, and it is named according to the number of fatty acids that are linked to it. For example, if one fatty acid is attached to the glycerin molecule it is called a monoglyceride, if two fatty acids are attached to a glycerin molecule it is called a diglyceride, and if there are three it is called a triglyceride. Vegetable oil which has ester functional groups like biodiesel has three long rows of carbon and hydrogen atoms, making it about three times larger than normal diesel molecules. The larger size of vegetable oil makes it to gel in cold weather and hard to use in an engine. Converting it into biodiesel makes it a smaller molecule, closer to the size of regular diesel, so that it has to get colder than vegetable oil before it starts to gel (Goshen College, 2013). Hence, the direct use of

vegetable oils in diesel engines results in severe engine deposits, injector choking, piston ring sticking, and high exhaust emissions.

Animal fats are waste raw materials which are more abundant than frying oils. The application of waste animal fats produced in greater amounts at several slaughter houses and other meat processing industries is very appealing also because their use as animal feed strongly decreased, due to the possibility of transmission of severe animal disease (Dias *et al.*, 2009). Utilisation of animal fats for biodiesel production is a good alternative to recycle these wastes. The use of such raw materials adds value to the wastes, which otherwise need to be further eliminated. Different animal fats, as pig lard, beef tallow, chicken fat, yellow grease and brown grease were used for biodiesel production (Moser, 2009). In comparison with biodiesel from vegetable origin, biodiesel from animal fats has the advantage of a higher calorific value and cetane number. Disadvantages include being less stable to oxidation, due to the absence of natural antioxidants and have a higher cold filter plugging point, due to greater content of saturated fatty acids (Dias *et al.*, 2009). The obtained fuel might however be used 100% pure in boilers for heat generation or mixed with other raw materials, even improving some fuel characteristics. Animal fat waste feedstocks have high free fatty acid content (Leonard, 2007). The free fatty acids (FFA) present major problem when using a base catalyzed transesterification process since the FFA react with the base catalyst to form soaps, which leads to loss of catalyst and ester product and increases production costs. This reason makes it necessary to use acid catalyst for transesterification of triglycerides and esterification of FFA (Lotero *et al.*, 2005). The FFA can react with alcohol to form ester (biodiesel); this reaction is very useful for handling oils or fats with high FFA, as is shown in equation 2.1.



Equation 2.1: Transesterification of free fatty acids with alcohol

2.2 Fatty Acid Composition of Some Oils

The triglyceride molecules consist of three long chain fatty acids that are bonded to a single glycerol molecule that makes up 90% of the total mass of a triglyceride molecule. Thus, the fatty acids have the greatest impact on the physical properties of oil.

There are many different kinds of fatty acids that differ in carbon chain length and in the number of carbon-carbon double bonds. The percentage of the different fatty acids in fats or oils varies depending on the source. Table 2.1 shows the fatty acid composition of some common vegetable oils (Goering *et al.*, 1982).

Table 2.1: Fatty acid composition in some vegetable oils (% weight) (Goering *et al.*, 1982)

Fatty acid	Formula	Cottonseed	Safflower	Soybean	Sunflower	Peanut
Myristic 14:0	C ₁₄ H ₂₈ O ₂	0.00	0.00	0.00	0.00	0.00
Palmitic 16:0	C ₁₆ H ₃₂ O ₂	28.33	8.60	11.76	6.08	11.38
Stearic 18:0	C ₁₈ H ₃₆ O ₂	0.89	1.93	3.15	3.26	2.39
Oleic 18:1	C ₁₈ H ₃₄ O ₂	13.27	11.58	23.26	16.93	48.28
Linoleic 18:2	C ₁₈ H ₃₀ O ₂	57.51	77.89	55.52	73.72	31.95
Linolenic 18:3	C ₁₈ H ₂₈ O ₂	0.00	0.00	6.31	0.00	0.93
Arachidic 20:0	C ₂₀ H ₄₀ O ₂	0.00	0.00	0.00	0.00	1.32
Behenic 22:0	C ₂₂ H ₄₄ O ₂	0.00	0.00	0.00	0.00	2.52
Lignoceric 24:0	C ₂₄ H ₄₈ O ₂	0.00	0.00	0.00	0.00	1.23

2.3 Biodiesel

ASTM International (originally known as the American Society for Testing and Materials) defines biodiesel as a mixture of long-chain monoalkylic esters from fatty acids obtained from renewable biological resources. It is obtained from triglycerides through transesterification with lower alcohols or by esterification of fatty acids (Srivastava and Prasad, 2000). Biodiesel fuel (fatty acid methyl ester (FAME) from vegetable oil, which primarily contains triglycerides (TGs) and free fatty acids (FFAs), is considered the best candidate for diesel fuel substitute in diesel engines and is used neat (100% biodiesel) or can be blended with petroleum diesel (Romano, 1982).

It has been reported by researchers that biodiesel is an ecologically friendly fuel because it is biodegradable and non-toxic, with low emission profiles (Ma and Hanna, 1999; McCormick and Alleman, 2001) than petrodiesel and decreases the greenhouse gas emissions from combustion ignition engines. The reasons for these environmental benefits are that it is an oxygenated and a biodegradable fuel (Knothe, 2005). In addition, it contains little or no sulfur or carcinogenic polyaromatic components, and decreases soot emission considerably which is safer to handle. However, biodiesel has higher values of viscosity and density that may cause injection system and combustion anomalies (Tat and Van Gerpen, 2000).

A typical biodiesel molecule would have a long chain of carbon atoms, with an ester functional group. Diesel engines can burn biodiesel fuel with no engine modifications. This is possible because biodiesel is chemically similar to fossil diesel. The fossil diesel also has the long chain of carbon and hydrogen atoms, but does not have the ester functional group in biodiesel.

2.4 Historical Development of Biodiesel

It is generally known that vegetable oils were tested as diesel fuels well before the energy crises of the 1970's. Rudolf Diesel conducted engine tests on plant oils at the World's Exhibition in Paris in 1900 (Shay, 1993), with apparently excellent results (Knothe *et al.*, 2001) and received the *Grand Prix* (highest prize). 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. Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan and China have been reported to have tested and used vegetable oils as emergency diesel fuels and other purpose fuels during the 1920s and 1930s and later during World War II.

Work on vegetable oils as diesel fuel ceased in India when petroleum-based diesel fuel became available again plentifully at low cost (Amrute, 1947). 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 which could result in engine break down on long term usage (Srivastava and Prasad, 2000). This was due to the high viscosity of vegetable oils compared to petroleum diesel fuel. Attempts to overcome these problems included heating of the vegetable oil, blending it with petroleum derived diesel fuel or ethanol, pyrolysis and cracking of the oils.

The first account of the production of what is known as "biodiesel" today was on August 31, 1937, when G. Chavanne of the University of Brussels (Belgium) was granted a patent for a

"Procedure for the transformation of vegetable oils for their uses as fuels". This patent described the alcoholysis (often referred to as transesterification) of vegetable oils using methanol and ethanol in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa in 1979 and by 1983, the process for producing engine-tested quality biodiesel fuel was completed and published internationally (Wei *et al.*, 1983). The three most widely used technologies are Pyrolysis, Microemulsification and Transesterification

2.5 Biodiesel Feedstocks

Biodiesel can be produced from a variety of renewable lipid sources, including soybeans, rapeseed, sunflower, cottonseed, palm seed and palm kernel, corn, mustard seed oil and peanut (Schuchardt *et al.*, 1998; Ajiwe *et al.*, 2003; Ajiwe, 2004).

However, the food industry imposes a direct competition for some of these oil sources and this may be critical for a world whose population is increasing exponentially. For these and other reasons, non-edible oil sources are preferable for biodiesel production, particularly those requiring low agronomic demand for cultivation, a reasonable plant cycle, favorable geographic adaptability, high oil content and a low cost for cultivation and harvesting (Ezeanayanso, 2010). Other sources from various non- edible vegetable oils like Copaiba, Honge oil, *Jatropha curcas* and neem seed), waste vegetable oil (WVO) and animal fats (like tallow, lard, yellow grease, chicken fat and so on) have been tested (Leonard, 2007).

Microorganisms especially microalgae, have been selected for biodiesel production because of their high biomass, higher lipid content and environmental friendliness. Microalgae is also a non-edible material, therefore, there will be no impact on the human food supply chain.

Fossil diesel (PD) and biodiesel from the microalgae *Chlorella protothecoides* (B20) blend have been found to give good performance with a significant reduction in CO, CO₂ and NO emissions (Al-lwayzy and Yusaf , 2013).

A number of microorganisms belonging to the genera of yeast, fungi, bacteria and microalgae have been investigated as sources of oils and found to have substantial amounts of oil, sometimes up to and even in excess of 70% of their biomass weight under specific cultivation conditions (Huang *et al*, 2010; Kais *et al*, 2011; Thevenieau and Nicaud, 2013). Yeast, for its easy availability, rapid growth, high lipid accumulation capacity, capability to grow on a variety of materials has been used for oil extraction (Gohel *et al*, 2013). Today, with the great progress of metabolic and genetic engineering, the developments are focused on the high value oils containing important polyunsaturated or specific fatty acids.

2.5.1 *Jatropha curcas*

Jatropha curcas L. is a non-edible oil-bearing plant widespread in arid, semi-arid and tropical regions of the world (Bosswell, 2003) that produces a significant amount of oil from its seeds in the range of 30 to 50% by weight of the seed and range of 45 to 60% by weight of the kernel itself (Pramanik, 2003).

2.5.2 Yellow oleander

In Nigeria, notable among the non-edible less known seeds are castor, *jatropha* and yellow oleander. The yellow oleander (*Thevetia peruviana*) is an ever – green ornamental dicotyledonous shrub or small tree that belongs to the order apocynales and Apocyanaceae family (Dutta, 1964). It is commonly found in the tropics and sub-tropics but it is native to Central and South America. *Thevetia peruviana* made its way to Nigeria over fifty years ago, and has been grown as an ornamental plant in homes, schools and churches by missionaries and

explorers (Ibiyemi *et al.*, 2002). It is a drought resistant plant, with yellow trumpet like flowers (Plate 2.1) and grows well in all parts of Nigeria. It can be grown in arid zones as well as in higher rainfall zones and even on land with thin soil cover. It will tolerate most kinds of soil as long as they are well drained and is situated in full sun in a sheltered area. In fact it is a popular hedging and once established needs no care besides the annual pruning.

The yellow oleander flowers and fruits (Plate 2.2) all year round providing a steady supply of seeds (Plate 2.3). Grown as hedges, they can produce between 400 – 800 fruits per annum depending on the rainfall pattern and plant age. It grows to about 10-18 feet high; the leaves are spirally arranged, linear and about 13 – 15cm in length (Olisakwe *et al.*, 2015).



Plate I: Yellow oleander flowers



Plate II: Fruits of yellow oleander plant



Plate III: *Thevetia* nuts containing *Thevetia* seeds

The fruits are somewhat globular, with fleshy mesocarp and have a diameter of 4 – 5 cm. The fruits are usually green in colour and become black on ripening. Each fruit contains a nut which is longitudinally and transversely divided. The fruit contains between one to four seeds in its kernel, and the plants bears milky juice in all its organs. All parts of the plant, especially the seeds are toxic due to the presence of glycosides. It contains a milky sap containing a compound called thevetin that is used as a heart stimulant but in its natural form is extremely poisonous. The seed contains 60 – 65 % oil and the cake comprises of 30 – 37% protein (Ibiyemi *et al.*, 2002). According to Oluwaniyi (2007) the crude lipid ranges from 4.40 to 4.80/100 g. Despite the fact that there is high level of oil and protein in the seed, it remains non – edible because of cardiac glycoside (toxins). The physicochemical properties of *Thevetia peruviana* oil can be used for the preparation of oleo chemicals such as soap, shampoos, alkyd resin and biodiesel (Usman *et al.*, 2009). The above stated properties of this plant suggest that it can be used as feedstock for production of biodiesel in Nigeria.

2.5.3 Lard

Lard is pig fat in both its rendered and unrendered forms. Lard can be obtained from any part of the pig as long as there is a high concentration of fatty tissue. Lard is one of the few edible oils with relatively high smoke point, attributable to its high saturated fatty acids content (Rohman *et al.*, 2012). Lard contains considerable proportions of palmitic acid, stearic acid, oleic acid and linoleic acid. There are small amounts of palmitoleic acid and traces of linoleic acid, arachidonic acid and myristic acid (Rohman *et al.*, 2012).

Lard is an important dietary item, and was widely used to produce shortenings, margarines and other speciality food oils (Marikkar *et al.*, 2005). It has been an important cooking and baking staple in cultures where pork is allowed. In certain countries, the producers

of food products prefer to blend vegetable oils with lard in order to reduce the production cost (Rohman and Che Man, 2010). Lard is commonly used to manufacture soap (Davidson, 2002). By the late 20th century, lard had begun to be considered less healthy than vegetable oils because of its high saturated fatty acid and cholesterol content. Many restaurants in the western nations have for this reason and health-related dietary restrictions, eliminated the use of lard in their kitchens. The diminishing uses of lard as food have rendered it available as feedstock for production of biodiesel in Nigeria. Pig waste were transformed to biodiesel by sulphuric acid pretreatment (esterification) and sodium hydroxide transesterification; a purity of 99.6wt. % was obtained (Dias *et al.*, 2009).

2.6 Methods of Oil Extraction

Extraction is the first step in the refining process of oils. It is the isolation of oil from animal by-products, fleshy fruits such as the olive and palm, and oilseeds such as cottonseed, sesame seed, soybeans, and peanuts. Oil is extracted by three general methods: rendering, mechanical pressing and extracting with volatile solvents.

Available work done on the extraction of oil from oil seeds includes work by Khan and Hanna (1983) who observed that oil yields from jatropha seeds were improved by increasing temperature, pressure and pressing time. Investigation was carried out by Orhevba, *et al.*, (2013) to determine the effect of pressure on the yield of neem seed kernel oil expressed using a multiseed oil expeller. An improvement in neem seed kernel oil yield was recorded with increase in pressure. Some of the methods usually employed for the extraction of oil are briefly discussed below.

2.6.1 Traditional methods

A traditional oil press comprises of a container with bored holes and rods fitted at the sides. A rotating wood is fitted in the centre of the container serving the role of a compressor. Oil is extracted from fresh coconut, olives, palm fruit, shea butter and so on, by separating the flesh and boiling it in water. In palm oil processing the fruit is first heated in a 'digester'. The boiled palm nuts are poured into the traditional pressing machine where they are crushed. During the crushing of the nuts warm water is poured into the machine. The juice seeps through the bore holes of the container and drains into the basin. The collected juice which floats on water can now be separated easily. The juice is boiled until the water completely evaporates (Nyanjou, 2008).

2.6.2 Manual methods

In this method, the oilseeds, usually pre-ground, are pressed in manual screw presses. Oil can be extracted by pressing softer oilseeds and nuts, such as groundnuts, melon, *Jatropha* and sheabutter, whereas harder, more fibrous materials such as copra and sunflower seed are processed using ghanis. A ghani consists of a large pestle and mortar rotated either by animal power or by a motor. Seed is fed slowly into the mortar and the pressure exerted by the pestle breaks the cells and releases the oil. This is more efficient at removing oil than traditional hand squeezing, allowing higher production rates (Achaya, 1993)

2.6.3 Mechanised extraction

Mechanical pressing is the oldest and simplest method for oil extraction. No chemical is used for oil extraction. Continuous screw-presses replaced the conventional hydraulic presser equipment (Bargale, 1997). Mechanical extraction of the oil is accomplished by exerting sufficient force on confined seed. Under this condition, pressure is high enough to rupture the

cells and force oil from the seed to “escape”. Extraction is accomplished by compressing the material in a container that has small perforations, either round or slotted, that allow the liquid component to leave (Antony *et al.*, 2011).

Motorized presses are faster than manual or animal types but are more expensive. Expellers are continuous in operation and work by grinding and pressing the raw material as it is carried through a barrel by a helical screw. The pressure inside the barrel, and hence the yield of oil, are adjusted using a ‘choke’ ring at the outlet. The equipment has higher production rates than similar sized presses but is more expensive to buy and operate. The production rate of expellers depends on the size of the equipment, the speed of the screw and the setting of the choke ring (Deli *et al.*, 2011).

2.6.4 Solvent extraction method

Solvent extraction is achieved by first grinding the seed before it is purged with petroleum distillate which releases the oil in the seed. The solvent is then distilled off by heating the oil in a sealed chamber. Oils have been extracted from various seeds: *Jatropha curcas*, *Pentaclethra macrophylla* and soybean, using petroleum ether (Akinsiku, 2013).

Hexane solvent extraction can be used in isolation or it can be used along with the oil press/expeller method. After the oil has been extracted using an expeller, the remaining pulp can be mixed with cyclo-hexane to extract the remaining oil content. The oil dissolves in the cyclohexane, and the pulp is filtered out from the solution. The oil and cyclohexane are separated by means of distillation. These two stages (cold press and hexane solvent) together will be able to derive more than 95% of the total oil present in the seed.

2.6.5 Soxhlet extraction method

Soxhlet extraction is a method that uses chemical solvents. Oils from the seeds are extracted through repeated washing, or percolation, with an organic solvent such as hexane or petroleum ether, under reflux in special glassware (Ana-Godson and Udofia-Bassey, 2015). The Soxhlet extractor consists of a glass reservoir which is between a lower flask at the bottom and a condenser at the top. Inside the reservoir sits a thimble-shaped filter in which the seed sample is placed at the start of the procedure. Once the sample for extraction is placed in the thimble of the extractor, the flask is heated at 60°C with the use of an electric mantle. As the solvent (n-hexane) is heated up from the lower flask in the boiler, the pure vapor will rise through a by-pass and into the top part of the Soxhlet container (thimble) where the sample to extract is contained. In the condenser, the vapors condensed and drip steadily into the sample-containing thimble. This allows the oil components of the seed sample to be extracted. When the level of liquid reaches the same level as the top of the siphon, the liquid containing the extracted material is siphoned back into the boiler.

2.6.6 Ultrasonic-assisted extraction (UAE)

Oil extraction method based on ultrasonic waves involves the disintegration of cell structures by means of ultrasound for the extraction of intra-cellular compounds. Using an ultrasonic reactor greatly accelerates extraction processes. The process of extracting oil through this method is known as cavitations. Cavitations occur when vapour bubbles of a liquid form in an area where pressure of the liquid is lower than its vapour pressure (Paula and Roberto, 2011).

Ultrasound assisted extraction (UAE) is an emerging potential technology that can accelerate the heat and mass transfer and has been successively employed in the extraction field (Karami *et al.*, 2013). UAE allows better yields and a lower extraction temperature as

compared to the conventional methods.

Ultrasonic extraction has proven to be equally or more efficient than soxhlet extraction. Soxhlet extraction is a time consuming method, involving large volume of solvent and exposure to the hazard of boiling solvents. Compared to soxhlet method, ultrasonic technique usually provides a relatively low cost method, low extraction time, using small volume of organic solvent and simplicity of the apparatus and extraction procedure. Ultrasonic irradiation has proven to have almost no harmful intermediates of concern to humans (Kitajima *et al.*, 2006).

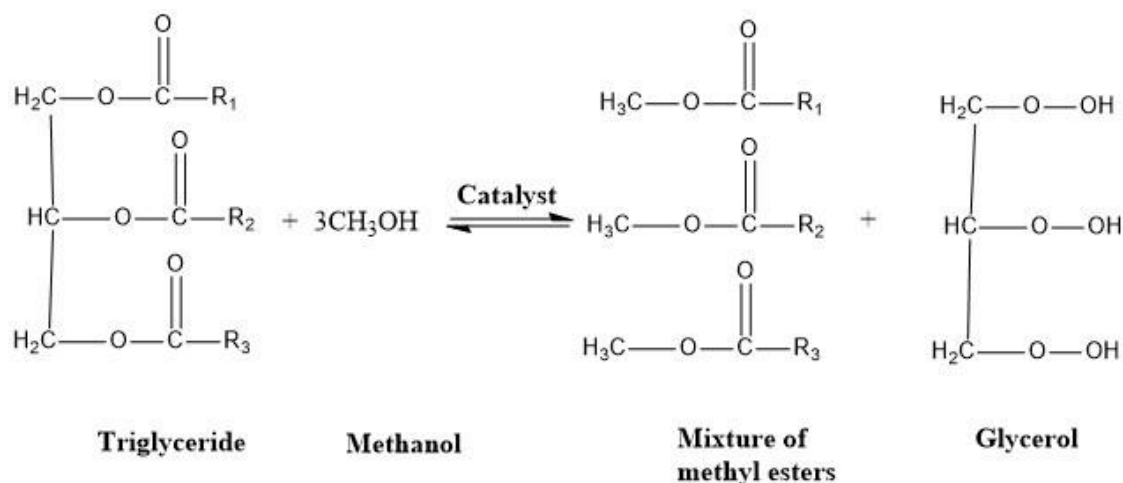
2.7 Production of Biodiesel

2.7.1 Transesterification process

Transesterification has been reported as the key and foremost important step in the production of cleaner and environmentally safe fuel from vegetable oils (Shahid and Jamal, 2007; Canoira *et al.*, 2006; Ashri and Kumar, 2014). Transesterification or alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that alcohol is used instead of water (Srivastava and Prasad, 2000). This process has been widely used to reduce the high viscosity of triglyceride. In the reaction, the triglyceride reacts with an alcohol in the presence of a catalyst to form another ester through interchange of the alkoxy moiety. This lowers the viscosity of the oil by way of transforming the large, branched molecular structure of the bio-oils into smaller, straight chain molecules of the type required in regular diesel combustion engines.

In the transesterification process, an alcohol is deprotonated with a base to make it a stronger nucleophile. The reaction has no other inputs than the triglyceride and the alcohol. Methanol and ethanol are commonly used in transesterification process, especially methanol because of its low cost and its physical and chemical advantages (polar and short chain alcohol).

It can quickly react with triglycerides and NaOH is easily dissolved in it. In this case, the reaction is referred to as methanolysis. The stoichiometry of methanolysis reaction requires 3 moles of methanol and 1 mole of triglyceride to give a mixture of three fatty acid methyl ester and 1 mole of glycerol as shown in equation 2.2.



Equation 2.2: Transesterification reaction of vegetable oils or animal fats

The symbols R₁, R₂ and R₃ represent straight chain fatty acids. The alcohol reacts with the fatty acids to form the mono-alkyl ester (biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so excess alcohol must be added to ensure complete conversion. The transesterification process can be done in a number of ways such as using an alkali catalyst, acid catalyst, biocatalyst or heterogeneous catalyst.

After transesterification of triglycerides, the products are a mixture of fatty acid methyl esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics (Srivastava and Prasad, 2000).

Under normal conditions, the reaction will proceed either exceedingly slowly or not at all, so heat, and catalysts (acid and/or base) are used to speed up the reaction. Common catalysts for transesterification include sodium hydroxide, potassium hydroxide and sodium hydroxide.

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids) (Stidham *et al.*, 2007; Aliyu *et al.*, 2013). Biodiesel produced from other sources or by other methods may require acid catalysis, which is much slower (Ataya *et al.*, 2007). The transesterification reaction is given in equation 2.3.

2.7.2 Base catalysed transesterification

In a base catalysed transesterification, alkaline metal hydroxides like sodium hydroxide (NaOH) or potassium hydroxide (KOH) are used as a catalyst (Meher *et al.*, 2006), as well as sodium or potassium carbonates (Vargha and Truter, 2005) along with methanol or ethanol. In the process, the triglycerides with low free fatty acids content (< 0.5%) are readily transesterified batchwise at atmospheric pressure and a temperature of approximately 60 – 70°C in the presence of an excess of methanol (Srivastava and Prasad, 2000; Zhang *et al.*, 2003). In the transesterification process, the catalyst first of all reacts with the alcohol to form an alkaline metal alkoxide, which in turn reacts with the triglyceride to form biodiesel and glycerol (Freedman *et al.*, 1986; Schwab *et al.*, 1987) as shown in scheme 1.

Pre-step:

Scheme 2. 1: Mechanism of base catalysed transesterification of vegetable oils

For an alkali-catalyzed transesterification, the glycerides and alcohol must therefore be substantially anhydrous because water makes the reaction partially change to saponification. The soap produced lowers the yield of biodiesel and renders the separation of ester and glycerol as well as the water washing difficult (Ma and Hanna, 1999). However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the

hydroxide with the alcohol. Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water, which does not hydrolyse the esters. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification (Fukuda *et al.*, 2001; Barnwal and Sharma, 2005).

It has been investigated and reported that in base-catalysed transesterification of oils from *Jatropha curcas*, *Azadirachta indica* and *Hevea brasiliensis*, alkaline metal alkoxides are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if applied at low molar concentrations (0.5M) (Ezeanayanso *et al.*, 2011; Helwani *et al.*, 2009). Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are good alternatives since they give the same high conversions of the oils when the catalyst concentration is increased to 1 or 2 mol % (Schuchardt *et al.*, 1998).

Base catalyzed transesterification is much faster than acid-catalyzed transesterification, and is the most common commercial method for production of biodiesel (Ma *et al.*, 1998; Ahmad *et al.*, 2009). In the base transesterification reaction, the catalysts (e.g. potassium and sodium hydroxide) which are hazardous, caustic, and hygroscopic must be neutralized and discarded as an aqueous salt waste stream. Removal of these catalysts from the product is technically difficult and could add extra cost to the final product (Ma *et al.*, 1998; Ahmad *et al.*, 2009).

2.7.3 Acid-catalysed transesterification

The second conventional way of producing biodiesel is using an acid catalyst instead of a base. If more water and free fatty acids are in the triglycerides, acid catalyzed transesterification can be used (Keim, 1945). Any mineral acid can be used to catalyze the

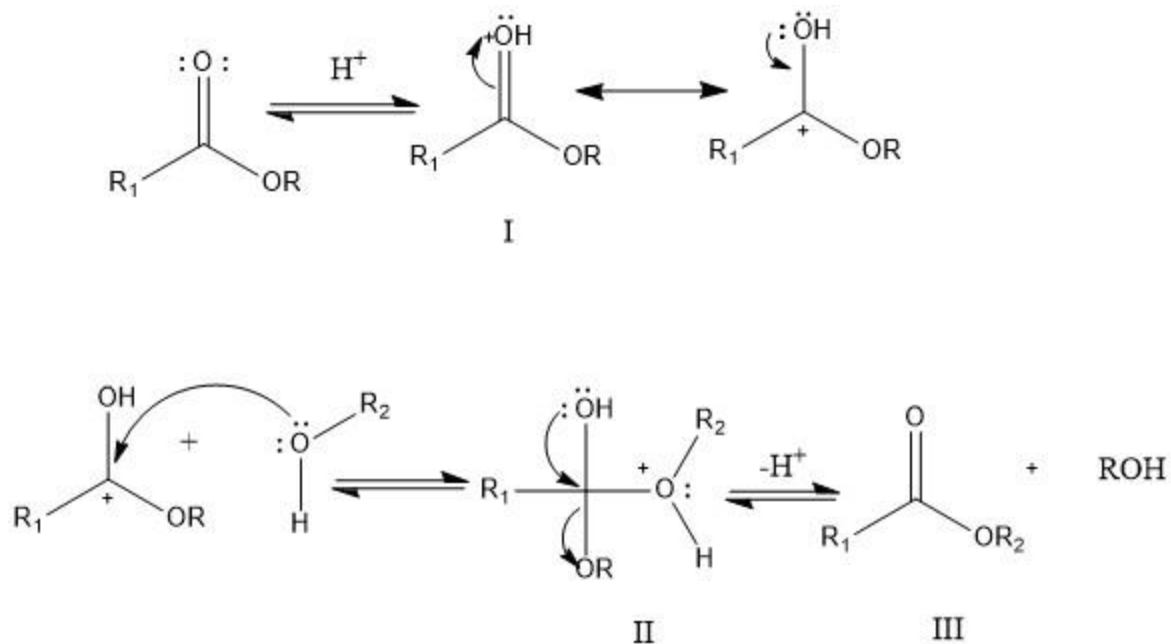
production of biodiesel. The most commonly used acids for this process are sulphuric acid and sulphonic acid. Acid catalysed transesterification of the triglycerides give very high yields of alkyl esters, but the acids, being corrosive, may cause damage to the equipment. The reaction rate of acid catalysed transesterification has been observed to be low and hence requires very high temperature and might take several days to complete the conversion (Freedman *et al.*, 1984).

For oils with high concentration of free fatty acids (acid value higher than 2 mg KOH/g), an esterification reaction step is recommended. Good results concerning the reduction of the acid value were achieved even with high initial percentages of free fatty acids (Canakci and Gerpen, 2001; Pereda Marin *et al.*, 2003). The initial step for the transesterification is protonation of the carbonyl group of the ester by the acid to give a carbocation intermediate (**I**) which undergoes a nucleophilic addition reaction with the alcohol forming a tetrahedral intermediate (**II**) which breakdown by proton migration and eliminates alcohol to form the new ester (**III**), and to regenerate the catalyst H^+ .

Each step in the process is reversible, but in the presence of a large excess of the alcohol (oil to methanol molar ratio > 6), the equilibrium point of the reaction is displaced so that transesterification proceeds virtually to completion (Pathak, 2015). Soap formation is not a problem because there are no alkali metals in the reaction medium.

According to an acid catalysed mechanism for esterification, the presence of water in the reaction mixture can readily form carboxylic acids by hydrolysis of the carbocation intermediate formed upon protonation of the ester. This ultimately stops the reaction; usually well before reaching completion (Ejikeme *et al.*, 2013). Therefore an acid-catalyzed transesterification

should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduces the yields of alkyl esters.



Equation 2.3: Acid catalysed transesterification of triglycerides

2.7.4 Two-step acid-base catalyzed transesterification

This involves acid catalysis followed by alkali catalysis. This approach solves the reaction rate problem by using each technique to convert high free fatty acid (FFA) feedstocks quickly and effectively. Since acid catalysis is relatively fast for converting the FFAs to methyl esters, it is used as a pretreatment for the high FFA feedstocks. Then, when the FFA level has been reduced to 0.5%, or lower, an alkali catalyst is added to convert the triglycerides to methyl esters. Water formation due to the presence of free fatty acids is still a problem during the pretreatment phase. One approach is to simply add so much excess methanol during the pretreatment that the water produced is diluted to the level where it does not limit the reaction. Molar ratio of alcohol to free fatty acid as high as 30:1 may be needed to reduce the free fatty

acid to 1% using hydrochloric acid catalyst (Alptekin *et al.*, 2011). The disadvantage of this approach is that more energy will be required to recover the excess methanol.

2.7.5 Transesterification using lipase-catalyst

The high energy cost of the conventional chemical process and additional purification step of glycerol, have made the application of lipase in the biodiesel industry to be more attractive (Selmi and Thomas, 1998). It has been found that enzymes such as lipase can be used to catalyze transesterification process by immobilizing them in a suitable support (Mendes *et al.*, 2012). The advantage of immobilization is that the enzyme can be reused without separation. Also, the operating temperature of the process is low (50°C) compared to other techniques. Disadvantages include inhibition effects which were observed when methanol was used and the fact that enzymes are expensive (Nelson *et al.*, 1996; Shimada *et al.*, 2002).

The common aspects of these studies include optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems.

2.7.6 Transesterification using heterogeneous catalyst

Heterogeneous catalysts such as amorphous zirconia, titanium-, aluminum-, and potassium-doped zirconias have also become popular for catalyzing the transesterification of vegetable oils. This process, which is referred to as heterogeneous catalysis, utilizes fixed-bed reactors, and the catalyst stays in the reactor and is used for an extended time. Sulfonic resins such as Nafion® NR50, sulphated zirconia (SZ) and tungstated zirconia (WZ) have sufficient acid site strength to catalyze biodiesel forming transesterification reactions as efficiently as sulphuric acid (Lopez *et al.*, 2005; Sharma *et al.*, 2011). Alkaline earth metal oxides, various

alkaline metal compounds supported on alumina or zeolite can also catalyze transesterification reactions. In general, heterogeneous catalysis systems are designed for continuous operation and produce high-purity glycerine (greater than 98 percent). The product, fatty acid esters, does not require water washing, and yields are generally high. It has been reported that the conversion to methyl ester reaches 87% with the potassium-loaded alumina catalyst, when a mixture with a molar ratio of methanol to oil of 15:1 is refluxed for a reaction time of 7 h (Xie *et al.*, 2006; Jitputti *et al.*, 2006).

The heterogenization of guanidines on organic polymers and their use in the transesterification of vegetable oils were tested (Schuchardt *et al.*, 1988; Crabbe *et al.*, 2001) and shown to be efficient catalysts.

2.7.7 Non-catalytic conversion techniques

Due to poor methanol and oil miscibility, use of a co-solvent that is soluble in both methanol and oil may improve reaction rates. Saka and Kusdiana have firstly proposed that biodiesel may be prepared from vegetable oil via non-catalytic method with supercritical alcohol. In the presence of a co-solvent, the reaction is 95 percent complete in 10 minutes at ambient temperatures and does not require a catalyst. (Saka and Kusdiana, 2001).

Supercritical fluids (SCFs) are good solvents for many substances when compressed into its state of above the critical temperature and critical pressure. SCFs have both gas-like viscosities and liquid-like densities. Compared with the traditional chemistry method, this novel method requires no catalyst and nearly complete conversion can be achieved in a very short time. So it successfully overcomes most problems in conventional chemical processes. However, the synthesis of biodiesel by supercritical methanol has a drawback with high cost of apparatus due to the high temperature and pressure, which are not viable in the large practice in industry.

Because supercritical methanol method has so many advantages, many researchers have focused on how to improve the reaction conditions (such as shorten reaction time, decrease reaction temperature, and pressure).

Co-solvent process is another option in non-catalytic biodiesel production. Use of co-solvent is a way to obtain a single-phase system for non-catalytic transesterification but at potentially lower temperatures and pressures than the values for supercritical alcohol. Co-solvent options are designed to overcome slow reaction time caused by the extremely low solubility of the alcohol in the triglyceride phase. This system is also known as BIOX process which makes use of a co-solvent that helps to overcome the slow reaction time. (Cao *et al.*, 2005) used propane as a co-solvent for biodiesel production from soybean oil with methanol. In their study, the critical point of the mixture is reduced with increasing amounts of propane which is a good solvent for vegetable oil, allowing a single phase to be formed in the mixture. This use of propane reduces the amount of methanol required and results in a significant reduction in the system pressure. The reaction conditions that gave the best results (98% yield in 10 min) in their study were a temperature of 280°C, propane to methanol molar ratio of 0.05, methanol to oil ratio of 24 and a system pressure of 12.8 MPa (Cao *et al.*, 2005).

Another approach is to use either tetrahydrofuran (THF) or Methyl Tetra-Butyl Ether (MTBE) as a co-solvent to generate a one-phase system (Sawangkeaw *et al.*, 2007). The result is a fast reaction, on the order of 5 min and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. This system requires a rather low operating temperature, 303 K (30°C) (Balt and Balat, 2010). Han *et al.*, (2005) used CO₂ as co-solvent and reported that about 0.98 of FAME

yield was obtained from a batch reactor in 10 min at 553 K, 14.3 MPa, methanol to oil molar ratio of 24:1 and CO₂ to methanol molar ratio of 1:10. There is a clean separation of glycerol and the ester. The products obtained finally are water and catalyst free. The excess methanol and co-solvent are easily recovered in a single step after the reaction is complete and the co-solvent recycled (Singh and Taggar, 2014). Adding proper co-solvent may lower the critical points of the reacting mixtures which may result in decrease of required temperature and pressure in the reactor.

2.7.8 Non-ionic base-catalyzed processes

Among the non-ionic bases frequently used in organic synthesis are amines such as triethylamine, piperidines like 1,2,2,6,6-pentamethyl piperidine, pyridines like 2,6-ditert-butylpyridine and 4-dimethyl-amino pyridine (DMAP) (Schuchardt *et al.*, 1998). The activity and efficiency of such non-ionic bases as catalysts for the transesterification of vegetable oils were studied (Ejikeme *et al.*, 2010). The catalytic activity of some guanidines was compared to that observed using other bases such as the amidines. It was observed that guanidines such as 1,5,7-triazabicyclo (4,4,0) dec-5-ene (TBD), even if applied at only 1 mol % produces more than 90% of methyl ester after 1 hour. Using the other bases, under the same experimental conditions, the yields were not higher than 66%.

The good performance of TBD, when compared to triamino (imino) phosphoranes, is related to its catalytic site (unshared electron pair of the sp² N), which is practically unhindered allowing an easy access of the methanol for proton transfer, while the steric hindrance shown by the triamino (imino) phosphoranes is so significant that they are practically inert to alkylating agents (Schuchardt *et al.*, 1998).

2.8 Factors Affecting Transesterification Process

Transesterification reaction is strongly affected by several factors, including the type and concentration of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, reaction temperature, reaction time, purity of the reactants (mainly water content) and free fatty acid content.

2.8.1 Effects of moisture and free fatty acids

The water and Free Fatty Acid (FFA) contents are critical factors for transesterification. Base-catalyzed transesterification requires water free and low acid value (< 1) raw materials (Demirbas, 2009) for biodiesel production. If the oil samples have high FFA content (more than 1%) then the reaction requires more alkali catalyst to neutralize the FFA. Presence of water gives greater negative effect than that of FFAs because water can cause soap formation and frothing which cause increase in viscosity. In addition formation of gels and foams hinders the separation of glycerol from biodiesel (Demirbas, 2009). Water and FFA also lead to the reduction of methyl ester yield.

To overcome this problem, Demirbas, 2002 and Balat, 2008 studied the transesterification reaction using supercritical methanol and the best methyl ester yield was 95%. The supercritical transesterification method is more tolerant to the presence of water and FFAs than the conventional alkali-catalyzed technique, and hence more tolerant to various types of vegetable oils, even for fried and waste oils (Demirbas, 2007).

2.8.2 Effect of molar ratio of methanol to oil

According to Mathiyazhagan and Ganapathi (2011), molar ratio of alcohol to triglyceride plays a vital role in biodiesel yield. The stoichiometric ratio for transesterification requires three

moles of alcohol and one mole of glyceride to yield three moles of fatty acid methyl ester and one mole of glycerol. Excess amount of alcohol increases conversion of fats into esters within a short time. So the yield of biodiesel increases with increase in the concentration of alcohol up to certain concentration. However further increase of alcohol content does not increase the yield of biodiesel but it rather increases the cost of alcohol recovery (Leung and Guo, 2006).

The molar ratio is associated with the type of catalyst used. An acid catalyzed reaction needs a 30:1 ratio of butanol to soybean oil, while an alkali-catalyzed reaction requires only a 6:1 ratio to achieve the same ester yield for a given reaction time (Freedman *et al.*, 1986).

Akhihiro *et al.*, (2013) studied the effect of molar ratio variation on the yield of biodiesel from the transesterification of *Jatropha* seed oil with methanol using various concentrations of sodium hydroxide catalysts. The result showed that a methanol/oil molar ratio of 8:1 with NaOH concentration of 1% w/w gave the optimum yield of biodiesel. Biodiesel yield was found to reduce with increasing NaOH concentration and higher methanol/oil ratio. This is because at higher methanol/oil ratio, the excess methanol reacted with the NaOH to form soap instead of speeding up the production of biodiesel.

2.8.3 Effect of catalyst type

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed (Freedman *et al.*, 1984; Zhang *et al.*, 2003). However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable. This is due to the fact that acid catalyst reduces the FFA content and water content present in the oil samples.

Currently, most biodiesels are prepared using alkaline catalysts such as sodium hydroxide and potassium hydroxide. Even though transesterification is feasible using homogeneous base

catalysts, the overall base catalysed process suffers from serious limitations that translate into high production cost for biodiesel. Leung *et al.* (2010) used KOH as catalyst in the transesterification process and obtained a maximum yield of biodiesel at 0.5 wt% of KOH, but the yield decreases as wt% of KOH increases beyond 0.5 wt % due to soap formation .

However, Freedman *et al.* (1984) found that sodium methoxide would be more effective because mixing of sodium hydroxide with methanol produces a small amount of water which inhibits the formation of the biodiesel as a result of hydrolysis reaction (Umaru *et al.*, 2014). This is one of the reason for mixing of catalyst with methanol first before adding to the oil or fats. Sodium hydroxide was also chosen to catalyze the transesterification because it is cheaper. Ester conversions at the 6:1 ratio for 1% (w/v) NaOH solution and 0.5% NaOCH₃ were almost the same after 60 min (Aransiola *et al.*, 2010; Freedman *et al.*, 1984). The transesterification of soybean oil with methanol, ethanol and butanol, using 1% concentrated sulphuric acid, was unsatisfactory when the molar ratios were 6:1 and 20:1 (Canakci and Van Gerpen, 1999). A 30:1 ratio resulted in a high conversion to methyl ester. More recently, an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion greater than 98% (Jackson and King, 1997).

2.8.4 Effect of catalyst concentration

Catalyst concentration can affect the yield of the biodiesel product (Leung *et al.*, 2010). Usually, the conversion of triglycerides and the yield of biodiesel increase with the catalyst concentration increasing. This is because an insufficient amount of catalyst results in an incomplete conversion of the triglycerides into the fatty acid esters (Leung and Guo, 2006). However, if the catalyst amount is in excess of the optimal concentration, the biodiesel yield

would decrease a little, which is due to the excess alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Dorado *et al.*, 2002).

The effect of different catalyst concentrations on base-catalyzed transesterification during biodiesel production from vegetable oil by means of ultrasonic energy has been investigated by Stavarache *et al.* (2005). Best yields were obtained when the catalyst was used in a small concentration of 0.5 % (w/w) of oil.

2.8.5 Effect of reaction time

The yield of biodiesel is nearly independent of reaction time but the methyl ester concentration increases with increased reaction time. This is due to the increasing of mixing and dispersion of methanol in oil phase with reaction time, which is in accord with the work of Freedman *et al.* (1984). The reaction time will be directly proportional to the percent yield of biodiesel obtained. The rate of conversion increases with the length of reaction time. Diglycerides and monoglycerides at the beginning of the reaction time, will increase and then decrease. In the end, the amount of monoglycerides will be higher than diglycerides. And monoglycerides required for the transesterification reaction (Ma and Hanna, 1999).

Liu and Wang, (2013) observed that in the beginning, the reaction is slow due to the mixing and the dispersion of methanol into oil, but with time the biodiesel yield increases very quickly in the reaction time range of 30 – 60 min. Moreover, excessive reaction time leads to a bit reduction in the product yield due to the backward reaction, resulting in a loss of esters as well as causing more fatty acids to form soaps (Gashaw and Teshita, 2014).

2.8.6 Effect of reaction temperature

Reaction temperature is another important factor that affects the yield of biodiesel. For example, increasing reaction temperature increases the reaction rate and shortens the reaction time due to the reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides (Mathiyazhagan and Ganapathi, 2011) and causes methanol to vaporise resulting in decreased yield (Anitha and Dawn, 2010).

Usually the transesterification reaction temperature should be below the boiling point of the alcohol in order to prevent it from evaporation. The range of optimal reaction temperature may vary from 50°C to 60°C depending upon the oils or fats used (Mathiyazhagan and Ganapathi, 2011). Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion (Jagadale and Jugulkar, 2012) . According to Ogbu and Ajiwe, 2013, appreciable transesterification of up to 78% can be achieved at room temperature after 60 minutes. Temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in much faster reactions.

2.8.7 Effect of agitation speed

Oils and alcohols are not totally miscible, thus reaction can only occur in the interfacial region between the liquids and transesterification is a moderately slow process. So, adequate mixing is very important in the transesterification process, to promote contact between these two feedstocks. Mechanical mixing is commonly used in the transesterification process. The intensity of the mixing could be varied depending on its necessity in the transesterification process. When vegetable oils with high kinematic viscosity are used as the feedstock, intensive mechanical

mixing is required to overcome the negative effect of viscosity to the mass transfer between oil, alcohol and catalyst (Jagadale and Jugulkar, 2012; Kansedo, 2009).

In transesterification reaction, agitation speed plays an important role in the formation of the end product (biodiesel). At a mixing speed of 400 rpm, higher conversion to biodiesel was obtained (Mathiyazhagan and Ganapathi, 2011). Due to the reverse behaviour of transesterification reaction, lower agitation speed slows down the end product formation; however, higher stirring speed favors formation of soap (Mathiyazhagan and Ganapathi, 2011).

2.9 Biodiesel Blends

Biodiesel's physical properties are similar to those of petroleum diesel, but the biodiesel significantly reduces greenhouse gas emissions and toxic air pollutants. Biodiesel can be used in its pure state or blended with petroleum based diesel fuel. Biodiesel can be blended in many different ratios. These include B100 (pure biodiesel), B20 (20% biodiesel, 80% petroleum diesel), B5 (5% biodiesel, 95% petroleum diesel), and B2 (2% biodiesel, 98% petroleum diesel) (Ali *et al.*, 2013). The most common biodiesel blend is B20, which qualifies for fleet compliance under the Energy Policy Act (EPA Act) of 1992. Biodiesel blended up to B20 can work in any diesel engine with few or no modifications to the engine or the fuel system

The current mandates regarding the use of biodiesel around the world are mostly based on a biodiesel–diesel blend up to 20% biodiesel. The B20 blend provides a superior diesel fuel with a higher cetane rating, superior lubricity and significant emission reductions. Cold weather can cloud and even gel any diesel fuel, including biodiesel, but using a 20 percent biodiesel blend will cause an increase of the cold flow properties (cold filter plugging point, cloud point, pour point) by approximately 1 ° C. Biodiesel blends have powered thousands of vehicles, in the

United States and is used both as a 5 % blend in France up to 100% neat fuel in Austria and Germany (National Biodiesel Board, 1996). The use of biodiesel blends could reduce CO₂ accumulated in the atmosphere by 78% due to CO₂ recycling by growing plants. In addition, other harmful substances such as particulate matter (PM), hydrocarbons (HC), and carbon monoxide (CO) are considerably reduced (U.S. Department of Energy, 2004).

The biodiesel energy content is less than that of mineral diesel, therefore using of additive must not worsen the energy content of the blend fuel. Because biodiesel has lower energy content compared to diesel resulting from its chemical structure, the blending of biodiesel with additive that have less energy content usually causes the energy content of the fuel to decrease depending on the additive energy content and portion. Currently, the energy content is one of the major technical issues in the use of biodiesel–diesel blends, as it relates to the engine power (Ali *et al.*, 2013).

2.10 Fuel Properties of Oils and Biodiesels

In order to test the quality of biodiesel as a diesel fuel substitute, the American Society of Testing and Materials (ASTM) has set a standard for biodiesel as a fuel for use in diesel engines. Numerous properties are included in the standard, such as kinematic viscosity, cetane number, flash point, sulfur content, water content, free glycerol, total glycerol. It is important to control the quality of biodiesel to meet the ASTM standard shown in Table 2.4 before using it in a diesel engine.

2.10.1 Cetane number

The cetane number of the fuel, specified by ASTM D-613, is a measure of its ignition quality. Cetane numbers measure the ignition of diesel, much like octane numbers measure the ignition of gasoline. Cetane number represents the time from when fuel is injected into an engine

and when the combustion process starts. This time for combustion figure serves as an effective means of measuring fuel quality, as better-quality fuels will ignite more quickly. A fast-igniting fuel generally contains fewer contaminants and impurities than one that takes longer to ignite.

Biodiesel has a higher cetane number than fossil diesel, largely because of its higher oxygen content (Jackson and King, 1996). Hence, biodiesel may provide cetane enhancement when used neat or in blends, and may provide emission benefits that have been correlated to cetane number. Higher cetane numbers (as high as 55 to 60) generally improve diesel emissions, but above that level little improvement is demonstrated.

It is important to note that biodiesel's cetane number can vary widely, based on differences in fatty acid composition of the feedstock oil and the saturation level of the fatty acids (Saka and Kusdiana, 2001). Cetane number increases with chain length, decreases with number and location of double bonds, and changes with various locations of the carbonyl group. Cetane numbers increase from 47.9 to 75.6 when the number of carbons increases from 10 to 18 in the fatty acids of biodiesel. When the number of carbons in the fatty acid chains exceeds C12, the cetane number exceeds 60.

For soy methyl ester, reported cetane numbers range from 45.8 to 56.9. The variation is due to the distribution of carbon chain lengths in each fuel tested. The average of the available data is 51.3 (Freedman and Bagby, 1990). Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion.

Table 2.2: ASTM D6751 requirement for biodiesel and blends (NREL, 2008)

Property	Test Method	Specification	Units
Flash point, closed cup	ASTM D93	130°C Min	°C
Water and sediment	ASTM D2709	0.050 Max	Vol. %
Kinematic viscosity, 40°C	ASTM D445	1.9-6.0	mm ² /s
Sulfated ash	ASTM D874	0.020 Max	Mass %
Sulfur	ASTM D5453	0.0015 Max	Mass %
Copper strip corrosion	ASTM D130	No. 3, Max	-
Cetane number	ASTM D613	47, Min	-
Cloud point, °C	ASTM D2500	No established limit	°C
Carbon residue	ASTM D4530	0.050 Max	Mass %
Oxidation stability	EN14112	3 min.	H

2.10.2 Acid value

Acid number (value) determines the acidic or basic constituents in petroleum products and lubricants. The total acid number is the quantity of base expressed in milligram of KOH that is required to neutralize all acidic constituents present in 1g sample and is measured using the AOCS Method (1990). The acid value is often a good measure of the breakdown of the triacylglycerol into free fatty acids, which has an adverse effect on the quality of many fats (MPOB, 2005). It reflects the amount of free fatty acid content in biodiesel ester. This is done by dissolving the sample and titrating with alcoholic potassium hydroxide (AOCS, 1990).

For biodiesels, the acid number is an indicator of the quality of the product. Specifically, it detects the presence of any unreacted fatty acids still in the fuel, or of any acids that were used

in processing. This is also an indication of the condition of the stability of the fuel, because the acid number increases as the fuel ages (NREL, 2001). For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Total acidity should be low in order that corrosion of metals in contact with the fuel during storage and distribution is minimised.

2.10.3 Cold flow properties

Cold flow properties are the parameters for low temperature applications of a fuel and are controlled by the cloud point (CP) and pour point (PP). The CP of a fuel is defined by ASTM-D2500 as the temperature at which wax crystals first become visible in the form of a haze, and is related to the warmest temperature at which these will form in the fuel when it is cooled under prescribed conditions. In the case of biodiesel, the haze is made up of crystallized fuel molecules, specifically crystallized stearic and/or palmitic methyl esters (Knothe and Dunn, 2001).

The pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. The pour point as defined by ASTM-D97 is always lower than the cloud point. At this temperature the fuel can no longer be pumped. The pour point and cloud point are both higher for biodiesel fuel than for gasoline-based diesel, indicating that biodiesel will tend to gel at higher temperatures than diesel, causing engine problems. (Lee *et al*, 1996).

Cloud point values vary depending on the type of mix of esters in the feedstock used, with animal fat generally having a higher cloud point temperature due to the presence of saturated (i.e. single bond) fatty acids. The monoglycerides cause turbidity (crystals) in the mixture of esters. This problem was very obvious, especially for transesterification of animal fats such as beef tallow (Ma, 1998). The impurities raised the cloud and pour points. Also a large

proportion of saturated fatty acid esters in beef tallow esters (almost 50% w/w) make the cloud and pour points higher than that of vegetable oil esters. A reduction in the cloud point can be achieved through the use of anti-gel additives. Additives called flow improvers do not generally affect the cloud point of convectional diesel however; they do reduce the size of the crystallites formed when the fuel cools.

2.10.4 Kinematic viscosity

Kinematic viscosity is referred to as the thickness of the oil (flow properties) and is defined as resistance to flow of liquid due to internal friction between the liquid and the surface, under a reproducible driving head and at a closely controlled temperature. It plays an important role in the performance of the fuel system of engine operating through wide range of temperatures. It affects the fuel injection system as low viscosity can result in an excessive wear in injection pumps and power loss due to pump leakage whereas high viscosity may result in excessive pump resistance, filter blockage, coarse atomization and fuel delivery rates.

Viscosity is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Kinematic viscosity is increased with the carbon chain length in biodiesel containing free fatty acids and hydrocarbons. However, the kinematic viscosity of diesel is lower, and the increasing trend in viscosity over time is lower as diesel is less oxygenated than biodiesel (Lin and Li, 2009).

The ASTM-D445 specification for viscosity at 40°C of 4 centistokes is generally met by biodiesel and biodiesel blends. However, the kinematic viscosity of biodiesel and its blends is higher than diesel. Soy methyl ester is reported to have a kinematic viscosity ranging from 3.8 – 4.1 centistokes at 40°C (Bajpai and Tyagi, 2006). Fuel atomization is also affected by fuel viscosity. Highly viscous fuel would take longer time to mix with air since the quality of the

vaporization and atomization of the fuel is reduced. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions. The kinematic viscosity of biodiesel and biodiesel blends also increases more rapidly than diesel as temperature is decreased. Certain impurities also tend to significantly increase the viscosity of biodiesel (McGowan, 2011).

2.10.5 Heat of combustion

Heat of Combustion is the amount of heat energy released by the combustion of a unit volume of fuel. The bomb calorimeter requires the burning of a certain mass of oil sample in the presence of oxygen at a certain temperature and time and then determining the heat involved. This heat value is called the Gross Calorific Value (GCV) or Performance Energy content. The energy content of diesel fuel is the heat released when a known quantity of fuel is burned under specific conditions. The energy content of biodiesel that meets the ASTM standard is more dependent on the raw materials used during biodiesel production than the particular process. One of the most important determinants of heating value is moisture content. However, the energy content of biodiesel is much less variable than fossil diesel.

The heat of combustion is an important parameter for estimating fuel consumption. The greater the heat of combustion, the lower is the fuel consumption (Knothe *et al.*, 2008). The heat of combustion increases with increasing chain length and decreases with increasing unsaturation. Generally, fuel consumption is proportional to the volumetric energy density of the fuel based on the lower or net heating value. The energy content of biodiesel and diesel is 37 MJ/kg and 45MJ/kg respectively (Bajpai and Tyagi, 2006).

2.10.6 Flash point

Flash point as defined by ASTM-D93 is a measure of the temperature to which a fuel must be heated such that a mixture of the vapour and air above the fuel can be ignited (Bajpai and Tyagi, 2006). It is the minimum temperature at which the fuel's vapour catches fire inside the cup. This is achieved by ASTM D-93 test method, where a fuel sample is heated inside a Flash cup closed tester with continuous/interruptive stirring and a small flame brought near to it at regular interval (ASTM, 2008). All convectional diesel fuels have high flash points, 54°C minimum and 71°C typical. The flash point of neat biodiesel is typically greater than 93°C and a flash point below 93°C is considered to be out of specification (ASTM, 2008). The U.S. department of transportation considers a material with a flash point of 93°C and above to be non-hazardous. (Divya and Iyago, 2006). If the biodiesel has not flashed at 160°C, the test is finished and the result is reported as >160°C (ASTM, 2008).

Flash point has no bearing on performance but is important largely from the point of view of safety in handling the fuel and minimum values are usually specified. Flash point measures the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. Flash point is used in shipping and safety regulations to determine flammable and combustible materials. Flash point can indicate the possible presence of highly volatile materials in a relatively non-volatile material.

2.10.7 Specific gravity and density

Density is the measure of the mass per unit volume, which is expressed in gram per cubic centimeter (g/cm^3). Fuel density generally increases with increasing molecular weight of the fuel molecules. Specific gravity is the ratio of the density of a liquid to the density of water at a stated temperature. Specific gravity is usually quoted at 15° C, which is 15 °C / 15 °C. Biodiesel

exhibits specific gravity between 0.86 – 0.90 depending on the feed-stock used. The specific gravity of most oils and their methyl esters is higher than that of diesel fuel. That is, specific gravity of vegetable oils and methyl ester depends on their molecular weight and chemical structure (free fatty acid content) (Saeid *et al.*, 2008,; Pramanik, 2002). Also some important performance indicators such as Cetane number and heating value are correlated with specific gravity (Tat and Van Gerpen, 2000). It is also an important parameter in connection with fuel storage and transportation (Alamu, 2007a). The variation in densities and viscosities of methyl esters of some fatty acids has been studied and was observed to vary linearly with temperature (Tate *et al.*, 2006; Liew *et al.*, 1992).

2.10.8 Iodine value

Iodine value (IV) is a measure of the total number of double bonds present in fats and oils. It is expressed as the "number of grammes of iodine that will react with the double bonds in 100 grammes of fats or oils". The determination is conducted by dissolving a weighed sample in a non-polar solvent such as cyclohexane, then adding glacial acetic acid. The double bonds are reacted with an excess of a solution of iodine monochloride in glacial acetic acid ("Wijs' solution"). Mercuric ions are added to hasten the reaction. After completion of the reaction, the excess iodine monochloride is decomposed to iodine by the addition of aqueous potassium iodide solution, which is then titrated with standard sodium thiosulphate solution. An increase in iodine value indicates high susceptibility of lipid to oxidative rancidity due to high degree of unsaturation.

2.11 Oxidative Stability of Biodiesel

The biodiesel quality is affected by large number of parameters including oxidation, thermal and storage stability. Although biodiesel is environmentally compatible, it is susceptible

to oxidation. Oxidative stability is measured by ASTM D2274 and when compared to diesel fuels, biodiesel fuels are far more prone to oxidation. Stability of fatty compounds is influenced by factors such as presence of air, heat, traces of metal, peroxides, and structural features of the compounds themselves, mainly the presence of double bonds. The degree of saturation of the fatty acid chains tends to be correlated with its stability. The trend of increasing stability is linolenic acid < linoleic acid < oleic acid which are present in significant amounts in almost all biodiesels (Knothe and Dunn, 2003). The corresponding esters undergo auto-oxidation at different rates depending upon the number and position of the double bonds and results in formation of a series of by-products, like acids, esters, aldehydes, ketones, lactones, which limits the use of biodiesel as fuel (Barnwal, 2011; Madarasz and Kumar, 2011). As the linoleic (18:2) and linolenic (18:3) acids content in fatty oils or esters increases, the oxidation stability decreases and as fatty oils or the alkyl monoesters of fatty oils are oxidized, the hydroperoxide (ROOH) levels also increased indicating the drop in the quality of the oil or esters (Refaat, 2009).

Biodiesel is safe to store and the properties of biodiesel should conform to respective standards after it has been stored for a long time. There are several key factors that need to be considered for the storage of biodiesel, including exposure, temperature, oxidative stability, fuel solvency and material compatibility (Leung *et al.*, 2006). The storage temperature of most pure biodiesel is generally kept between 7 and 10°C to avoid the formation of crystals which can plug fuel lines and fuel filters (Lee *et al.*, 1995). Even in extremely cold climates, underground storage of pure biodiesel usually provides the storage temperature necessary for preventing crystal formation (Gerpen *et al.*, 2004). Bondioli *et al.*, (1995) noted that the stability of biodiesel is an important property when it is to be stored for a prolonged period. Poor stability can lead to

an increased acid value and fuel viscosity and to the formation of gums and sediments. Therefore, if the duration of storing biodiesel or biodiesel blends is more than 6 months, it should be treated with an antioxidant additive (Van Gerpen *et al.*, 2004). Moreover, because water contamination will lead to biological growth in the fuel, it should be minimized in the stored fuel by using biocides. Biodiesel storage tanks made of aluminium, steel, Teflon and fluorinated polyethylene or polypropylene should be selected. The tanks should minimize the possibility of water contamination and should be cleaned prior to use for biodiesel storage.

Thermal stability is related to the degree of unsaturation of the fatty acids constituting the oils. Normally, the higher the unsaturation in the oil, the lower is the thermal stability. This could be evidenced by the lower boiling point of the unsaturated fatty acids compared to their saturated equivalents (Sricharoenchaikul and Atong, 2009). Jain and Sharma, (2010) on the stability of biodiesel and their blends with fossil diesel under different conditions, reported that vegetable oil, fats and their biodiesel suffer with the drawback of deterioration of its quality during long term storage unlike fossil diesel. The low oxidation stability of biodiesel hinders its long-term storage (Kivevele *et al.*, 2011; Karavalakis *et al.*, 2011; Jain and Sharma, 2011; Dantas *et al.*, 2011).

2.12 Gas chromatography - mass spectrometry (GC-MS)

Gas chromatography- mass spectrometry (GC-MS) has been used to characterize biodiesels and to determine product yield (methyl esters) and conversion efficiency. Biodiesel from different or even from the same source may have different chemical structures and consequently different properties. Analysis using GC-MS can show specific fatty acids in the oils and biodiesel (Chin *et al.*, 2009). The composition of the fatty acids influences the fuel properties. The type and concentration of fatty acids has an outstanding effect on the specific

physico-chemical properties of biodiesel (Litty and Nithya, 2012; Knothe, 2009; Moser, 2009; Knothe and Steidly, 2005). Though the cost of the GC-MS equipment is prohibitive and its usage requires intensive sample preparation, it has the advantage of not requiring standard of samples to be analyzed. It is highly sensitive and can be used to identify a compound, and if there is noise in the analysis, it will not complicate the reading of analysis results (Suparman *et al.*, 2015).

CHAPTER THREE

3.0 MATERIAL AND METHODS

3.1 Chemicals

All chemicals and reagents used were of analytical grade purchased from Merck, Germany.

3.2 Sample Collection and Preparation

Yellow oleander pods were collected from the Ahmadu Bello University main campus Zaria and Rigachikun village, near National Teachers' Institute (NTI), Kaduna during the months of November and December, 2012. Lard from domestic pig (*Sus domesticus*) was purchased at the Mami Market, Basawa Army Barracks in Zaria.

The dry pods of yellow oleander were de-hulled manually by crushing the hard shell using a locally fabricated nut cracker machine. After which the shells were carefully separated from the kernels by hand. The seeds were crushed to produce fine seed powder to expose larger area from which oil was extracted. The extraction of the oil was achieved with the help of a manual hand-held grinder which was operated batch-wise.

The ground seeds (1.00 kg) were placed in an oil press machine and the oil extracted manually. The expelled oil was filtered using a cloth sieve into a beaker. The difference in weight of the seed sample just before and after the extraction of oil was taken as the weight of oil expelled. Percentage of oil yield was then calculated thus:-

$$\% \text{ Oil yield} = \frac{\text{weight of oil expelled in g} \times 100}{\text{Weight of ground seed used(g)}} \quad 3.1$$

3.3 Pig Lard Preparation

The pig fat was obtained from the part of the pig with a high concentration of fatty tissue that occurs in the abdominal cavity. The fatty tissues were cut into small pieces and a portion (1.00 kg) of the pig fat was weighed and rendered dry by melting it at 90–100°C for 30 min in a beaker in the absence of water under atmospheric pressure to avoid any degradation (Sharma *et al.*, 2013). The melted lard was strained through triple-folded muslin cloth, dried using anhydrous Na₂SO₄ and then centrifuged at 3000 rpm for 20 min. the content was filtered using Whatman filter paper (18µm). The filtrate was then weighed and repeated thrice and the average taken. The percentage yield of lard was determined as in equation 3.2. The processed pig lard was stored in air tight opaque plastic jars to prevent oxidation.

$$\% \text{ Lard} = \frac{\text{weight of lard} \times 100}{\text{Initial weight of pig fat (g)}} \quad 3.2$$

3.4 Determination of Fatty Acid Composition (Pearson, 1981).

The gas chromatographic analysis of the yellow oleander seed oil, pig lard and their respective biodiesels was made using Agilent 7890A series chromatograph equipped with a Mass Spectrometer Detector (Make No. 5975). For the ester concentration of the biodiesels to be analyzed, the gas chromatograph was equipped with a capillary column of dimension 30m x 250µm x 0.25µm packed with non-polar HP-5. The column temperature was programmed initially at 100°C for 20 min, and then increased to 180°C at the rate of 10°C/min, for 10 min and then increased to 290°C. The inlet temperature was set at 300°C. Acquisition was carried out using SCAN mode.

The samples were first methylated to the more volatile methyl esters by dissolving 0.125g of the oil in 5.0cm³ of n-hexane. This was then followed by the addition of 0.5 ml of 5M sodium methoxide solution and vigorously shaken. The methylated sample was diluted in hexane and 1µl of this solution was injected into the column at a temperature of 230°C, and a detector temperature of 240 °C, while the nitrogen gas was maintained at 5.5Psi. The injection was performed in split mode with a split ratio of 50:1. Helium was used as the carrier gas at a flow rate of 0.8cm³/m. The fatty acids were eluted as peaks. The identification of peaks was done by comparison of their retention times and mass spectra with NIST05 Library (Fu *et al.*, 2008).

3.5 Transesterification of the Oils

3.5.1 Preparation of reagents

Na₂S₂O₃ (0.1 M) Solution: Sodium thiosulphate (1.8 g) was weighed into a 50cm³ beaker and dissolved in 20cm³ distilled water and the solution transferred into a 1000cm³ volumetric flask and made up to the mark with distilled water.

KI Solution (10 % w/v): Potassium iodide (10 g) was dissolved in 20cm³ distilled water and the solution transferred into a 100cm³ volumetric flask and made up to the mark with distilled water.

Starch indicator (1%): Reagent grade starch (1 g) was dissolved in hot water in a beaker and the clear fraction was transferred into 100cm³ volumetric flask and made up to the mark.

Wijs' reagent : Wijs' solution was prepared by dissolving 8 g iodine trichloride in 200cm³ glacial acetic acid. Iodine (9 g) was also dissolved in 300 cm³ carbon tetrachloride and the two solutions mixed and diluted to 1000cm³ with glacial acetic acid. The Wijs' reagent was stored in a glass-stoppered amber bottle.

Alcoholic KOH (0.5 M): KOH (7.00 g) pellet was dissolved in 20 cm³ ethanol and the solution transferred into a volumetric flask (250 cm³) and made up to the mark with ethanol.

Phenolphthalein indicator: Phenolphthalein (0.25 g) was dissolved in a volumetric flask (250 cm³) and made up to the mark with ethanol.

3.5.2 Base - catalysed transesterification of yellow oleander seed oil and pig lard

The method of Meher *et al.* (2006) was adopted for the base - catalysed transesterification of the oils. Exactly 25cm³ methanol (20.0 g) was transferred into a 500cm³ conical flask and potassium hydroxide (1.0 g) was carefully added into the container and stoppered. The container was swirled round thoroughly for about 2 minutes until the potassium hydroxide was completely dissolved in the methanol to form potassium methoxide. The oil (100.0 g) was filtered into a clean dry conical flask and heated to 55 - 60°C on a hot plate equipped with magnetic stirrer, with the magnetic stirrer switched off. The prepared potassium methoxide was carefully added to the flask. The hot plate and the magnetic stirrer were then switched on and mixture stirred at low speed of 100 rpm and temperature maintained at 60°C for 90 minutes.

As soon as the transesterification process was completed, the mixture was transferred into a separating funnel and allowed to stand. The reaction mixture was allowed to stand for 24 hours while phase separation occurred by gravity settling. The glycerin by-product settled as a distinct layer at the bottom of the funnel, with a clear line of separation from the paler liquid above which is the biodiesel. The glycerin was carefully drained off, leaving the top layer of biodiesel in the separating funnel. The biodiesel was washed with water according to the method described by Alamu *et al.* (2007b) and Alamu *et al.*(2008) to neutralize and remove the catalysts. The

biodiesel was then carefully transferred into clean dry bottle and the yield determined. The procedure was replicated three times and the average biodiesel yield was then calculated.

$$\% \text{ biodiesel yield} = \frac{\text{weight of biodiesel produced(g)} \times 100}{\text{weight of raw oil used (g)}} \quad \mathbf{3.3}$$

Batch transesterifications of yellow oleander seed oil and pig lard (100 g each) were carried out in a 250 ml Erlenmeyer flask. This was done on a temperature regulatory hot plate with magnetic stirrer, keeping the rate of agitation low. Biodiesels were produced from the yellow oleander seed oil and pig lard using the same procedure of Meher *et al.*(2006) at different reaction temperatures of 30°C, 40°C, 50°C, 60°C, or 70°C. Different catalyst concentration of 1% w/w and 0.5 % w/w were used for each biodiesel production temperature. Each reaction was allowed to run for various periods of 30 min, 45 min, 60 min, 75 min and 90 min and biodiesel yield determined. Results were presented in Appendix v.

Biodiesel were also produced from a mixture of yellow oleander seed oil and pig lard, in the ratios of 1:1, 1:2 and 2:1 v/v proportions. These oil mixtures had FFA content of 0.87% , 1.43% and 1.19% respectively. Hence, esterification with an acid catalyst to bring down the FFA level of the oil mixture with FFA levels of 1.43% and 1.19% to around 1% was required. A two-step ‘acid-base’ process where an acid (H₂SO₄) pretreatment was followed by the main base-transesterification reaction described by Meher *et al.* (2006). The biodiesel produced were labeled as YO/PL(1:1) FAME, YO/PL(1:2) FAME and YO/PL(2:1) FAME respectively and their various fuel properties determined at room temperature using the ASTM methods. Results were presented in Tables 4.11-4.15

3.5.3 Biodiesel blending

Biodiesel-diesel blends were prepared by mixing biodiesel with fossil diesel in ratios of 10:90 up to 90:10 of biodiesel (incremental of 10% by volume) to fossil diesel (10% decreasing volume) and labeled as B10 – B90 respectively. The ink tank method (Krishna, 2003) of petrol blending was adopted. Samples of yellow oleander oil methyl ester and fossil diesel were prepared as B10 (10%vol. YOME + 90%vol. diesel), through mixing and blending using electrical magnetic stirrer. The mixtures were stirred continuously for 20 minutes and left for 30 minutes to reach equilibrium at room temperature before they were subjected to any test. The same procedure was followed for pig lard methyl ester to obtain blends of B10, B20, B30, up to B90. The blends were centrifuged for homogeneity before proceeding with fuel analysis using ASTM standards. Results were presented in Appendices vi-vii.

3.5.4 Temperature treatment of biodiesels

The method involved heating biodiesel samples of yellow oleander methyl ester and pig lard methyl ester and their blends in a closed vessel at elevated temperatures of 100°C, 150°C, 200°C and 250°C. The fuel properties of the treated biodiesels were then determined to test for their thermal stability at elevated temperatures. The same treatment was carried out on the biodiesel samples of YO:PL(1:1), YO:PL(1:2) and YO:PL(2:1) from mixed oils. Results were presented in Appendix viii - x

3.5.5 Storage of biodiesel

Biodiesel samples (100 g) each of yellow oleander methyl ester and pig lard methyl ester were taken into 250 cm³ conical flasks and stoppered. The storage of the biodiesel fuel samples was done at room temperature without addition of additives and agitation was avoided so as not to increase exposure to oxygen. At the end of 60 days storage period a portion of the biodiesel

sample was withdrawn and tested for fuel properties. The storage period was extended to 120 days and another test on the fuel properties was carried out to see the effect of storage period on biodiesels. Results were presented in Appendice xi –xv.

3.6 Determination of Physicochemical Properties of Yellow Oleander Seed Oil and Pig Lard

3.6.1 Preparation of reagents

Alcoholic KOH (0.5 M) solution: KOH (7.00 g) pellet was dissolved in 20 cm³ ethanol and the solution transferred into a volumetric flask (250 cm³) and made up to the mark with ethanol.

Phenolphthalein indicator: Phenolphthalein (0.25 g) was dissolved in a volumetric flask (250 cm³) and made up to the mark with ethanol

HCl (0.5 M) solution: From concentrated hydrochloric acid, 42.37cm³ was accurately measured and dissolved in a 1000cm³ volumetric flask and made up to the mark with distilled water.

3.6.2 Determination of saponification value (AOAC, 1980)

Procedure: The oil (2.0 g) was weighed accurately into a 250 cm³ conical flask containing 25 cm³ of 0.5 M alcoholic KOH solution. A reflux condenser was fitted to the flask and heated in a water bath for an hour, swirling the flask frequently to ensure that the sample was fully dissolved. The excess KOH solution was titrated hot with 0.5M HCl solution using 1 cm³ of phenolphthalein indicator until a pink endpoint was reached. A blank determination was also carried out. The saponification value was calculated using equation 3.4:

$$\text{Saponification value (mg KOH/g oil)} = \frac{56.1 \times C \times (V_0 - V)}{M} \quad 3.4$$

Where: V = Volume (cm^3) of the 0.5M HCl solution used in blank.

V_o = Volume (cm^3) of the 0.5M HCl solution used in assay with oil.

M = mass in g of oil used and

C = molar concentration of HCl solution used

56.1 = Relative molar mass of KOH

3.6.3 Acid value determination and free fatty acid (%FFA) (Pearson, 1991)

The oil was filtered and heated to about 100°C to remove traces of water. The oil sample (5.00 g) was then weighed into a clean dried 250cm^3 conical flask, containing 25cm^3 absolute ethanol. To this was added 2-3 drops of phenolphthalein indicator and the mixture heated with shaking in water bath for 10 minutes. It was allowed to cool and then titrated against 0.1 M alcoholic potassium hydroxide solution, shaking constantly until a pink colouration persisted for at least 10 seconds. The volume of KOH solution used was recorded and the acid value was determined according to equation 3.5:

$$\text{Acid value (mg KOH/g oil)} = \frac{56.1 \times C \times V}{\text{weight of oil sample(g)}} \quad \mathbf{3.5}$$

Where, V = Volume of the potassium hydroxide solution used (in cm^3)

C = Molar concentration of potassium hydroxide solution used

56.1 = Relative molar mass of KOH

The acid value determination was followed by the free fatty acid (%FFA) determination as:

$$\% \text{ Free Fatty Acid (FFA)} = \text{Acid Value} \times 0.503 \quad \mathbf{3.6}$$

3.6.4 Reduction of free fatty acid (% FFA)

Where the FFA was found to be higher than 1.0 %, acid esterification was employed to reduce the free fatty acid value to less than 1%. The oil (100g) in a 250 cm³ conical flask attached to a thermometer and placed in a hot plate with a temperature controller was heated to 60°C while being stirred mechanically at 800 rpm under atmospheric conditions to homogenize it.

To reduce the %FFA of the oil, a mixture of 2.25 g methanol and 0.05 g conc. sulphuric acid was added for each gram of free fatty acid in the oil and warmed for 15 minutes on a hot plate. This mixture was then transferred slowly into the 250 cm³ conical flask containing the oil followed by the addition of methanol (20.0g) and stirred (800 rpm) for 1 hour at 60°C to esterify.

The mixture was allowed to stand for 1 hour and the methanol-water mixture which rose to the top was decanted. The bottom fraction was now the pre treated oil and the FFA remaining was determined again as in section 3.6.3, in order to ensure it was less than 1.0% before base transesterification of the oil.

3.6.5 Determination of specific gravity (Williams, 1966)

A clean and dry stoppered density bottle of 25 cm³ capacity was weighed empty and the weight recorded as W_o . The density bottle was then filled with distilled water, stoppered and maintained in a water bath at 15°C for 10-15 min for the water to assume the bath temperature. The outside of the bottle was wiped, dried and reweighed as W_1 . The bottle was emptied, washed with water and dried. It was then filled with the oil and equilibrated to 15°C in the water bath. The outside of the bottle was again wiped dry and weighed as W_2 .

The specific gravity of each sample was calculated using the expression below:

$$\text{Specific gravity at } 15^{\circ}\text{C} = \frac{(W_2 - W_o)}{(W_1 - W_o)} \quad \mathbf{3.7}$$

Where, $(W_2 - W_o)$ = mass of sample.

$(W_1 - W_o)$ = mass of an equal volume of water.

3.6.6 Determination of iodine value (AOCS, 1988)

Procedure: The oil (0.2g) was weighed in a dry 250cm³ conical flask and 10cm³ of chloroform was added and swirled until it dissolved. Wijs' solution (20cm³) was added and the stopper previously moistened with potassium iodide solution was inserted immediately, then swirled and allowed to stand in the dark for 30 min with occasional swirling. Any free iodine on the stopper was washed down using 10 cm³ 15% (w/v) potassium iodide solution and thoroughly mixed with 100 cm³ of freshly boiled and cooled distilled water. The mixture was swirled again and titrated against 0.1 M sodium thiosulphate solution using starch indicator. The titration was continued until the blue colour just disappeared after shaking. The titre value was recorded as V₁. A blank determination was carried out with 100 cm³ of chloroform (titre value = V₂). Iodine value was determined using the formula.

$$\text{Iodine value} = \frac{(V_2 - V_1) \times C \times 12.69}{\text{Weight of sample (g)}} \quad \mathbf{3.8}$$

Where, C = concentration of sodium thiosulphate solution used

V₁ = volume of sodium thiosulphate solution used for sample

V₂ = volume of sodium thiosulphate solution used for blank

3.6.7 Determination of refractive index (IUPAC, 1979)

Refractive index of oil samples was determined at temperatures of 30°C, 40°C and 60°C respectively using Abbe refractometer. A few drops of oil was placed on the surface of a prism of the refractometer and allowed to gently spread. The refractometer was closed and tightened for 15 minutes for the oil and the prism to attain a steady temperature. The refractive index was then read from the demarcation line after adjusting it to coincide with the diagonal crossing. The sum of the main scale reading and the venier scale reading gave the refractive index of the oil which was read off directly at the various temperatures. This was performed three times and the average determined.

3.6.8 Determination of peroxide value (AOAC, 2005)

The oil sample (5g) was weighed into a dry 250 cm³ conical flask and powdered potassium iodide (5.0 g) was added. A solvent mixture (20 cm³) of chloroform and glacial acetic acid (1:2) was then added and swirled to dissolve. The flask was stoppered, agitated for 1 min and placed in a boiling water bath so that the contents were boiled for 30 seconds. Thereafter, 35cm³ of distilled water was added, mixed and the free iodine liberated was titrated with 0.1 M sodium thiosulphate solution until the yellow colour of iodine disappeared. Soluble starch solution (1 %) was then added as indicator and the titration continued until the blue color of the solution just disappeared. The titre value was recorded as V₁. Blank determination was also carried out and the titre value recorded as V₀. The peroxide value was computed from the relationship:

$$\text{Peroxide value (meq/kg oil)} = \frac{(V_1 - V_0) \times C \times 12.69}{\text{Weight of sample (g)}} \quad \mathbf{3.9}$$

Where, M = mass(g) of oil sample used.

C = exact molarity of sodium thiosulphate solution.

V_1 = volume (cm^3) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution used for sample titration.

V_0 = volume (cm^3) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution used for blank titration.

3.7 Determination of Fuel Properties

3.7.1 Determination of kinematic viscosity (ASTM D445, 2006)

A Redwood viscometer was used to measure the kinematic viscosity of the samples. The determination of kinematic viscosity was carried out by introducing about 50 cm^3 of the sample into a clean dried viscosity tube. This was done by inverting the tube thinner arm into the sample and then using suction force to draw up the oil to the upper timing mark of the viscometer. The instrument measured the time of gravity flow in seconds of fixed volume of the fluid (50cm^3) through specified orifice made in an agate piece.

The viscometer was placed into a holder and inserted into a constant temperature bath set at 40°C temperature and allowed for 30 minutes for the sample to come to the bath temperature. The suction force was then applied to the thinner arm to draw the sample slightly above the upper timing mark. The afflux time was recorded by timing the flow of the sample as it flowed freely from the upper timing mark to the lower timing mark. The kinematic viscosity (ν) was calculated by means of the equation 3.10 adapted from Sandford *et al.* (2009).

$$V = C \times t \quad \quad \quad \mathbf{3.10}$$

Where, V = Kinematic Viscosity (mm^2/s)

t = Time for flow of 50 cm^3 sample in seconds

C = Viscosity tube constant (0.09757)

The viscosity in centistokes, at a given speed cylinder combination was obtained by multiplying the instrument readings with appropriate multiplying factor given on the calibration chart.

3.7.2 Flash point determination (ASTM D93, 2008)

The flash points were measured with a Pensky-Martens closed cup tester (Koehler Instrument Company, Inc. K16200). The sample was transferred into a flash point cup, to a level inscribed on the metal container. The cup was placed in the Pensky Marten's Tester, and the pilot flame lighted. With the aid of a shutter operating knob, the cup was lowered and heated at 5°C interval with a flame being passed over the surface of the sample to check when it flashed. A temperature reading was taken immediately a flash appeared on the surface of the sample. This temperature was taken to be the flash point of the oil.

3.7.3 Cloud point analysis (ASTM D2500, 2005)

The sample was filtered and about 50cm³ was placed in a conical flask and closed tightly with a cork carrying a test thermometer. The flask was heated to 130°C and maintained at this temperature for 5min to remove all moisture in the sample. The flask was cooled in a water bath filled with ice and stirred thoroughly to ensure temperature uniformity and to prevent super cooling and solidification of fat crystals at the side and at the bottom of the sample bottle. The flask was continuously monitored for cloud formation. To achieve this, the flask was removed periodically without disturbing the sample in order to inspect if the sample had turned cloudy. The cloud point was taken as the temperature at which the first crystals began to form in the normally clear fuel. The test was repeated with the temperature of the water bath set at 5°C below the cloud point of fossil diesel. The temperature that corresponds to the first formation of a cloud in the fuel sample was recorded as the cloud point. The results of repeated tests were recorded and the average value determined.

3.7.4 Determination of pour point (ASTM D-97)

The ASTM D-97 standard method was adopted for the pour point test. The sample (50 cm³) was filtered and poured into a test jar to the level mark. The sample was heated in a water bath until it was just sufficiently fluid to pour into the test jar. The heated sample in the test jar was kept at room temperature for 24 h before testing. The test jar was covered with the cork carrying the high-pour thermometer with its bulb immersed completely into the test sample and the beginning of the capillary was 3 mm below the surface of the sample. The sample was cooled inside a cooling bath to allow the formation of wax crystals and for every subsequent 3°C, the test jar was removed and tilted to check for surface movement or flow. When the oil failed to flow when tilted, the jar was held horizontally for 5 sec. If it failed to flow again, 3°C was added to the corresponding temperature and the result was the pour point temperature of the oil.

3.7.5 Sulphur content determination (ASTM D-5453)

Sulphur in the samples was determined by X-ray fluorescence according to ASTM D-5453 method. The test sample (10cm³) was placed in an X-ray beam and the peak intensity of the sulphur K_α - line at 5.373 Å was measured. The background intensity, measured at a recommended wavelength of 5.190 Å was subtracted from the peak intensity. The net resultant counting rate was then compared to a previously prepared calibration curve to obtain the concentration of sulphur in the sample.

3.7.6 Test for cetane number (ASTM D 613, 2010)

An Ignition Quality Tester (IQT), a single cylinder, indirect injection diesel engine that is similar to the Octane Test Engine used for rating gasoline was used to determine the cetane number of the biodiesels produced. The engine speed was fixed at 900 rpm and aspirated,

keeping the intake air temperature constant at 60°C. The fuel/air ratio and the compression ratio were carefully adjusted to produce a standard ignition delay of 13 degrees (the period between the start of fuel injection and the start of combustion) while operating on the test fuel. Then the engine was switched to operate on a blend of two reference fuels. Different blends were tested until a formulation was found that restored the ignition delay of 13 degrees. The primary reference fuel used was n-cetane (n-hexadecane), which has a cetane number of 100 and heptamethylnonane (HMN), which has a cetane number of 15. When the ignition delay was restored to 13 degrees, the cetane number was then determined using the relationship:

$$\text{Cetane number} = \% \text{ n-cetane} + 0.15 (\% \text{HMN}) \quad \mathbf{3.11}$$

3.7.7 Calorific value determination (ASTM, 2015)

The calorific value of the oil and its methylester was determined by placing 0.4 g of oil sample in a clean cup. A thread was fixed at the suspender just a little above the cup holder making sure the ends of the thread are immersed in the oil. About 300Kpa of oxygen was pumped into the vessel which was tightly fixed to the device until the calorimeter displayed 'insert' on the screen. The vessel was then inserted into the calorimeter, and the lid closed. After about 15 minutes, the energy content was seen displayed on the screen in MJ/kg.

3.8 Fourier Transform Infrared Spectroscopy Analysis

The plates were thoroughly cleaned using acetone. By using a syringe pipette, a drop of the oil sample was placed between the two KCl plates. The chloride plates were then attached to a Fourier Transform Infrared Spectrometer coupled to a computer with print out system. The sample in the plate was irradiated by infrared lamp source at one end of the spectrometer and

each sample was analyzed between ranges of 600 cm^{-1} to 4000 cm^{-1} . Similarly, each biodiesel, biodiesel- fossil diesel blend and the neat fossil diesel were analyzed for their functional groups.

CHAPTER FOUR

4.0 RESULTS

4.1 Extraction and Physicochemical Properties of Yellow Oleander Seed Oil (YO) and Pig Lard (PL)

The yield of the oil from yellow oleander (*Thevetia peruviana*) seeds (YO) and pig (*Sus domesticus*) lard (PL) as well as their physicochemical properties are presented in Table 4.1. The seed of yellow oleander seed contained 64.7 % oil while the pig fat was 85.4 % oil. Therefore, both feedstocks can be classified as high yielding. The values obtained for each parameter were as follows: acid value (1.26 and 2.24 mg/g), peroxide value (3.0 and 2.0 meqO₂/kg), iodine value (75.82 and 53.93 g/g), saponification value (197.75 and 195.64 mg KOH/g), specific gravity (0.8841 and 0.8808 g/cm³), Calorific value (13.78 and 12.02 MJ/kg) and refractive index (1.48 and 1.47) for yellow oleander oil and lard respectively. All physicochemical parameters values compared well with those of *Jatropha curcas*. These values were higher in yellow oleander seed oil except for free fatty acid.

4.2 Fuel Properties of Yellow Oleander Seed Oil and Pig Lard

The fuel properties of the yellow oleander seed oil and pig lard are presented in Table 4.2. Yellow oleander seed oil had higher value for flash point (192°C), cetane number (48°C) and kinematic viscosity (23.23 mm²/s) whereas higher value for cloud point (15°C) was recorded in pig lard.

Table 4.1: Physicochemical properties of yellow oleander seed oil and pig lard compared with those of *Jatropha curcas*

Property	Yellow Oleander seed oil	Pig Lard	* <i>Jatropha curcas</i>
Oil Yield (%)	64.70 ± 0.53	85.40 ± 0.97	63.16±0.35
Acid value (mg KOH/g)	1.26 ± 0.02	2.24 ± 0.02	13.97±0.05
Free fatty acid %	0.63 ± 0.02	1.12 ± 0.02	2.23±0.02
Saponification value(mg/g)	197.75 ± 0.72	195.64 ± 0.56	193.55±0.61
Iodine value(g/g)	75.82 ± 1.44	53.93 ± 1.14	103.62±0.07
Refractive index value	1.48 ± 0.02	1.47 ± 0.01	1.47±0.00
Specific gravity (g/cm ³)	0.884 ± 0.02	0.881 ± 0.01	0.91±0.00
Peroxide value (meq O ₂ /kg)	3.00 ± 0.36	2.00 ± 0.66	1.93±0.012
Calorific value (MJ/kg)	13.78 ± 0.58	12.01 ± 0.63	-

Values are presented as mean± SD and are for duplicate analysis of each sample.

*Abdullah *et al.*, 2013

Table 4.2: Fuel properties of yellow oleander seed oil and pig lard

Property	Yellow seed oil	Oleander	Pig Lard
Flash point (°C)	192		165
Viscosity mm ² /s	23.23		12.62
Cetane Number	48		43
Diesel index	25		25
ASTM colour	0.5		0.5
Cloud point °C	14		15
Sulphur (%)	<0.01		<0.01

4.3 Fatty Acid Profile of Yellow Oleander Seed Oil and Pig Lard

The results presented in Figures 4.1 and 4.2 are the Gas chromatograms of yellow oleander seed oil and pig lard. The major peaks of the GC chromatogram of oils were identified using the NIST05s library search and tabulated in Tables 4.3-4.4, while the percentage composition of the fatty acids are shown in Table 4.5. They consist of the following categories of fatty acids: saturated (myristic (14:0), palmitic (16:0), marganic (17:0), stearic (18:0), arachidic (20:0), behenic (22:0)), monounsaturated (palmitoleic(16:1), oleic (18:1), erucic (22:1), elaidic (18:1)) and polyunsaturated (linoleic (18:2), linolenic (18:3)) fatty acids.

The percentage compositions of palmitic acid (23.89 %), stearic acid (10.92%), oleic acid(16.11%) and elaidic acid (24.83) and lenoleic (19.79) were higher in yellow oleander seed oil than pig lard which recorded percentage compositions of fatty acids as: palmitic (17.34%), marganic (12.47%), stearic (7.01%), oleic (11.99) and elaidic (23.42) and linolenic (21.35%) acids.

4.4 FTIR Spectra of Yellow Oleander Seed Oil and Pig Lard

Figures 4.3- 4.4 are the FTIR spectra of yellow oleander seed oil and pig lard. The assignment of the FTIR peaks of yellow oleander seed oil and pig lard are shown in Table 4.6. The peaks observed include broadband peaks of -OH stretching vibration at $3461 - 3643\text{cm}^{-1}$ which was shown in pig lard. The symmetric and asymmetric stretching vibration bands of aliphatic $-\text{CH}_2$ and $-\text{CH}_3$ group at $2912- 2927\text{ cm}^{-1}$, the double bond of the ester carbonyl functional group at $1739 - 1745\text{ cm}^{-1}$ and the C-O stretching vibration peaks of the ester group in the finger print region ($1103 - 1166\text{ cm}^{-1}$) were shown in all the spectra of both yellow oleander seed oil and pig lard. At $1455-1457\text{ cm}^{-1}$ was shown the carbon-carbon double bond vibrations of the triglyceride.

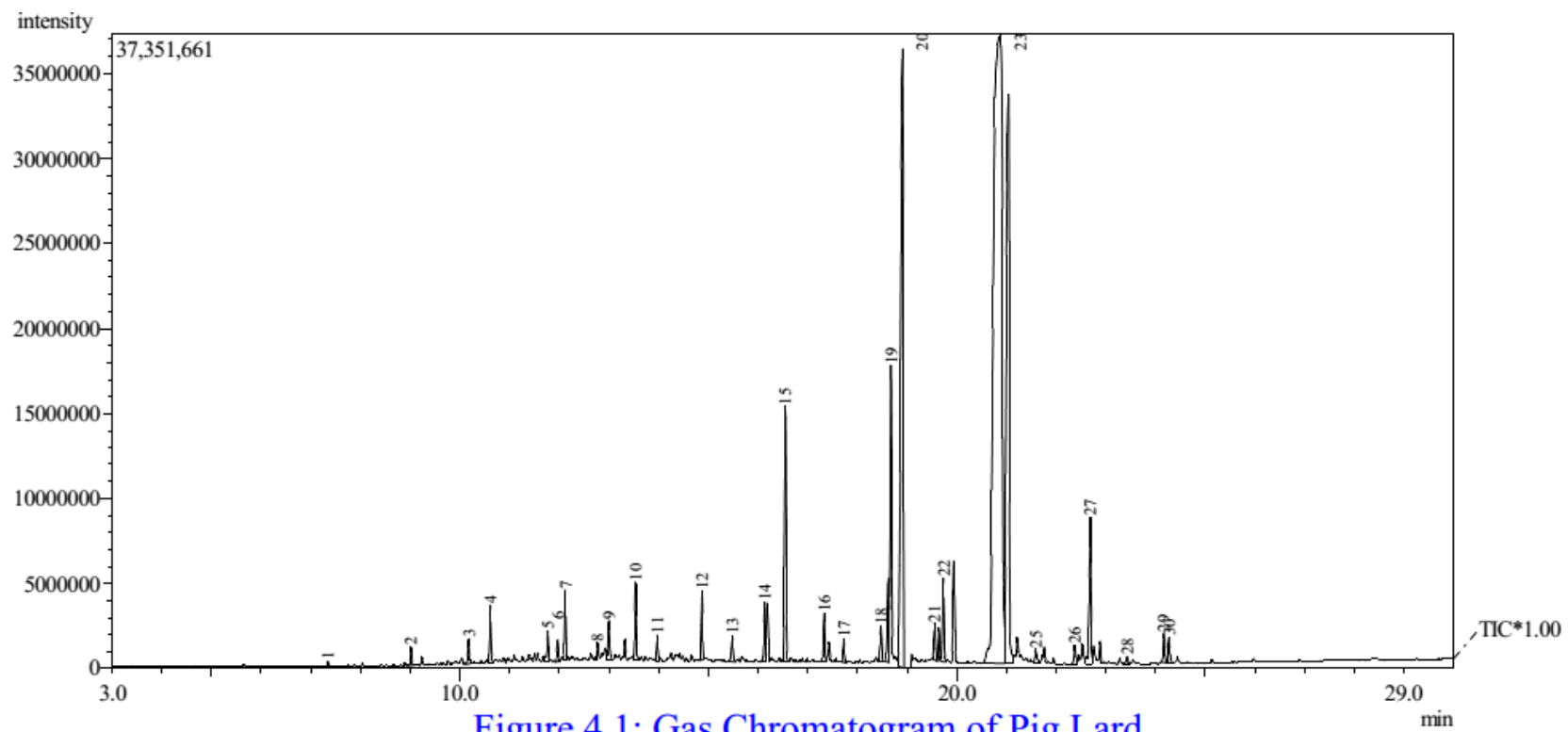


Figure 4.1: Gas Chromatogram of Pig Lard

Table 4.3: Major resolved peak areas of pig lard gas chromatogram and their suggested compounds from NIST05 library

Peak No.	Area%	Compound
15	3.51	Tetradecanoic acid, methyl ester (Myristic acid, methyl ester)
19	1.27	9-Hexadecenoic acid, methyl ester (Palmitoleic acid, methyl ester)
20	15.51	Hexadecanoic acid, methyl ester (Palmitic acid, methyl ester)
22	1.20	Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester
23	49.64	9-Octadecenoic acid, methyl ester
24	15.07	Octadecanoic acid, methyl ester (Stearic acid, methyl ester)
27	2.76	11-Eicosenoic acid, methyl ester

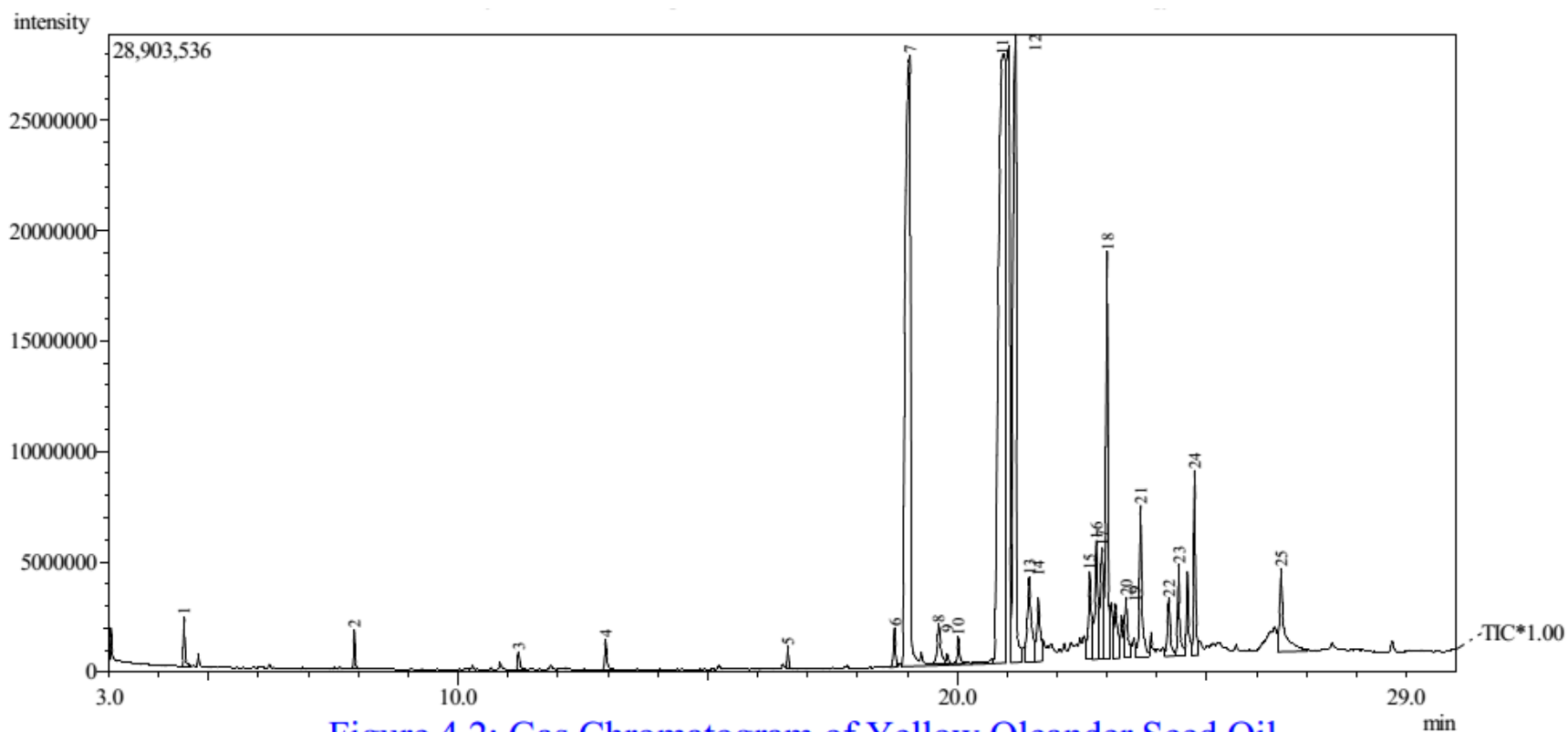


Figure 4.2: Gas Chromatogram of Yellow Oleander Seed Oil

Table 4.4: Major resolved peak areas of yellow oleander seed oil gas chromatogram and their suggested compounds from NIST05 library

Peak No.	Area%	Compound
7	23.23	Hexadecanoic acid methyl ester (Palmitic acid,methyl ester)
11	29.39	9,11-Octadecadienoic acid methyl ester
12	13.76	Octadecanoic acid, methyl ester (Stearic acid, methyl ester)
13	2.49	Oleic Acid 9-Octadecenoic acid
14	1.40	Octadecanoic acid (Stearic acid)
15	1.87	Oxiraneoctanoic acid, 3-octyl-, methyl ester
16	2.46	11-Eicosenoic acid, methyl ester
17	2.35	14-Methyl-8-hexadecenal
18	5.98	Methyl eicosanoate (Arachidic acid methyl ester)
21	2.82	14-Methyl-8-hexadecenal
23	1.53	9-Octadecenoic acid, 1,2,3-propanetriyl ester
24	2.43	Docosanoic acid, methyl ester (Behenic acid, methyl ester)
25	2.53	Methyl tetracosanoate (Lignoceric acid methyl ester)

Table 4.5: Fatty acid profile of yellow oleander seed oil and pig lard

Properties	*Yellow Oleander Seed Oil (%)	**Pig Lard (%)
Saturated acids	38.53	37.93
Myristic (14:0)	0.14	1.11
Palmitic (16:0)	23.89	17.34
Marganic (17:0)	—	12.47
Stearic (18:0)	10.92	7.01
Arachidic (20:0)	2.54	—
Behenic (22:0)	1.04	—
Mono-unsaturated acids	41.21	35.97
Palmitoleic(16:1)	0.27	—
Oleic (18:1)	16.11	11.99
Erucic (22:1)	—	0.56
Elaidic (23:1)	24.83	23.42
Polyunsaturated	20.26	26.10
Linoleic (18:2)	19.79	4.75
Linolenic (18:3)	0.47	21.35
Total Monounsaturated		
+Saturated	79.64	73.90
Total polyunsaturated	20.26	26.10

*See Appendix I for the Mass Spectra of yellow oleander seed oil.

**See Appendix II for the Mass Spectra of pig lard.

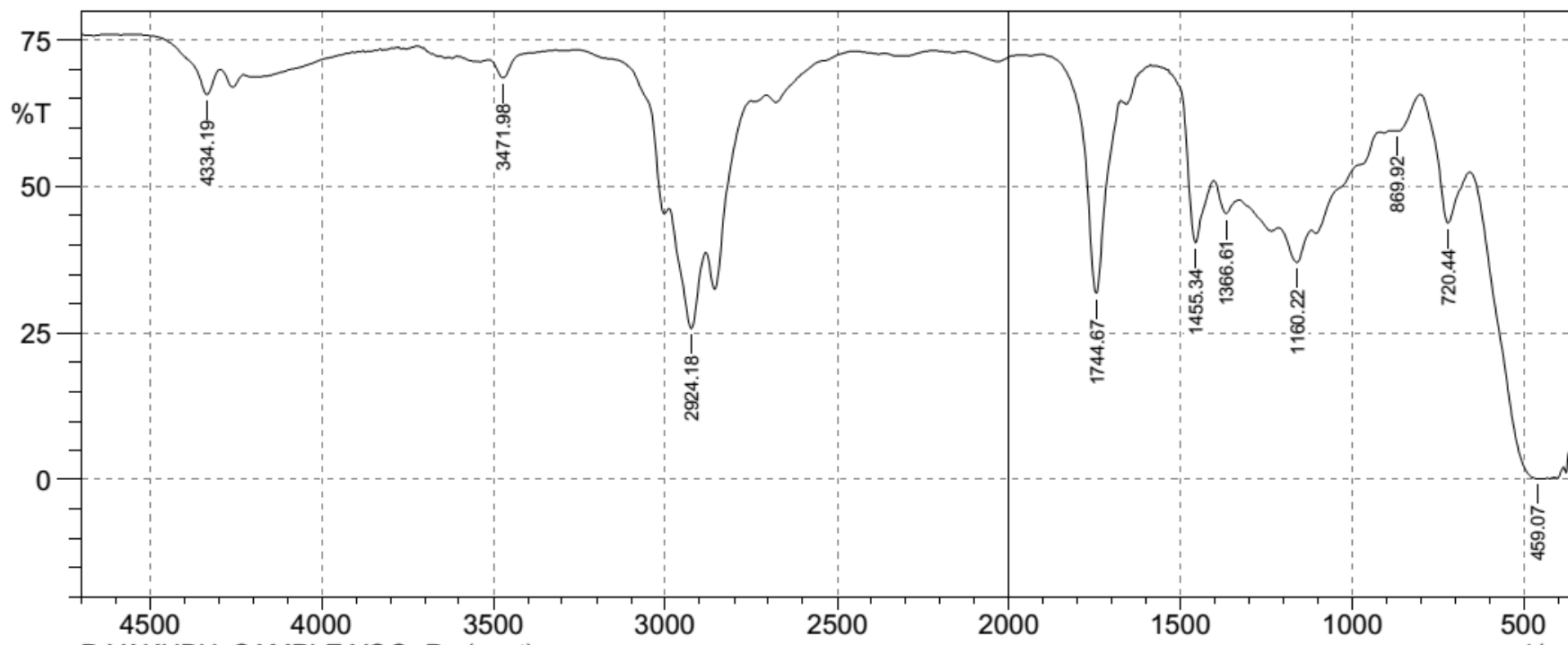


Figure 4.3: FTIR spectrum of yellow oleander seed oil

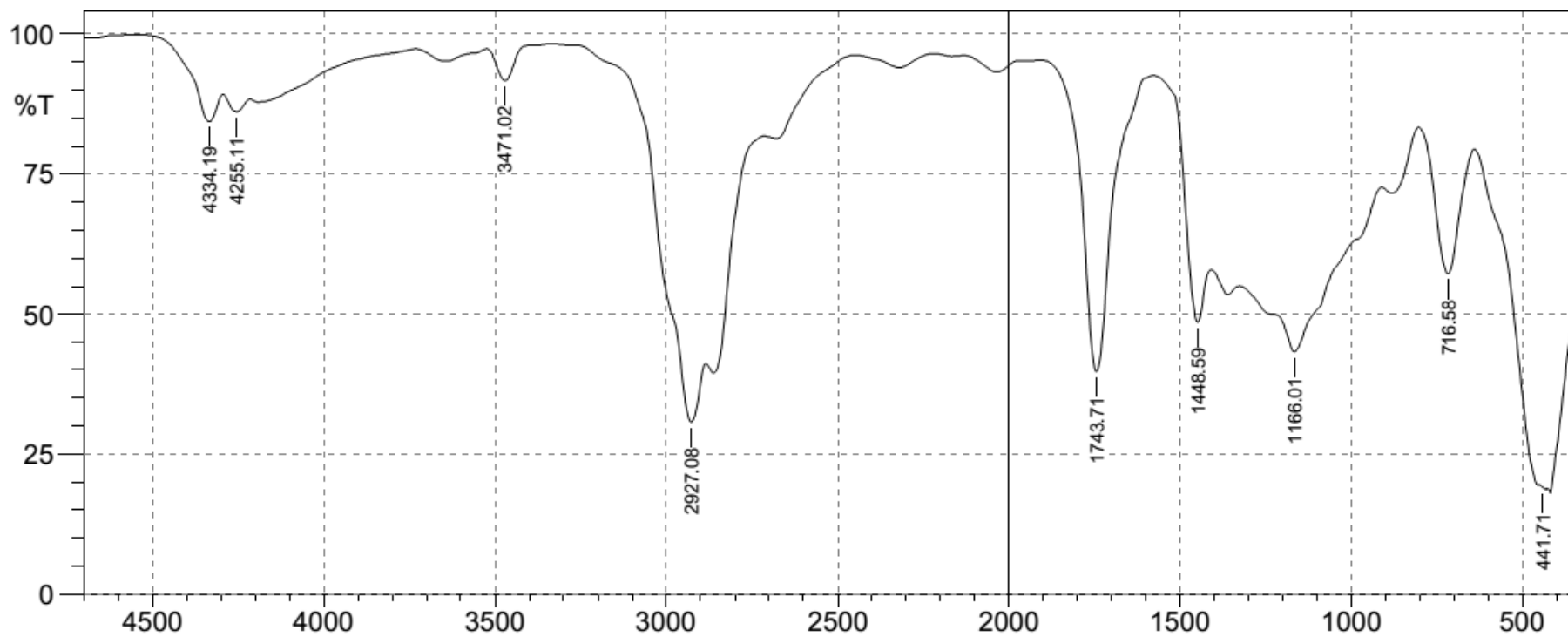


Figure 4.4: FTIR spectrum of pig lard

Table 4.6: Assignment of FTIR peaks (cm⁻¹) in yellow oleander seed oil and pig lard

Yellow Oleander seed oil	Pig Lard	Assignment
3471.98	3471	Region of hydroxyl group stretching. -OH stretching vibration of the triglycerides
2924.18	2927	-Symmetric and asymmetric stretching vibrations of the aliphatic -CH ₂ and -CH ₃ groups.
1744.67	1743	Region of double bond stretching -ester carbonyl functional group of the triglycerides
1455.34	1448	-C=C stretching vibration of olefins
		Region of other bond deformations and bendings
-	-	- Bending vibrations of CH ₂ groups
1160	1166	Fingerprint region -C-O stretching vibration of ester group
720.40	716	Overlapping of the CH ₂ rocking vibration and the out of plane vibration of disubstituted olefins

4.5 Effect of Variation of Reaction Time, Temperature and Catalyst Concentration on Yellow Oleander Methyl Ester and Pig Lard Methyl Ester Yield.

Figures 4.5 to 4.13 show the effect of varying reaction time, temperature and catalyst concentration on yellow oleander methyl ester and pig lard methyl ester yield in base-catalysed transesterification.

The biodiesel yield from yellow oleander seed oil and pig lard was studied as a function of contact time (Figures 4.5 – 4.8), while their temperature and catalyst concentration were kept constant. Transesterification reactions conducted under the various reaction temperatures, and catalyst amount of 0.5 - 1.0 (% w/w) revealed that the biodiesel yield was strongly dependent on reaction time. In the beginning (30 to 45 min), the biodiesel yield was fast but beyond 45 min the biodiesel yield slowed down. Therefore, the optimum reaction time was 45 min.

Figures 4.9 to 4.12 show the effect of varying temperature on biodiesel yield with 1% and 0.5% (w/w) catalyst. The biodiesel yield increased with the increase of reaction temperature to nearly 91% at 40°C, but at higher temperatures ($T > 40$ °C), the rate of the biodiesel yield remained nearly constant. Thus, the optimum reaction temperature was 40°C. In all, an increase in temperature results in an increase in biodiesel yield.

Effect of catalyst dosage of 0.5% (w/w), 1.0% (w/w) and 1.5% (w/w) on biodiesel yield was investigated under varying conditions of reaction temperature and reaction time. The biodiesel yield was found to increase fast up to 60min with all catalyst dosages with the maximum obtained with 1.0% catalyst (Figure 4.13) at each temperature. The rate of biodiesel yield declined with further increase in catalyst concentration. For pig lard methyl ester the yield increased from 91.45 % to 95.12 % with 0.5% and 1.0%, but with 1.5% catalyst the yield dropped.

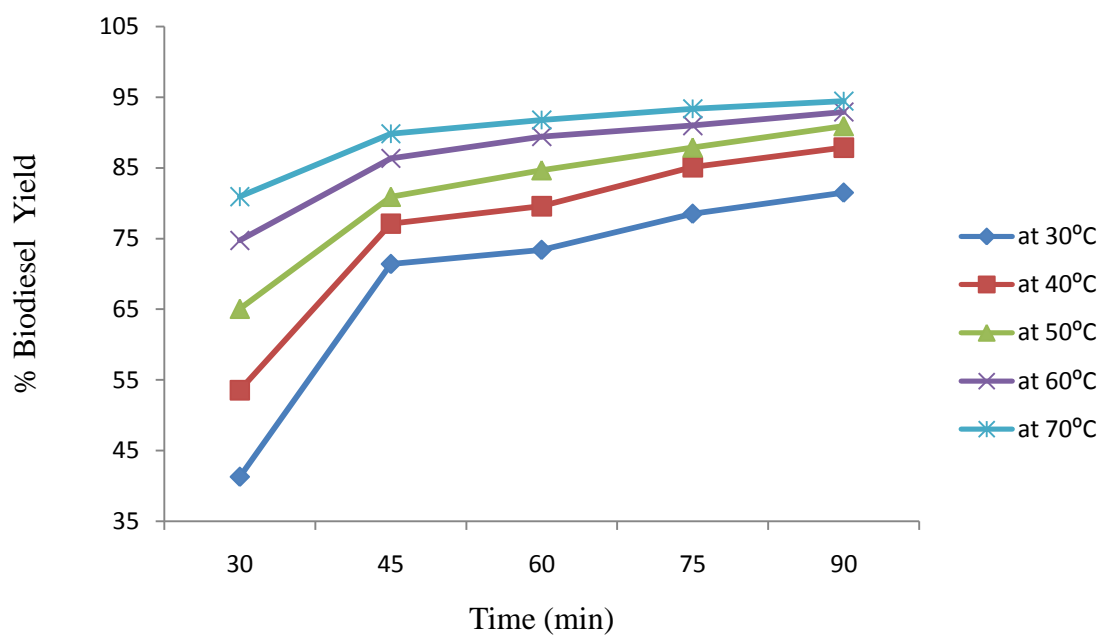


Figure 4.5: Effects of reaction time on yellow oleander biodiesel yield with 0.5% (w/w) catalyst and at different temperatures

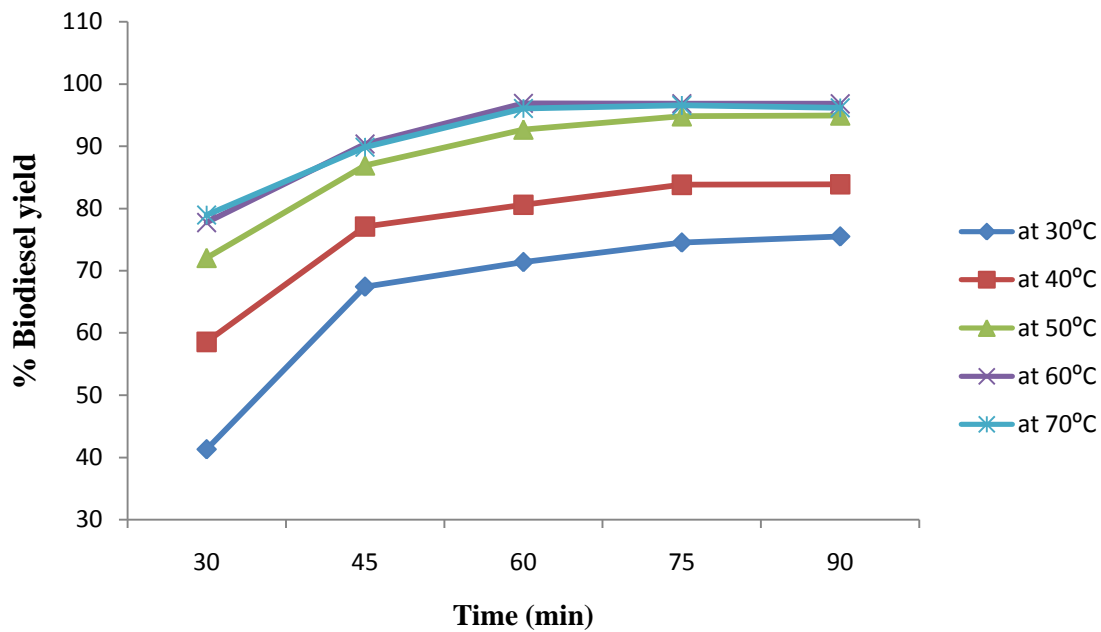


Figure 4. 6: Effects of reaction time on yellow oleander biodiesel yield with 1% (w/w) catalyst and at different temperatures

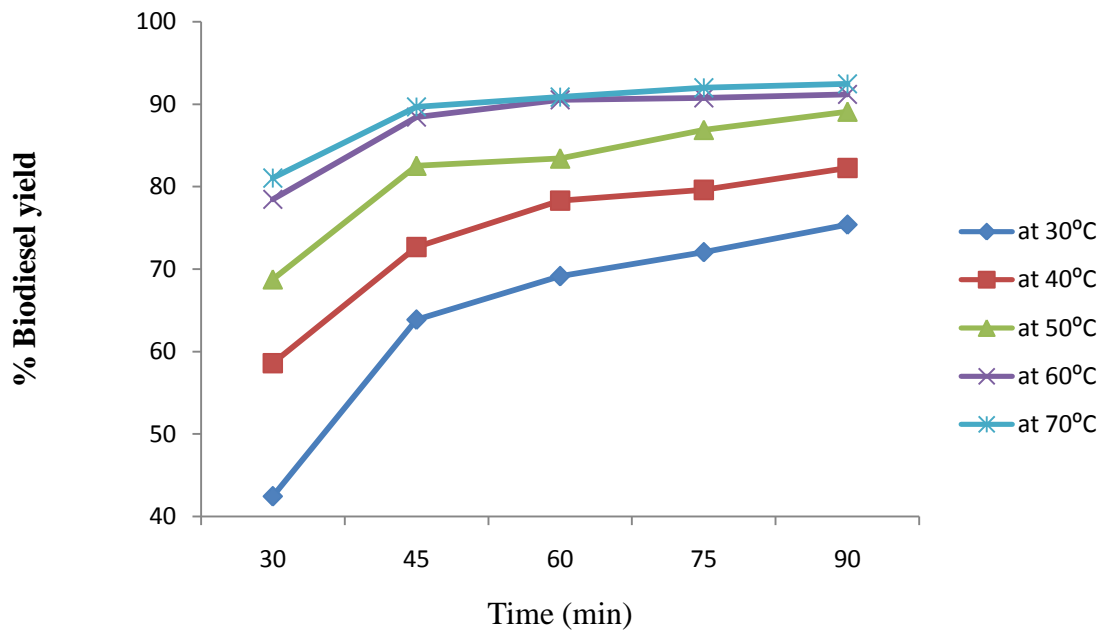


Figure 4.7: Effects of reaction time on pig lard biodiesel yield with 0.5 % (w/w) catalyst and at different temperatures

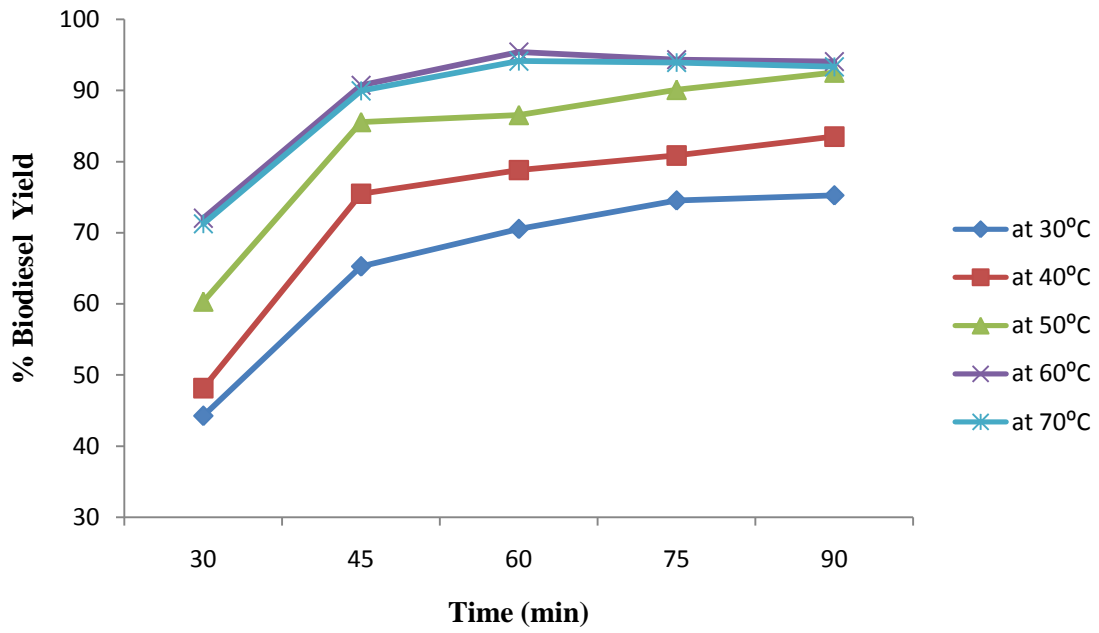


Figure 4.8: Effects of reaction time on pig lard biodiesel yield with 1% (w/w) catalyst and at different temperatures

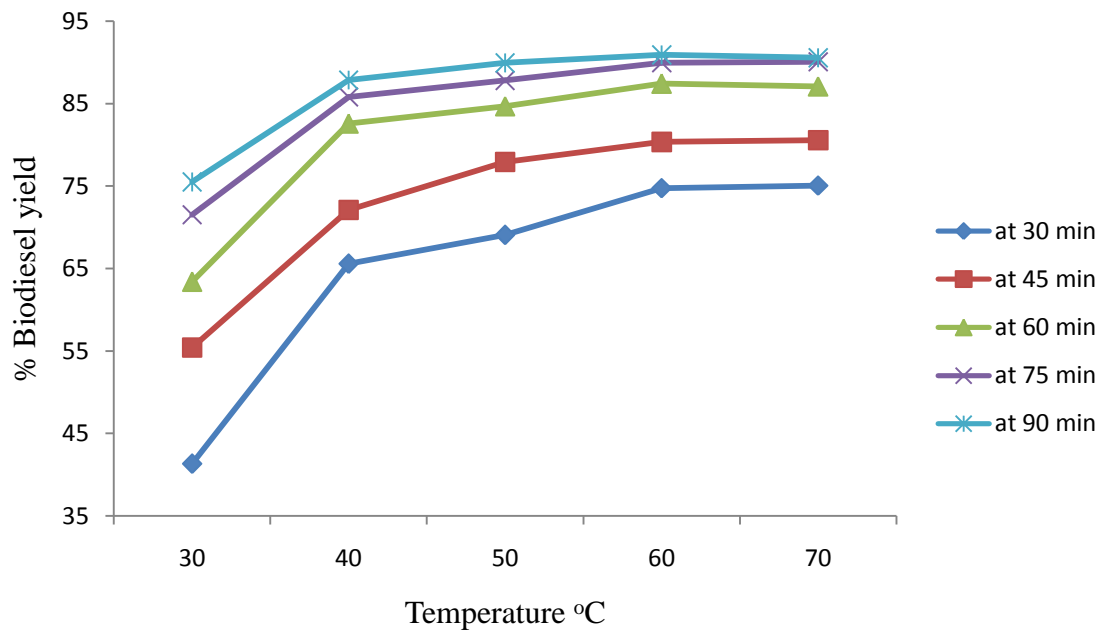


Figure 4.9: Effects of reaction temperature on yellow oleander biodiesel yield with 0.5 % (w/w) catalyst and at different time

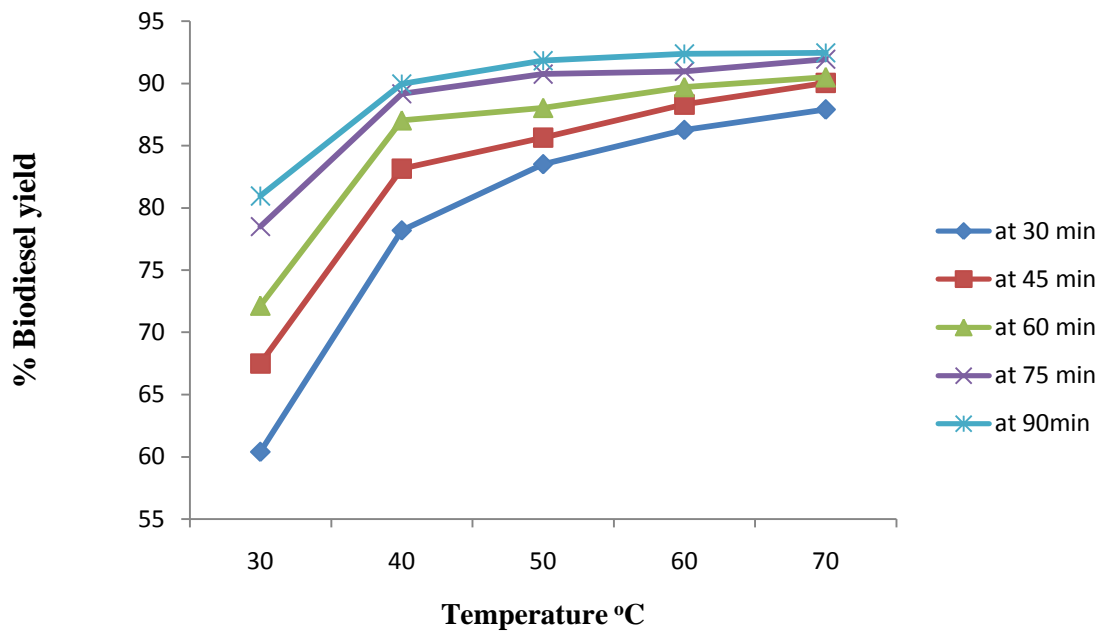


Figure 4.10: Effects of reaction temperature on yellow oleander biodiesel yield with 1% (w/w) catalyst and at different time

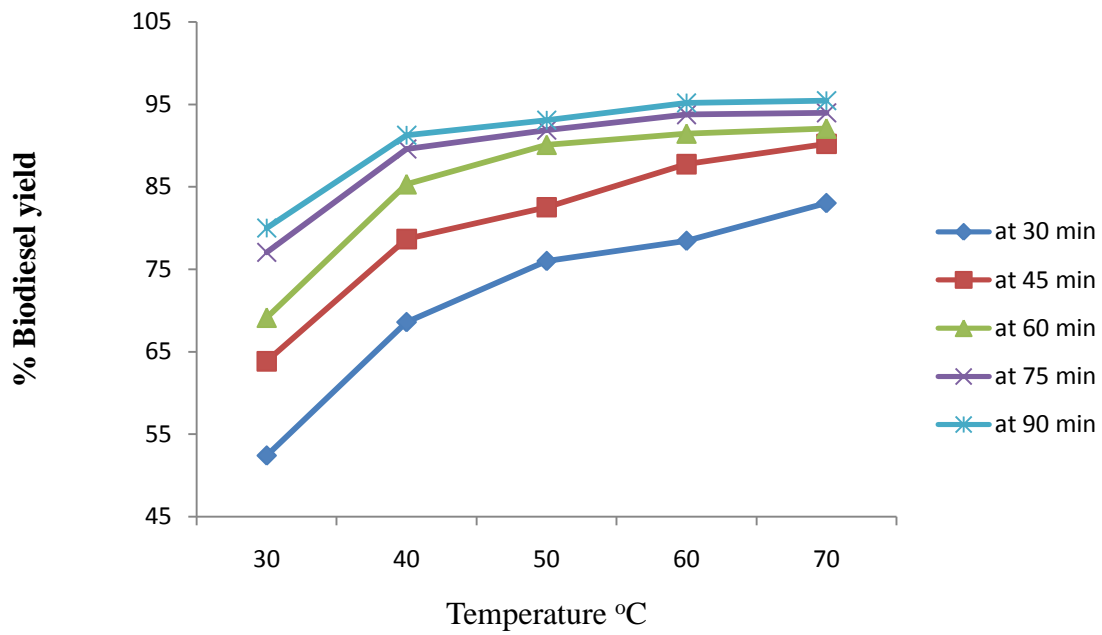


Figure 4.11: Effects of reaction temperature on pig lard biodiesel yield with 0.5% (w/w) catalyst and at different time

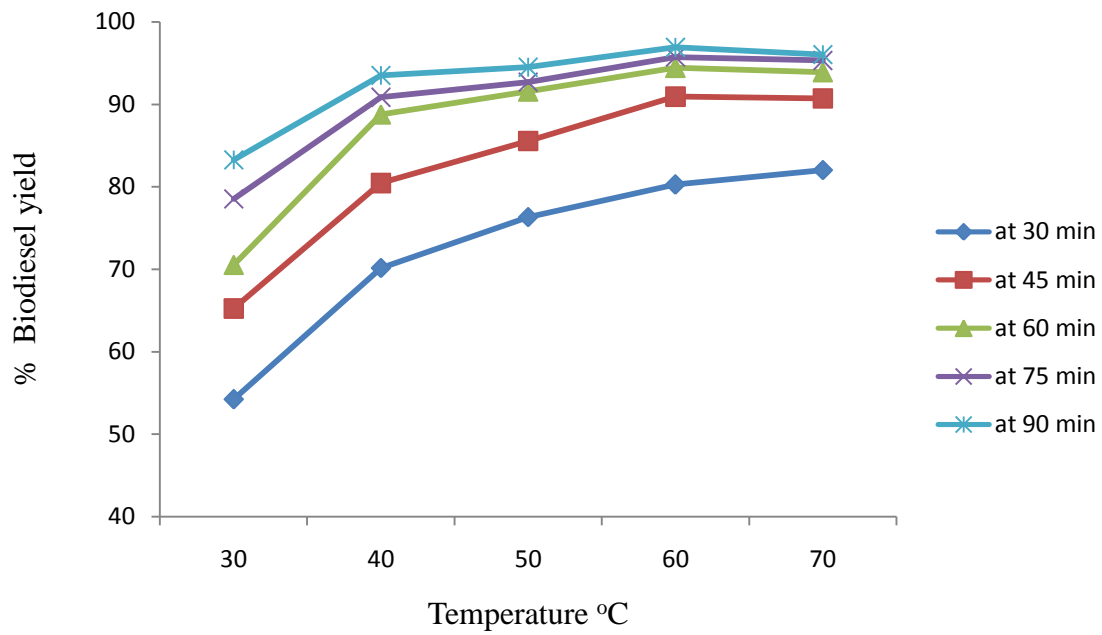


Figure 4.12: Effect of reaction temperature on pig lard biodiesel yield with 1% (w/w) catalyst and at different time

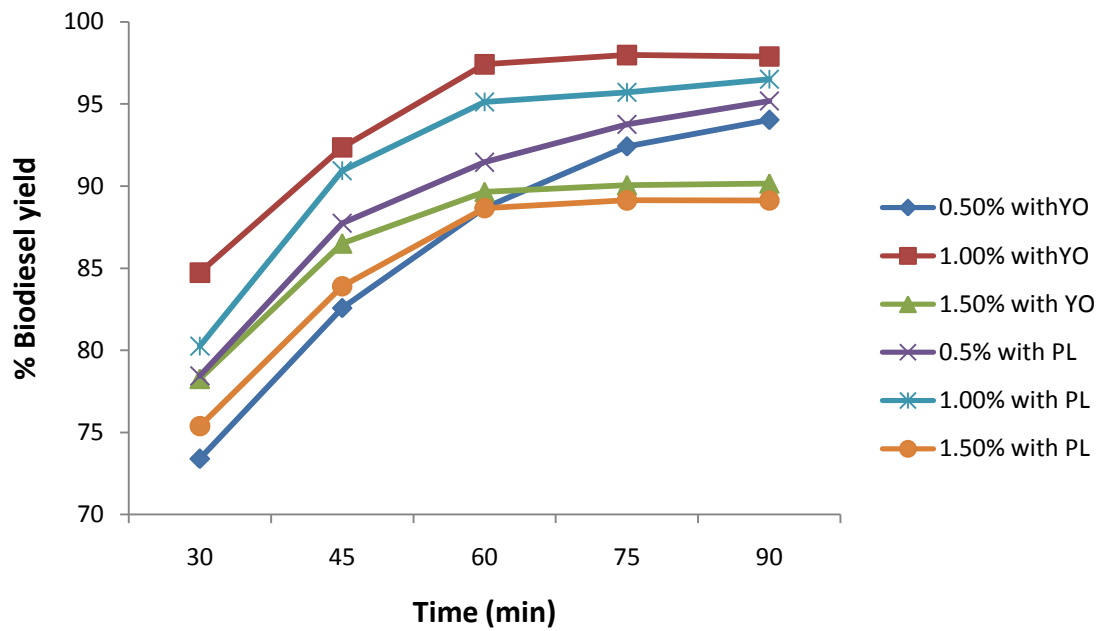


Figure 4.13: Effect of catalyst concentration (% w/w) on yellow oleander biodiesel and pig lard biodiesel yield at different time

PL = pig lard

YO = yellow oleander seed oil

4.6 FTIR Analysis of Yellow Oleander Methyl Ester and Pig Lard Methyl Ester

FTIR spectra of yellow oleander methyl ester and pig lard methyl ester are shown in Figures 4.14 and 4.15 respectively. A summary of the FTIR spectra are compared with those of yellow oleander seed oil and pig lard respectively in Table 4.7.

The yellow oleander seed oil, pig lard, yellow oleander methyl ester, pig lard methyl ester and fossil diesel show -CH_2 rocking bands at $716 - 722 \text{ cm}^{-1}$. The C - O stretching of $\text{-O-CH}_2\text{-C}$ was shown in the biodiesels from both feedstocks including fossil diesel at $1011 - 1033 \text{ cm}^{-1}$. The C-O vibration bands appeared at $1160 - 1186 \text{ cm}^{-1}$ in all the samples. The ester group appeared at $1448 - 1455 \text{ cm}^{-1}$ in yellow oleander seed oil, pig lard, yellow oleander methyl ester and pig lard methyl ester but absent in fossil diesel. Carbonyl -C=O stretch of the yellow oleander methyl ester and PLME were observed at $1740 - 1744$. The -CH_2 vibration peaks are shown in all samples and the fossil diesel at $2900 - 2929 \text{ cm}^{-1}$ (Figure 4.16).

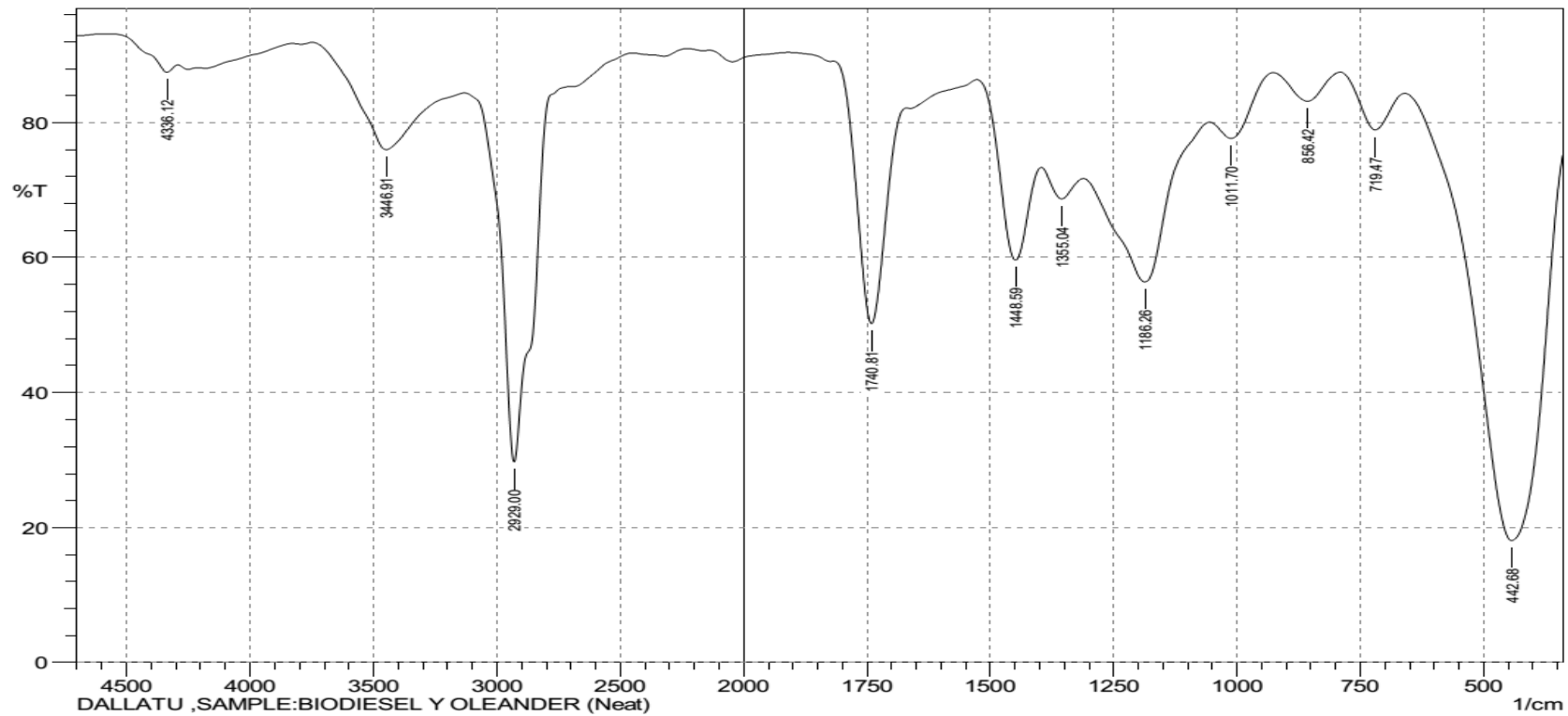


Figure 4.14: FTIR spectrum of yellow oleander methyl ester at room temperature

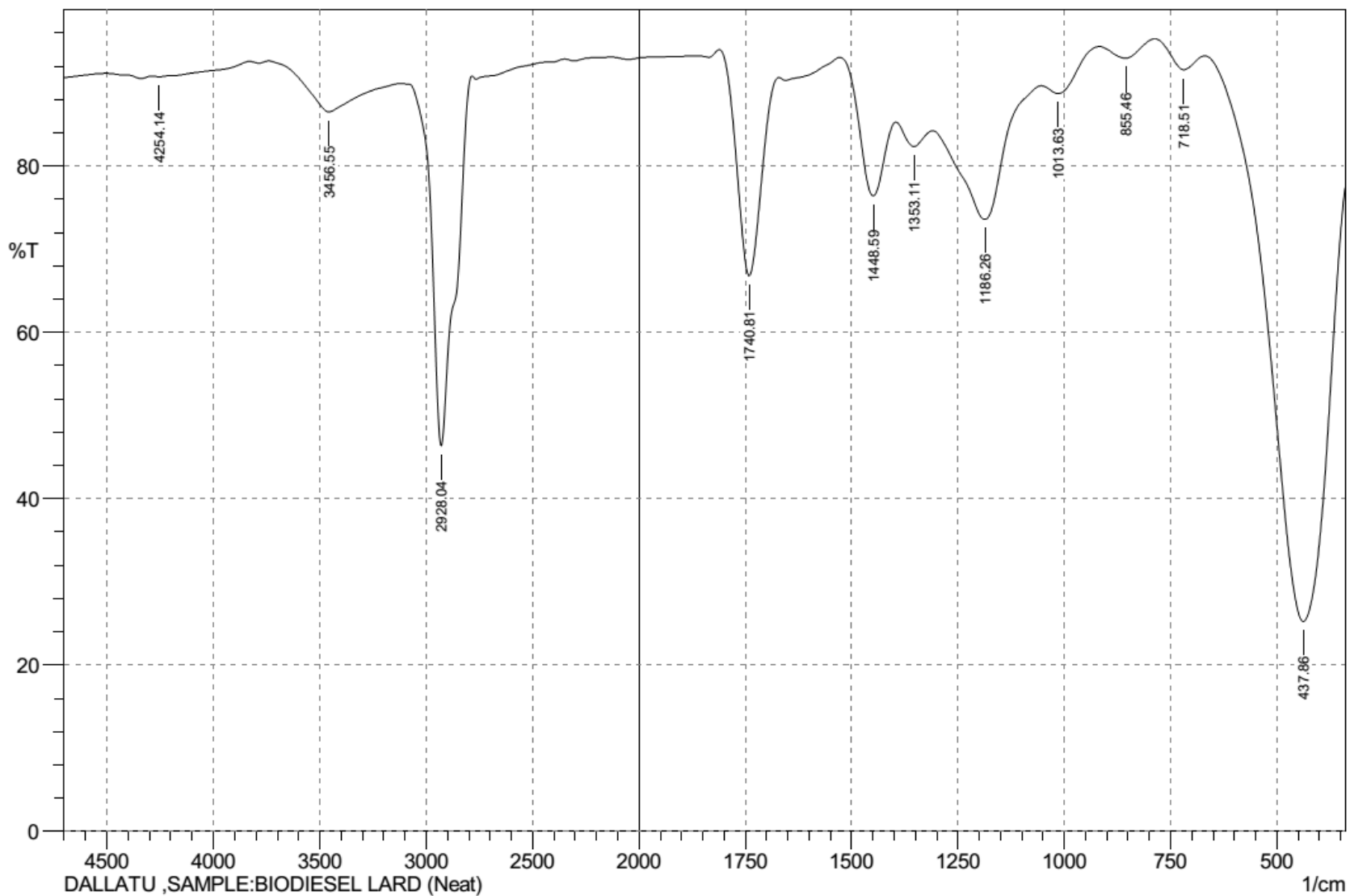


Figure 4.15: FTIR spectrum of pig lard methyl ester at room temperature

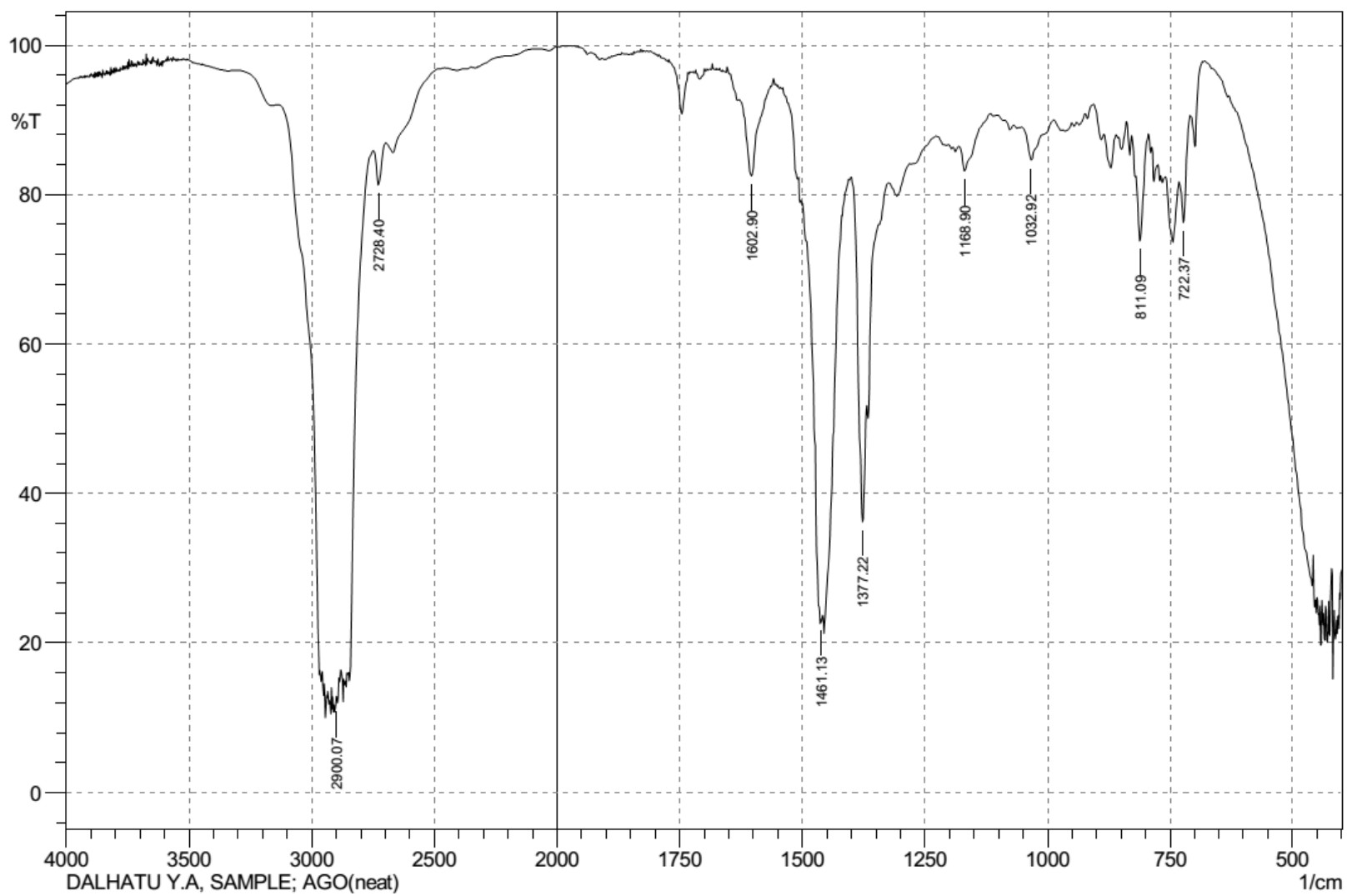


Figure 4.16: FTIR spectrum of fossil diesel at room temperature

Table 4.7 : A Summary of the FTIR spectra peaks (cm⁻¹) of yellow oleander seed oil, pig lard, yellow oleander methyl ester and pig lard methyl ester compared with fossil diesel

YO	YOME	PIG LARD	PLME	FOSSIL DIESEL	ASSIGNMENT
720	719	716	718	722	-CH₂ rocking
870	856	-	855	811	-CH₂ wagging in RCOCO-
-	1012	-	1013	1033	-C-O stretching of -O-CH ₂ -C
1160	1186	1166	1186	1169	-C-O vibration of hydrocarbon
1366	1355	-	1353	1377	-CH₃ bending
1455	-	1448	-	-	-C=C stretching vibration of olefins
-	1449	-	1448	-	-O-CH₃ of the methyl ester group
1741	1744	1743	1740	-	-C=O stretch of ester
-	-	-	-	2728	-CH₂
2924	2929	2927	2928	2900	-CH₂ vibration
3471	3447	3471	3456	-	-CH₃ vibration

YOME = yellow oleander methyl ester
 PLME = pig lard methyl ester

4.7 Fatty Acid Compositions of Yellow Oleander Methyl Ester and Pig Lard Methyl Ester

The Gas chromatograms show the fatty acid compositions in yellow oleander methyl ester and pig lard methyl ester (Figures 4.17 and 4.18), while their respective major peaks were identified and tabulated in Tables 4.8 – 4.9. A summary of the percentage compositions of the fatty acids is shown in Table 4.10. The predominant fatty acids are stearic acid, palmitic acid and oleic acid in both methyl esters. The profile show high percentage of saturated and monounsaturated fatty acids with stearic acid as 15.65% (yellow oleander methyl ester) and 15.98% (pig lard methyl ester), palmitic acid as 18.07% (yellow oleander methyl ester) and 15.58% (pig lard methyl ester) and oleic acid as 57.84% (yellow oleander methyl ester) and 57.82% (pig lard methyl ester).

Both yellow oleander methyl ester and pig lard methyl ester show higher percentage of unsaturated than the saturated fatty acids (Figures 4.19 and 4.20). The saturated fatty acids include caprylic acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid and lignoceric acid. The monounsaturated fatty acids identified were palmitoleic and oleic acids (62.85%) in pig lard methyl ester and oleic acid (57.65%) in yellow oleander methyl ester.

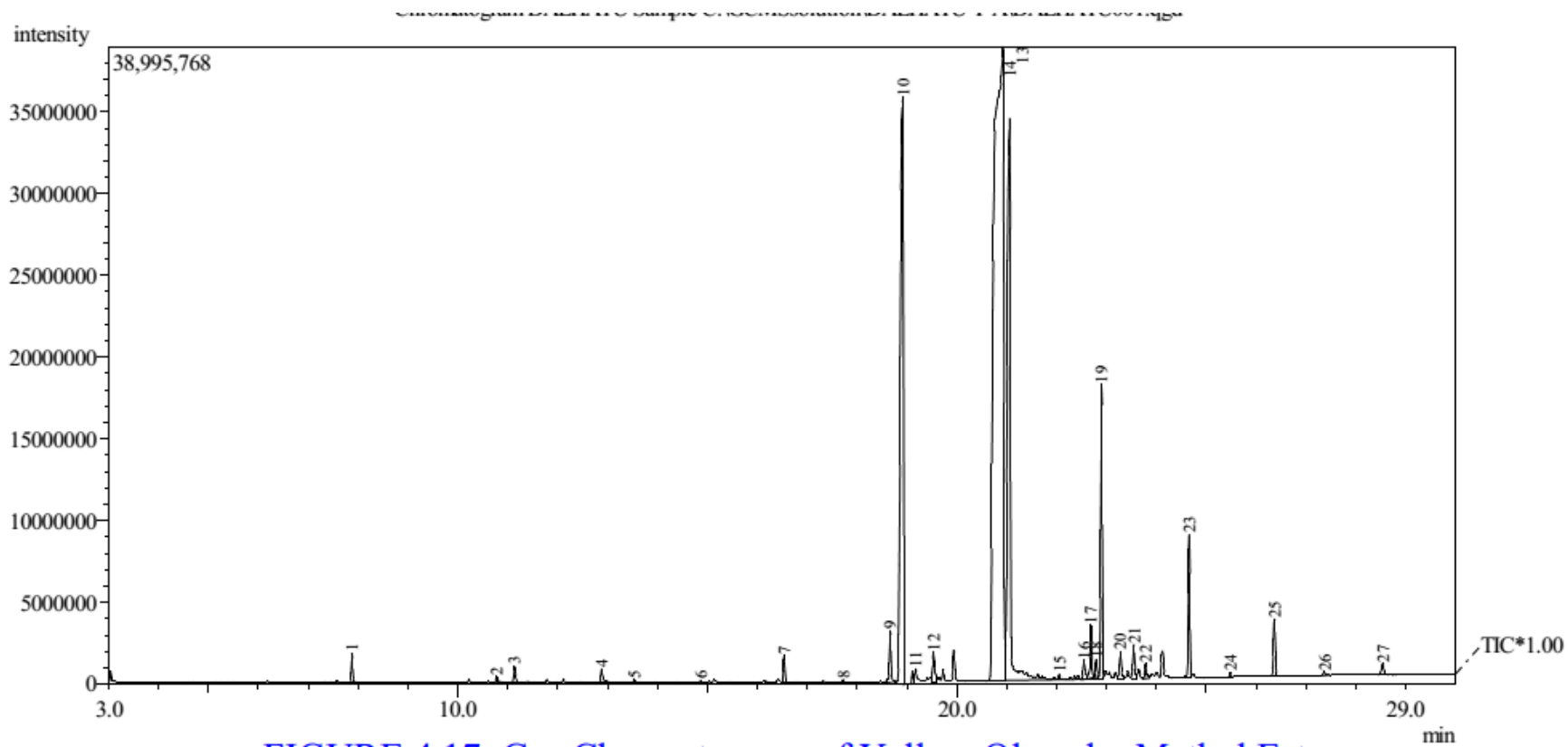


FIGURE 4.17: Gas Chromatogram of Yellow Oleander Methyl Ester

Table 4.8: Major resolved peak areas of yellow oleander methyl ester gas chromatogram and their suggested compound from NIST05 library

Peak No.	Area%	Compound
10	16.69	Hexadecanoic acid, methyl ester (Palmitic acid, methyl ester)
13	53.61	7-Octadecenoic acid, methyl ester
14	16.15	Octadecanoic acid, methyl ester (Stearic acid, methyl ester)
19	4.22	Eicosanoic acid, methyl ester (Arachidic acid methyl ester)
23	1.92	Docosanoic acid, methyl ester (Behenic acid, methyl ester)

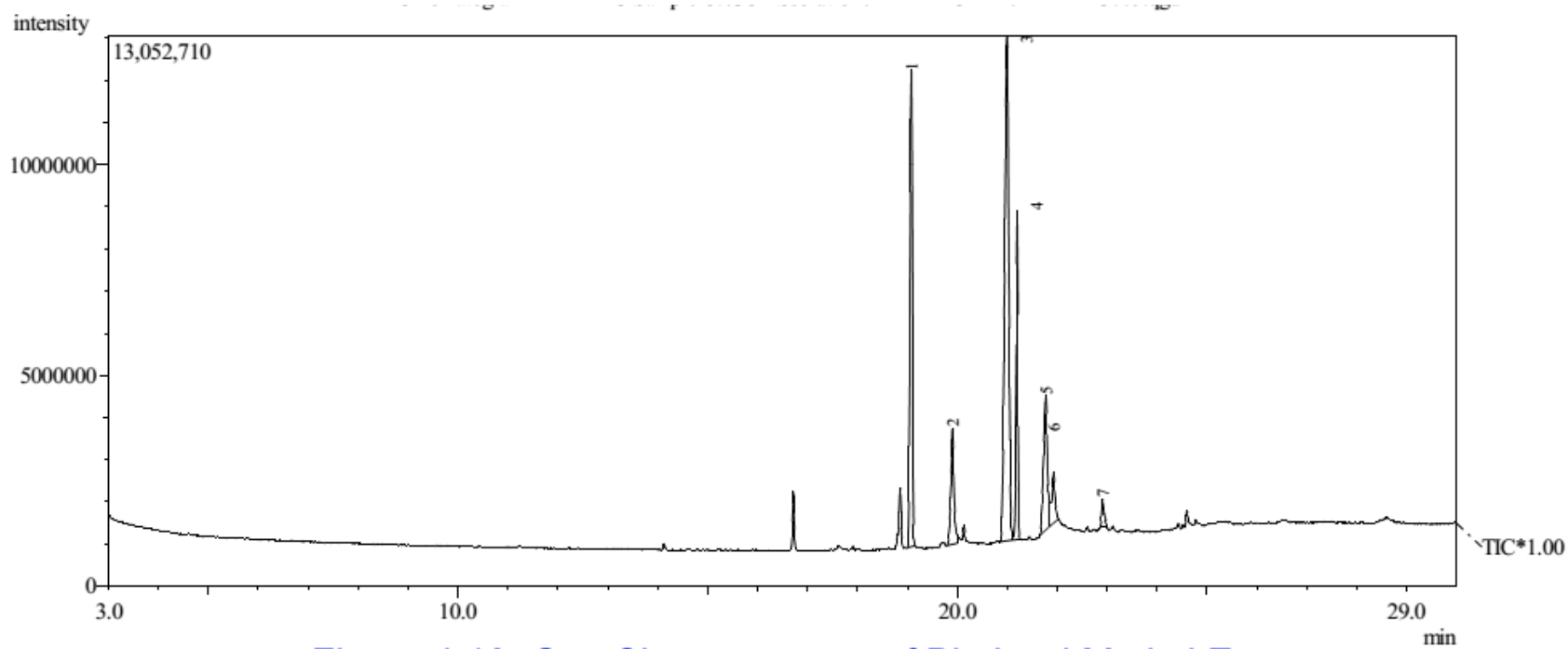


Figure 4.18: Gas Chromatogram of Pig Lard Methyl Ester

Table 4.9: Major resolved peak areas of pig lard methyl ester gas chromatogram and their suggested compound from NIST05 library

Peak No.	Area%	Compound
1	21.87	Hexadecanoic acid, methyl ester (Palmitic acid, methyl ester)
2	7.33	Octadecanoic acid (Stearic acid)
3	42.57	9-Octadecenoic acid, methyl ester (Elaidic acid, methyl ester)
4	12.41	Octadecanoic acid, methyl ester (Stearic acid, methyl ester)
5	11.00	Oleic Acid (9-Octadecenoic acid)
6	3.34	n-Hexadecoic acid (Palmitic acid)
7	1.48	13,16-Octadecadienoic acid, methyl ester

Table 4.10: Fatty acid profile of yellow oleander methyl ester and pig lard methyl ester

Fatty Acid	Molecular Formular	*YOME	**PLME
Caprylic Acid (9:0)	C ₉ H ₁₈ O ₂	0.40	-
Myristic Acid (14:0)	C ₁₅ H ₃₀ O ₂	0.36	3.86
Palmitic Acid (16:0)	C ₁₇ H ₃₄ O ₂	18.07	15.58
Palmitoleic Acid (16:1)	C ₁₇ H ₃₂ O ₂	-	5.03
Stearic Acid (18:0)	C ₁₉ H ₃₈ O ₂	15.65	15.98
Oleic Acid (18:1)	C ₁₉ H ₃₆ O ₂	57.84	57.82
Arachidic Acid (20:0)	C ₂₁ H ₄₂ O ₂	4.49	-
Behenic Acid (22:0)	C ₂₃ H ₄₆ O ₂	2.04	-
Lignoceric Acid (24:0)	C ₂₅ H ₅₀ O ₂	0.91	-

* See Appendix iii for the Mass spectra.

** See Appendix iv for the Mass Spectra.

*** Stacey, 2014

YOME = yellow oleander methyl ester

PLME = pig lard methyl ester

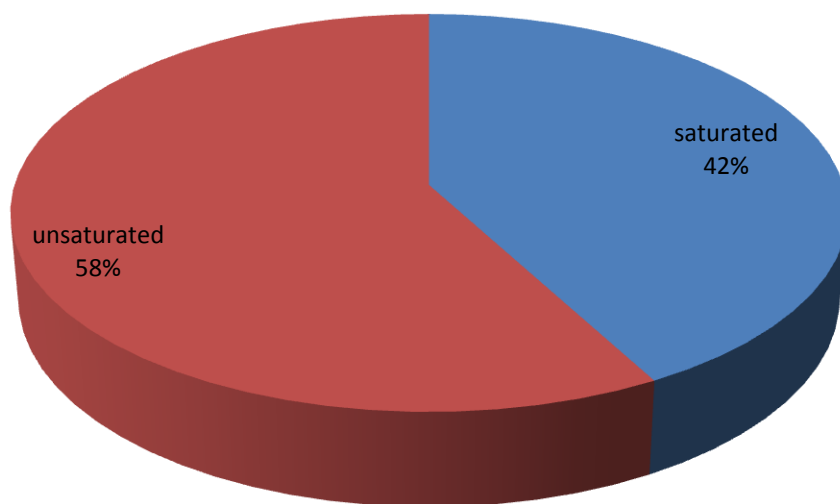


Figure 4.19: Compositions of saturated and unsaturated fatty acids of yellow oleander methyl ester

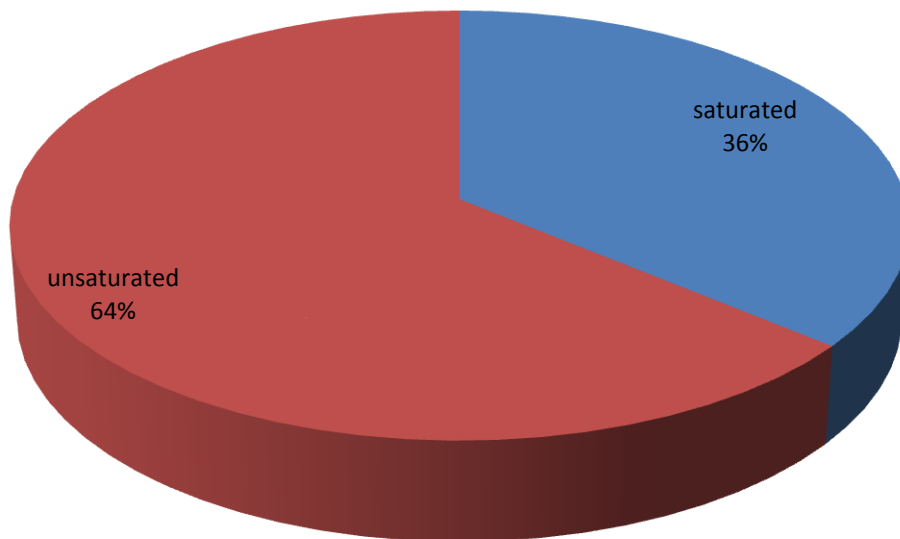


Figure 4.20: Compositions of saturated and unsaturated fatty acid of pig lard methyl ester

4.8 Fuel Properties of Yellow Oleander Methyl Ester and Pig Lard Methyl Ester in Comparison with Fossil Diesel

Tables 4.11 and 4.12 show the fuel properties of yellow oleander methyl ester and pig lard methyl ester compared with the fuel properties of fossil diesel. The flash point of pig lard methyl ester (86° C) was lower than that of fossil diesel (88° C). The cloud points were higher in the biodiesels compared with their respective oils and fossil diesel. The free fatty acid, the acid number and the density are all less than 1 unit.

4.9 Effects of Blending on Biodiesel Properties

Fuel properties (kinematic viscosity, density, flash point, cloud point, cetane number and calorific value) of the blended yellow oleander methyl ester and blended pig lard methyl ester with fossil diesel at different volumetric ratios are reported in Figures 4.21 – 4.27.

The kinematic viscosity of the blend increased as the biodiesel fraction increased in the fuel mixture (Figure 4.21). In yellow oleander methyl ester blends, the kinematic viscosity increased from 4.19 mm/s² in B10 to 6.53 mm/s² in B90 in yellow oleander methyl ester-fossil diesel blends and also increased from 3.76 mm/s² in B10 to 4.84 mm/s² in B90 in pig lard methyl ester-fossil diesel blends.

Figure 4.22 shows a constant density of 0.8805 in all the pig lard methyl ester-fossil diesel blends. With yellow oleander methyl ester-fossil diesel blends, there was an initial increase in the density.

The effect of blending on flash points of the biodiesel-fossil diesel blends is shown in Figure 4.23. The flash point of blends of both methyl esters generally increased with increase in percent biodiesel, resulting in high flash points of 88°C and 90°C in B90 of yellow oleander methyl ester and pig lard methyl ester blends respectively.

Table 4.11: Comparison of fuel properties of yellow oleander seed oil, yellow oleander methyl ester with fossil diesel

Properties	YO	YOME	FD	*ASTM LIMIT (Biodiesel)
Sp.gr at15/14 ⁰ C	0.8841	0.8821	0.8805	0.860 – 0.900
Free fatty acid %	1.96	0.63	-	-
Sulphur(%wt)	0.003	0.001	0.010	-
Flash point ⁰ C	192	98	88	Min 100
Cloud point ⁰ C	10	14	2	-1.0 – 4.0
ASTM colour	0.5	>0.5	2.5	-
Viscosity at40 ⁰ C (mm ² /s)	23.2	8.2	3.8	3.5 – 5.0
Diesel index	25	33	42	-
Cetane No.	48	60	41	-
Acid number	1.26	0.62	-	Max 0.5
Calorific value (MJ/Kg)	13.79	39.78	45.87	-

*Source: Antolin et al., 2002

ASTM = American society for testing and measurement

Sp.gr = specific gravity

YOME = yellow oleander methyl ester

FD = fossil diesel

YO = yellow oleander seed oil

Table 4.12: Comparison of fuel properties of pig lard, pig lard methyl ester with fossil diesel

Properties	PL	PLME	FD	*ASTM LIMIT (Biodiesel)
Sp.gr at 15/14 °C	0.8808	0.8805	0.8805	0.860 – 0.900
Free fatty acid %	2.24	0.81	-	-
Sulphur(% wt)	0.003	0.006	0.010	-
Flash point °C	165	86	88	Min 100
Cloud point °C	15	18	2	-1.0 – 4.0
ASTM colour	0.5	0.5	2.5	-
Viscosity at 40°C (mm ² /s)	12.6	7.3	3.8	3.5 – 5.0
Diesel index	25	25	42	-
Cetane number	43	56	41	-
Acid number	1.12	0.62	-	Max 0.5
Calorific value (MJ/Kg)	12.02	40.36	45.87	-

*Source: Antolin et al., 2002

ASTM = American society for testing and measurement

Sp.gr = specific gravity

PLME = pig lard methyl ester

FD = fossil diesel

PL = pig lard

The effect of blending on cloud point is shown in Figure 4.24. The cloud points of the lower blends of B10 and B20 of yellow oleander biodiesel blends were below 4°C. An increase in cloud point was observed with increase of methyl ester in the blends, hence, the higher the biodiesel fraction in the blend, the higher is the cloud point.

Figure 4.25 shows the cetane number of the methyl esters and their blends. A gradual increase in cetane number with increase ratio of biodiesel in the blends was observed.

The result showed large differences in calorific values between the biodiesels (B100) and their respective oils (Figure 4.26). The lowest calorific values were recorded in yellow oleander seed oil and pig lard. Figure 4.27 shows the variation of calorific values of yellow oleander methyl ester and pig lard methyl ester with blending. The calorific values of yellow oleander methyl ester- blends and pig lard methyl ester- blends decreased with increase in percentage fatty acid methyl ester.

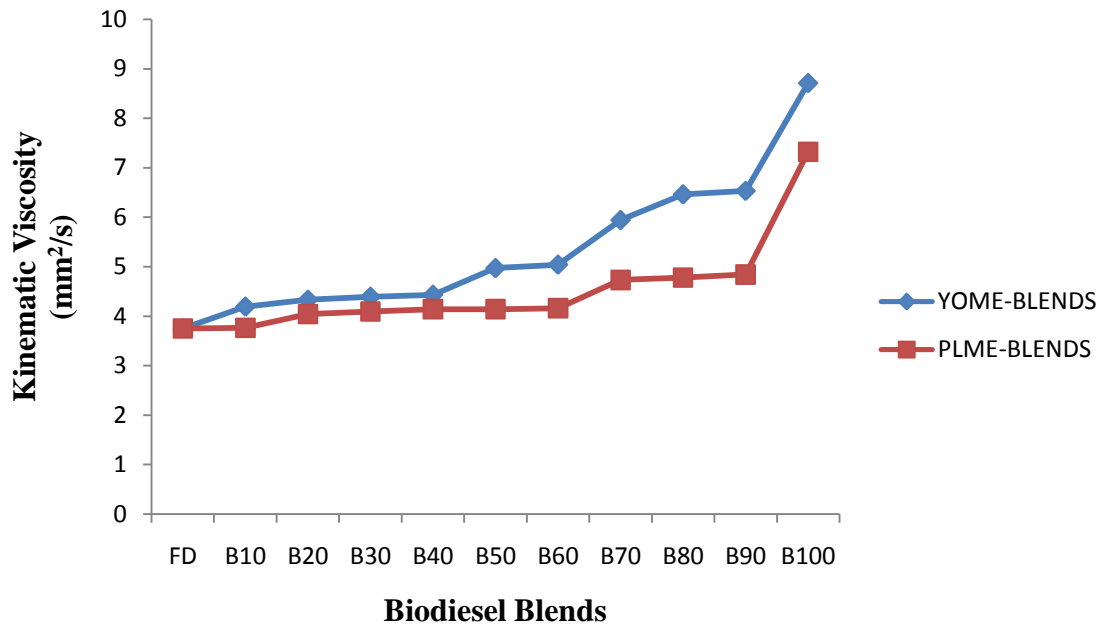


Figure 4.21: Effect of volumetric increment of methyl esters in blends on kinematic viscosity

FD = fossil diesel
 B10 = 10% biodiesel + 90% diesel
 B20 = 20% biodiesel + 80% diesel
 B30 = 30% biodiesel + 70% diesel
 B40 = 40% biodiesel + 60% diesel
 B50 = 50% biodiesel + 50% diesel
 B60 = 60% biodiesel + 40% diesel
 B70 = 70% biodiesel + 30% diesel
 B80 = 80% biodiesel + 20% diesel
 B90 = 90% biodiesel + 10% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester

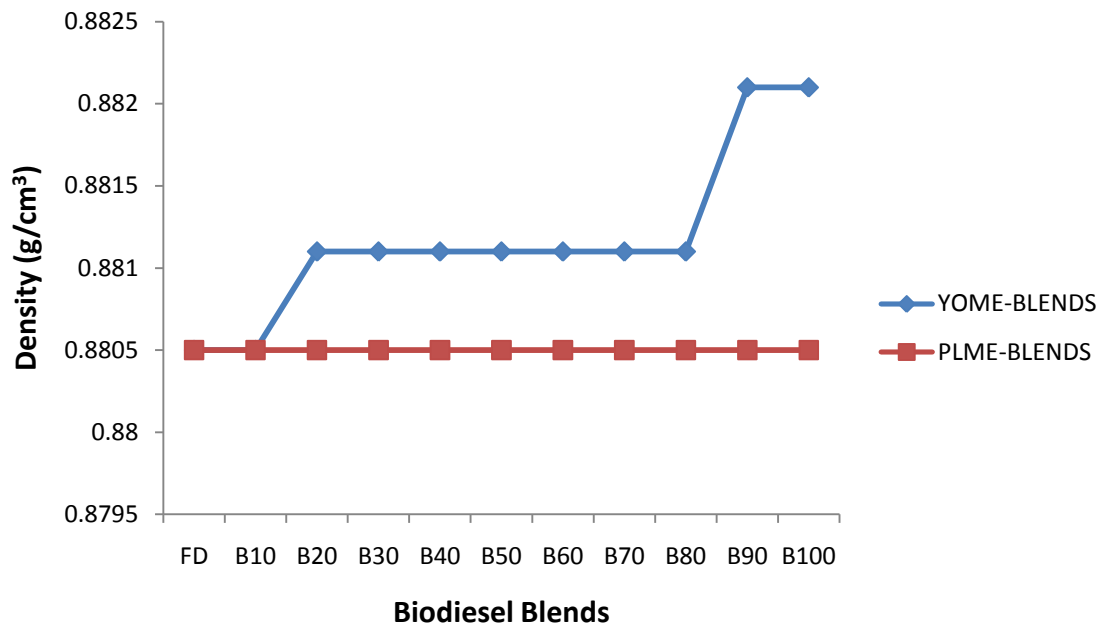


Figure 4.22: Effect of volumetric increment of methyl esters in blends on density

- FD = fossil diesel
- B10 = 10% biodiesel + 90% diesel
- B20 = 20% biodiesel + 80% diesel
- B30 = 30% biodiesel + 70% diesel
- B40 = 40% biodiesel + 60% diesel
- B50 = 50% biodiesel + 50% diesel
- B60 = 60% biodiesel + 40% diesel
- B70 = 70% biodiesel + 30% diesel
- B80 = 80% biodiesel + 20% diesel
- B90 = 90% biodiesel + 10% diesel
- B100 = 100% biodiesel
- PLME = pig lard methyl ester
- YOME = yellow oleander methyl ester

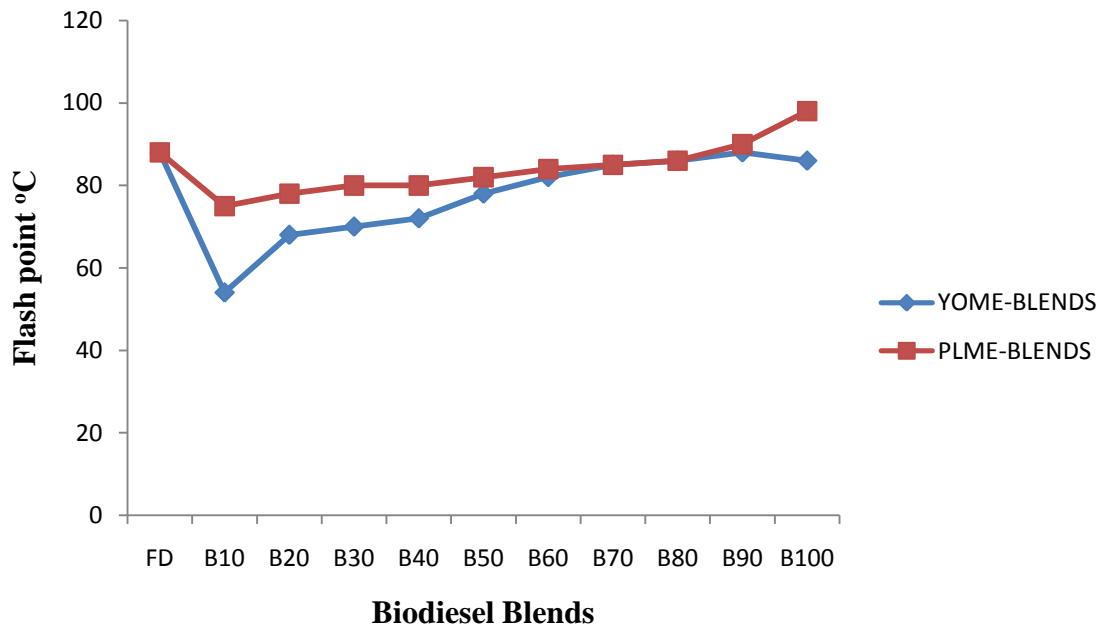


Figure 4.23: Effect of volumetric increment of methyl esters in blends on flash point

FD = fossil diesel
 B10 = 10% biodiesel + 90% diesel
 B20 = 20% biodiesel + 80% diesel
 B30 = 30% biodiesel + 70% diesel
 B40 = 40% biodiesel + 60% diesel
 B50 = 50% biodiesel + 50% diesel
 B60 = 60% biodiesel + 40% diesel
 B70 = 70% biodiesel + 30% diesel
 B80 = 80% biodiesel + 20% diesel
 B90 = 90% biodiesel + 10% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester

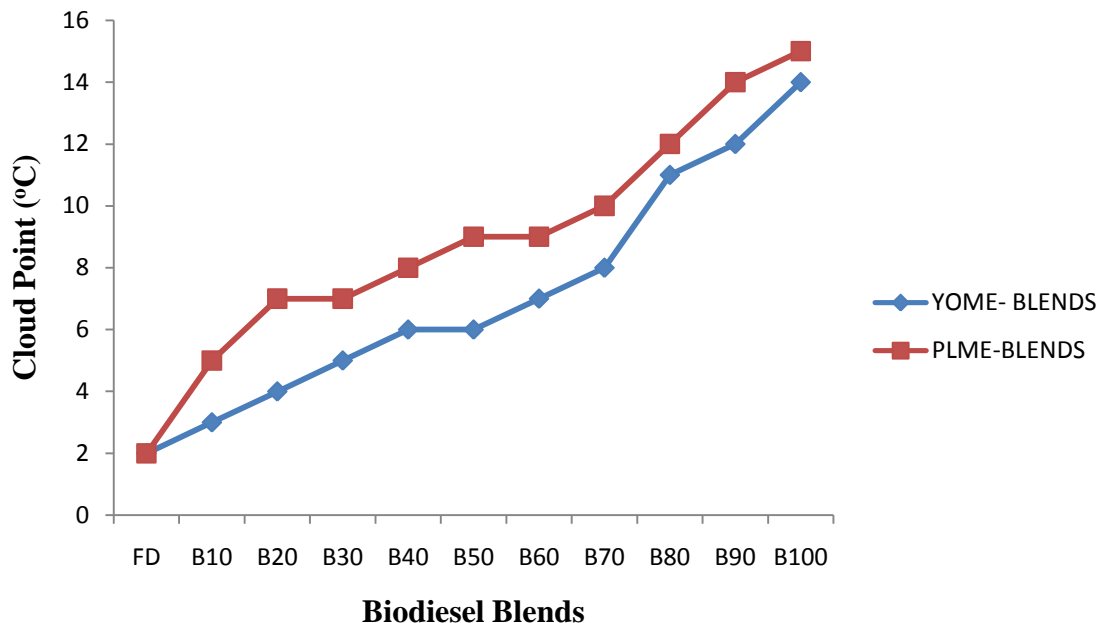


Figure 4.24: Effect of volumetric increment of methyl esters in blends on cloud point

FD = fossil diesel
 B10 = 10% biodiesel + 90% diesel
 B20 = 20% biodiesel + 80% diesel
 B30 = 30% biodiesel + 70% diesel
 B40 = 40% biodiesel + 60% diesel
 B50 = 50% biodiesel + 50% diesel
 B60 = 60% biodiesel + 40% diesel
 B70 = 70% biodiesel + 30% diesel
 B80 = 80% biodiesel + 20% diesel
 B90 = 90% biodiesel + 10% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester

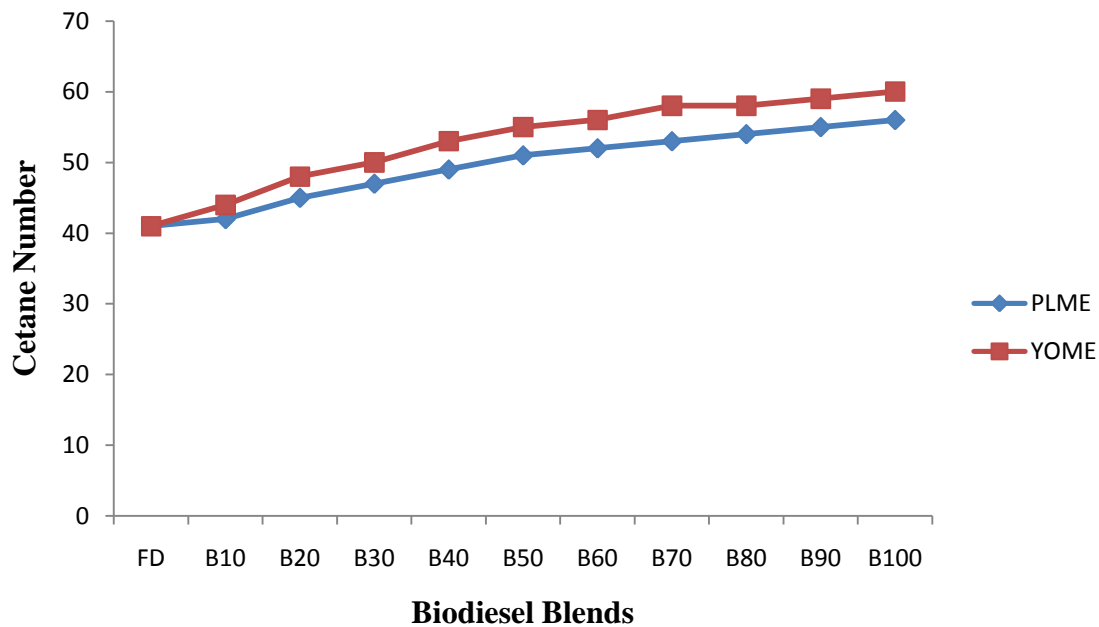


Figure 4.25: Effect of volumetric increment of methyl esters in blends of cetane number

- FD = fossil diesel
- B10 = 10% biodiesel + 90% diesel
- B20 = 20% biodiesel + 80% diesel
- B30 = 30% biodiesel + 70% diesel
- B40 = 40% biodiesel + 60% diesel
- B50 = 50% biodiesel + 50% diesel
- B60 = 60% biodiesel + 40% diesel
- B70 = 70% biodiesel + 30% diesel
- B80 = 80% biodiesel + 20% diesel
- B90 = 90% biodiesel + 10% diesel
- B100 = 100% biodiesel
- PLME = pig lard methyl ester
- YOME = yellow oleander methyl ester

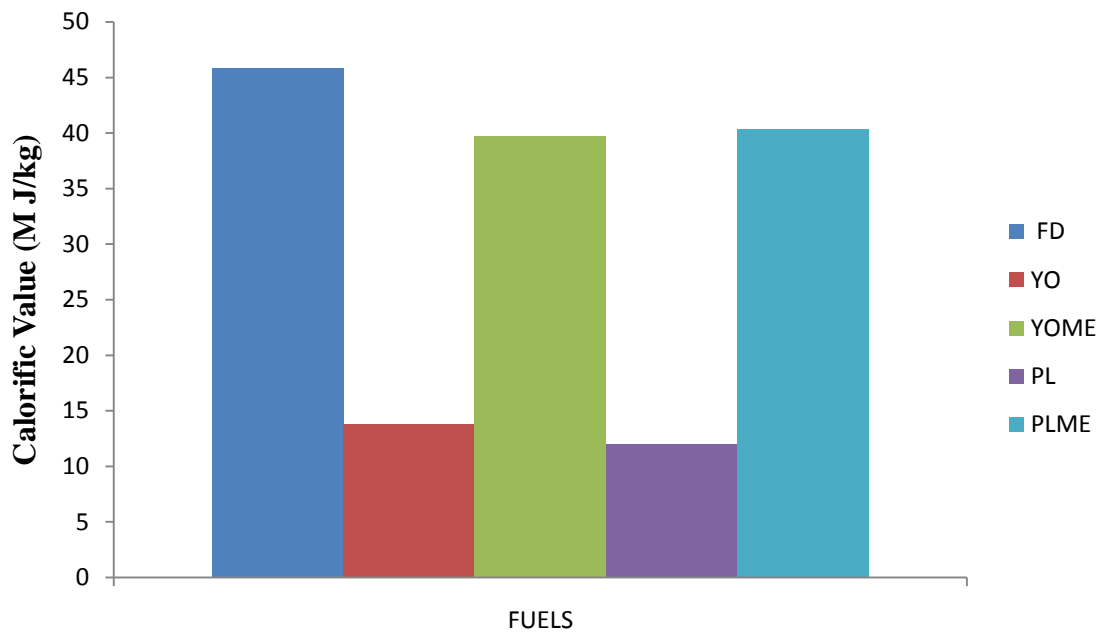


Figure 4.26: Comparison of calorific value of pig lard, yellow oleander seed oil, yellow oleander methyl ester and pig lard methyl ester with fossil diesel

FD = fossil diesel
 PL = pig lard
 YO = yellow oleander seed oil
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester

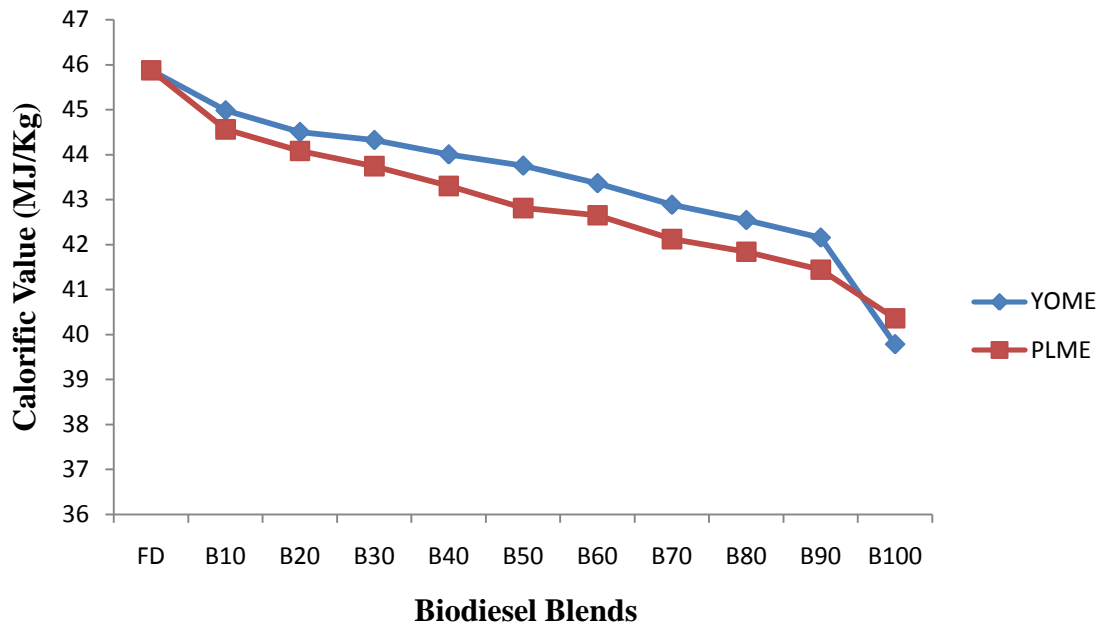


Figure 4.27: Effect of volumetric increment of methyl esters in blends on calorific value

- FD = fossil diesel
- B10 = 10% biodiesel + 90% diesel
- B20 = 20% biodiesel + 80% diesel
- B30 = 30% biodiesel + 70% diesel
- B40 = 40% biodiesel + 60% diesel
- B50 = 50% biodiesel + 50% diesel
- B60 = 60% biodiesel + 40% diesel
- B70 = 70% biodiesel + 30% diesel
- B80 = 80% biodiesel + 20% diesel
- B90 = 90% biodiesel + 10% diesel
- B100 = 100% biodiesel
- PLME = pig lard methyl ester
- YOME = yellow oleander methyl ester

4.10 Correlation Coefficient Analysis of Blends from Yellow Oleander Methyl Ester and Pig Lard Methyl Ester

Tables 4.13 - 14 present the correlation analysis results for Yellow Oleander Methyl Ester and Pig Lard Methyl Ester blends respectively. High positive correlation coefficients in ASTM Colour and sulphur, Calorific and sulphur, calorific value and cetane number were shown in pig lard biodiesel blends and in yellow oleander biodiesel blends, the correlation coefficient of ASTM Colour and Sulphur was 0.796 in YOME blends at 99% confidence limit. A strong negative correlation coefficient of -0.673 existed between cetane number and ASTM colour at 99% confidence limit. Calorific value show a negative correlation of -0.484 with ASTM colour at 95% confidence limit. In Table 4.10 the sulphur contents of PLME blends show highly significant negative correlation with flash point, cloud point, kinematic viscosity and cetane number at 99% confidence limit. Flash points were significantly positively correlated at 99% confidence level with cloud point and cetane number. Other properties that negatively correlate with the flash point are ASTM colour and calorific value. Calorific value of the PLME blends shows a strong negative correlation of - 0.951 with cetane number at 99% confidence limit.

Table 4.13: Correlation analysis of the physicochemical properties of yellow oleander methyl ester blends

PROPERTY	SPG-Y	S-Y	FP-Y	CP-Y	ASTMC-Y	KV-Y	DI-Y	CV-Y	CN-Y
SPG-Y	1								
S-Y	-.299	1							
FP-Y	-.096	.325	1						
CP-Y	.248	-.323	.043	1					
ASTMC-Y	-.232	.796**	.005	-.114	1				
KV-Y	.145	-.403	-.368	.049	-.121	1			
DI-Y	.048	-.160	-.284	.057	-.322	.415	1		
CV-Y	.343	-.278	-.186	-.135	-.484*	-.041	.422	1	
CN-Y	.077	-.673**	-.170	.015	-.673**	.076	-.169	.369	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

SPG-Y = specific gravity of yellow oleander methyl ester blend
S-Y = %sulphur content of yellow oleander methyl ester blend
FP-Y = flash point of yellow oleander methyl ester blend
CP-Y = cloud point of yellow oleander methyl ester blend
ASTMC-Y = colour of of yellow oleander methyl ester blend
KV-Y = kinematic viscosity of yellow oleander methyl ester blend
DI-Y = Diesel index of yellow oleander methyl ester blend
CN-Y = cetane number of yellow oleander methyl ester blend

Table 4.14: Correlation analysis of the physicochemical properties of pig lard methyl ester blends

PROPERTY	SPG-P	S-P	FP-P	CP-P	ASTMC-P	KV-P	DI-P	CV-P	CN-P
SPG-P	1								
S-P	.203	1							
FP-P	-.150	-.796**	1						
CP-P	.024	-.655**	.657**	1					
ASTMC-P	.091	.861**	-.839**	-.778**	1				
KV-P	.211	-.594**	.533*	.796**	-.751**	1			
DI-P	-.227	.118	-.178	-.482*	.217	-.261	1		
CV-P	-.115	.825**	-.796**	-.794**	.934**	-.795**	.379	1	
CN-P	.161	-.748**	.709**	.778**	-.882**	.719**	-.486*	-.951**	1

*. Correlation is significant at the 0.05 level (2-tailed).

** . Correlation is significant at the 0.01 level (2-tailed).

SPG-P	=	specific gravity of pig lard methyl ester blend
S-P	=	%sulphur content of pig lard methyl ester blend
FP-P	=	flash point of pig lard methyl ester blend
CP-P	=	cloud point of pig lard methyl ester blend
ASTMC-P	=	colour of of pig lard methyl ester blend
KV-P	=	kinematic viscosity of pig lard methyl ester blend
DI-P	=	Diesel index of pig lard methyl ester blend
CN-P	=	cetane number of pig lard methyl ester blend

4.11 Effect of Temperature on Kinematic Viscosity, Acid Value and Peroxide Value of Methyl Esters at 100, 150, 200 and 250°C

A comparison of kinematic viscosity, acid value and peroxide value measured before and after the biodiesels were heated to different temperature range is shown in Figures 4.28- 4.30.

Kinematic viscosities of the methyl esters initially decreased with increase in temperature up to 150°C and then start to increase with increase in temperature (Figure 4.28).

The acid values of both yellow oleander methyl ester and pig lard methyl ester were found to increase with increase in temperature. A comparison of acid values showed those of yellow oleander methyl ester to be lower than those of pig lard methyl ester at each temperature measurement (Figure 4.29).

There was an initial increase in peroxide values in yellow oleander methyl ester and pig lard methyl ester with increase in temperature up to 100°C, but on further increase in temperature, the peroxide values decreased (Figure 4.30).

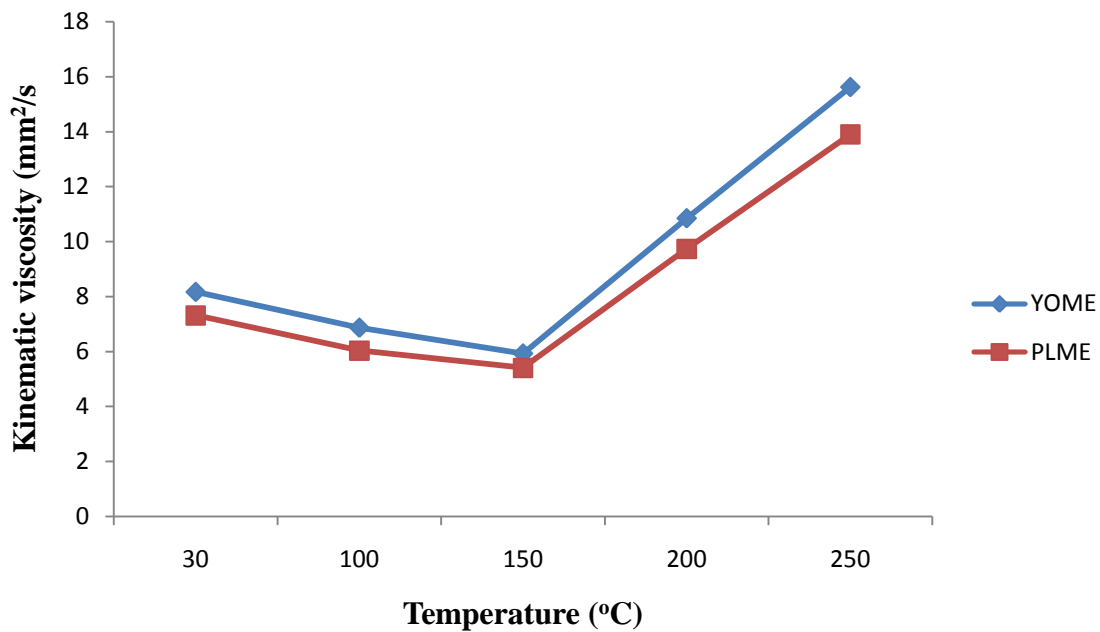


Figure 4.28: Effect of temperature on kinematic viscosity of methyl esters

PLME = pig lard methyl ester
YOME = yellow oleander methyl ester

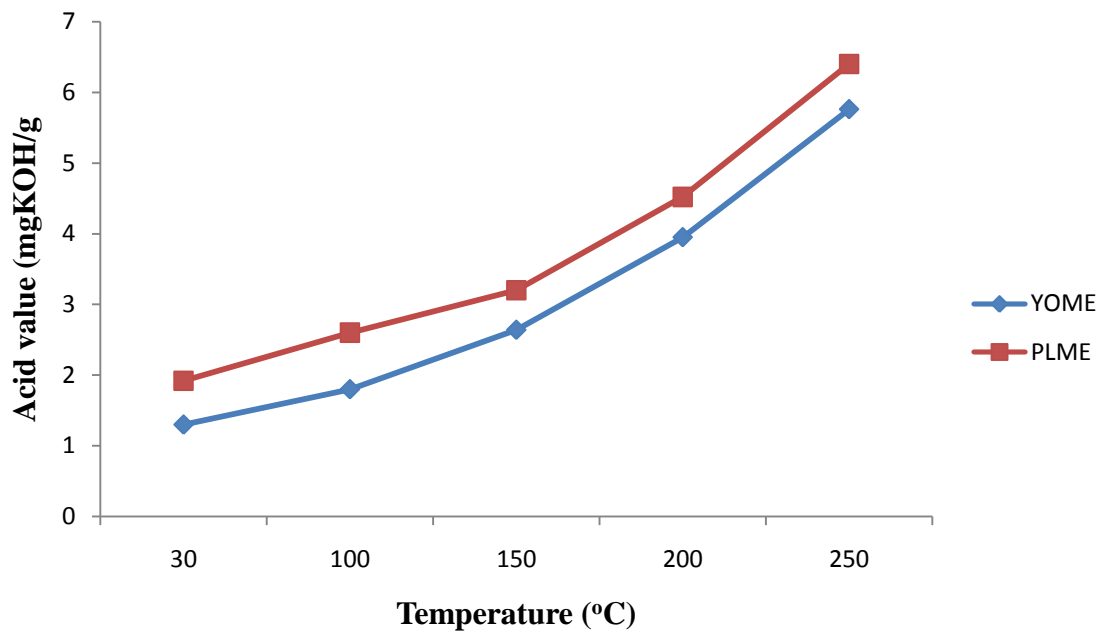


Figure 4.29: Effect of temperature on acid value of methyl esters

PLME = pig lard methyl ester
YOME = yellow oleander methyl ester

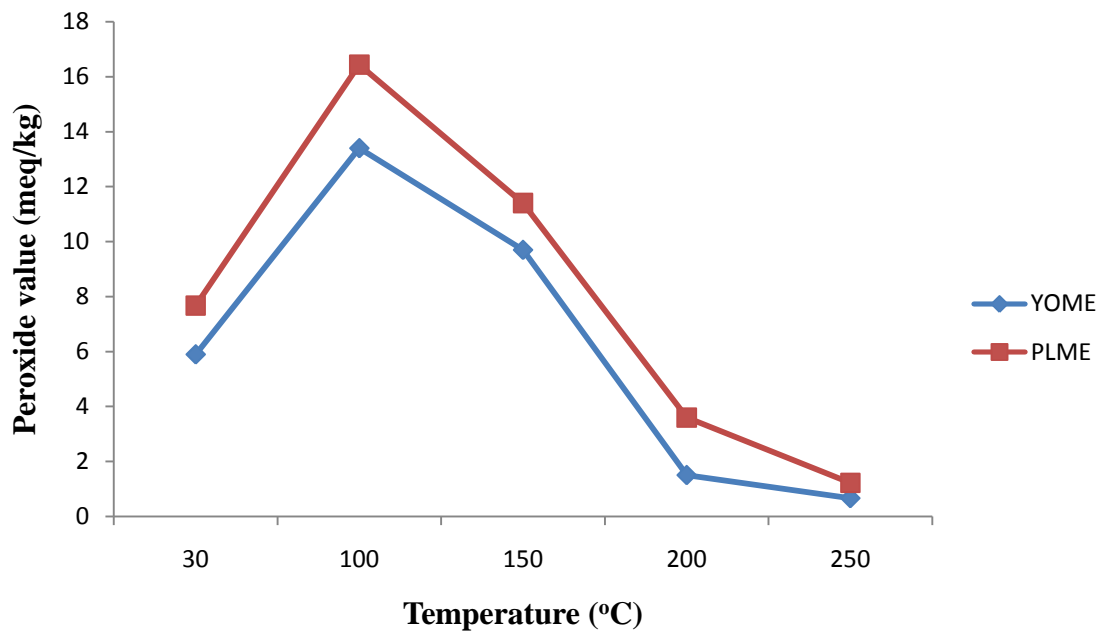


Figure 4.30: Effect of temperature on peroxide value of methyl esters

PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester

4.12 Effect of Storage on Methyl Esters and Methyl Ester-Blends

The effects of storage on the fuel properties of the methyl esters and their blends are shown in Figures 4.31 to 4.38.

There was a general decrease in calorific values in all the biodiesels and their blends with increase of storage period. Fossil diesel did not show any effect on its calorific value over the storage period. Blends with high fractions of biodiesel experienced higher decrease in calorific values as storage period increased. In B20 of yellow oleander methyl ester-fossil diesel blend, calorific value decreased by 1.10% and in other blends B40, B80 and B100 calorific value decreased by 2.43 %, 2.63 %, and 3.19 % respectively after 60 days (see Appendix VII).

In Figures 4.33 and 4.34, there was an increase in flash point with increase in storage period in both biodiesels and their blends. These increments in flash point were higher in blends containing high proportion of methyl ester.

From Figures 4.35 and 4.36, an increasing trend of density for all the fuel samples and their blends was observed with increase in storage time. The increasing trend of density in pig lard methyl ester blends was more than that for yellow oleander seed methyl ester blends.

The effect of storage on the kinematic viscosity of yellow oleander methyl ester and pig lard methyl ester and their blends is shown in Figures 4.37 and 4.38. The kinematic viscosity of the biodiesels and their blends increased with increase in storage period. The viscosity of yellow oleander methyl ester (B100) increased from 8.17 mm²/s to 8.29 mm²/s after a storage period of 60 days, then to 8.40 mm²/s after 120 days of storage.

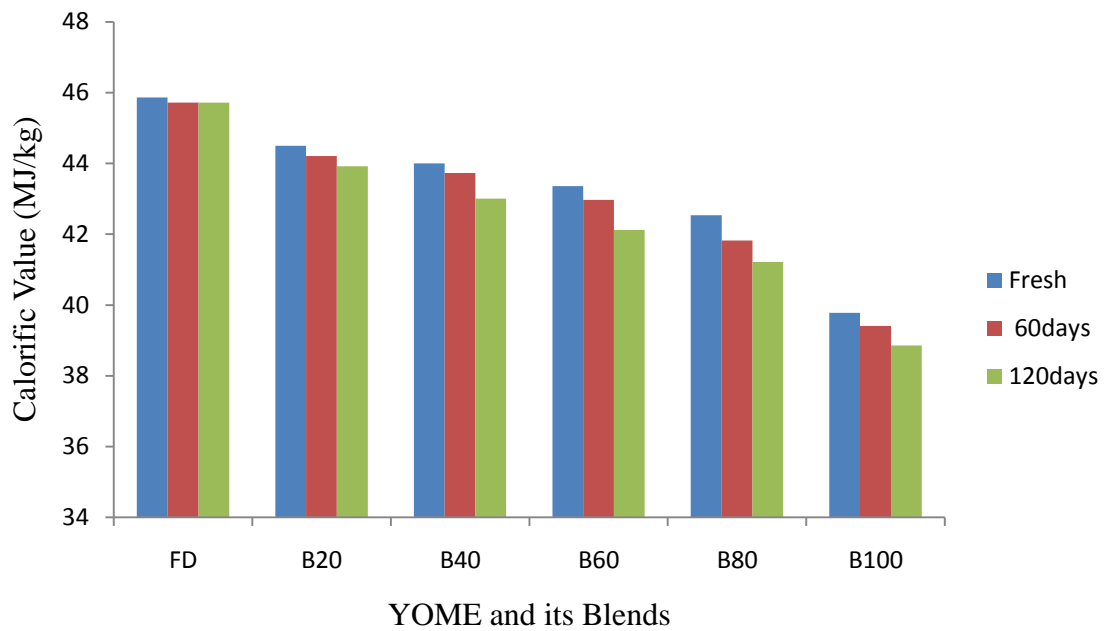


Figure 4.31: Effect of storage on calorific value of yellow oleander methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

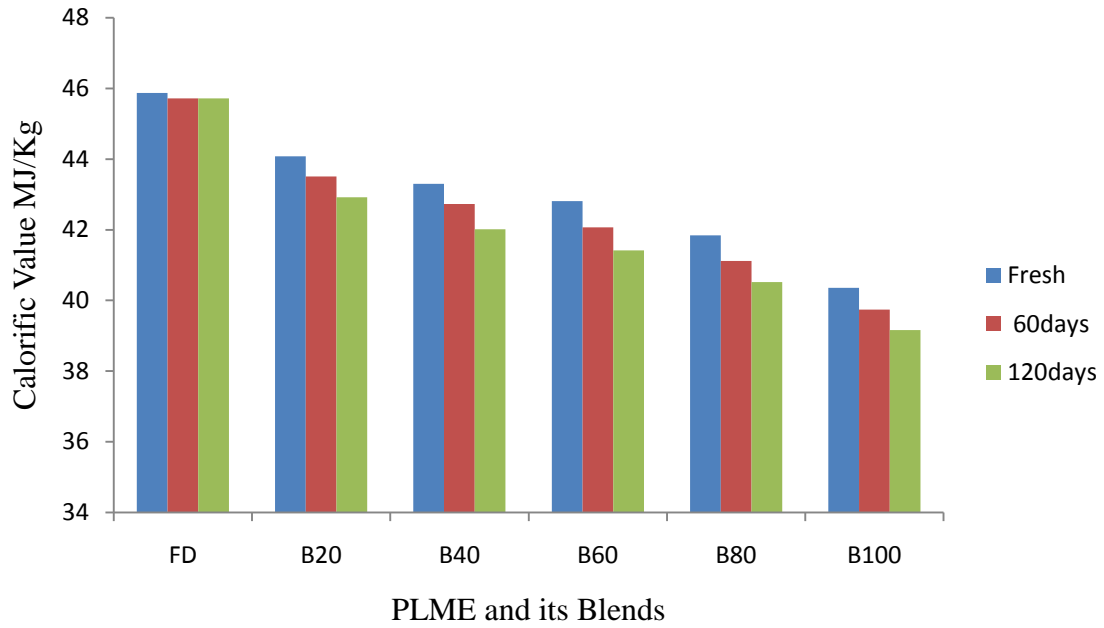


Figure 4.32: Effect of storage on the calorific value of pig lard methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

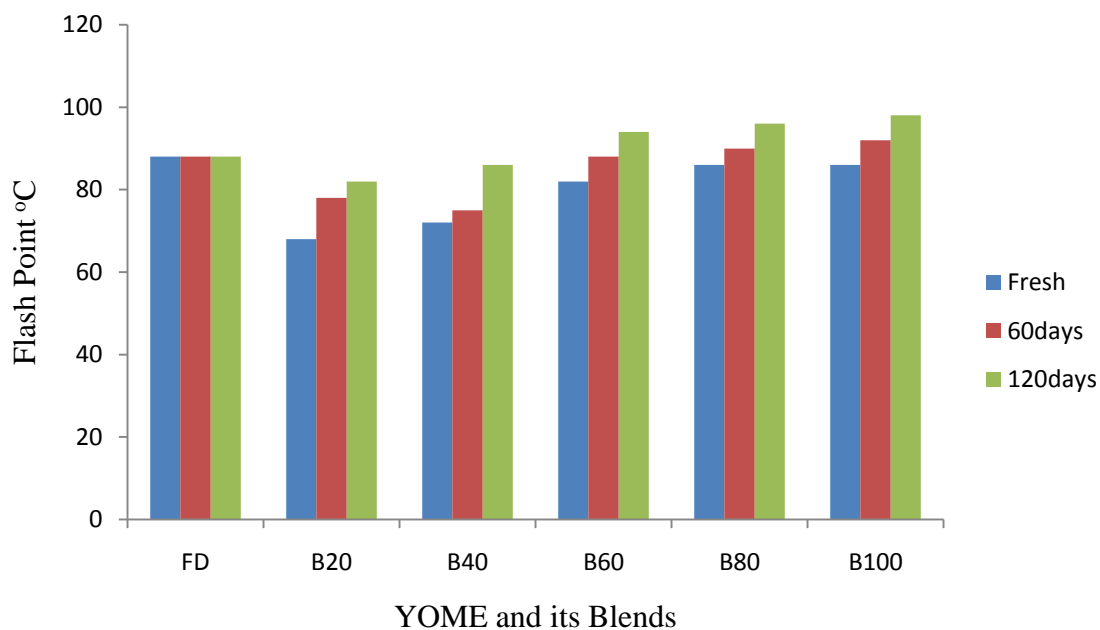


Figure 4.33: Effect of storage on the flash point of yellow oleander methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

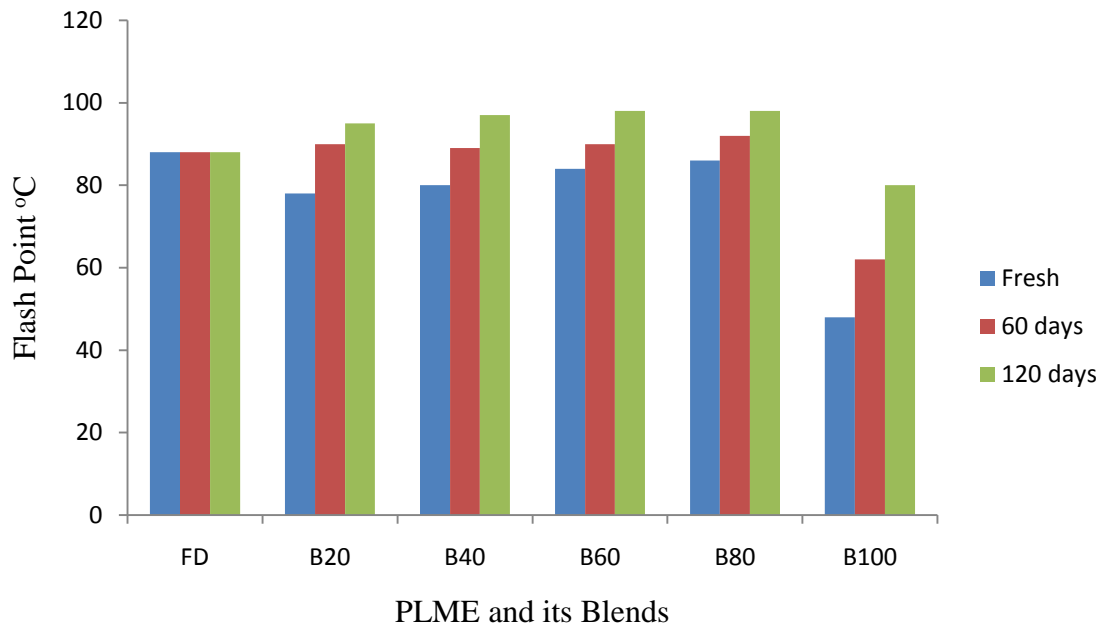


Figure 4.34: Effect of storage on the flash point of pig lard methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

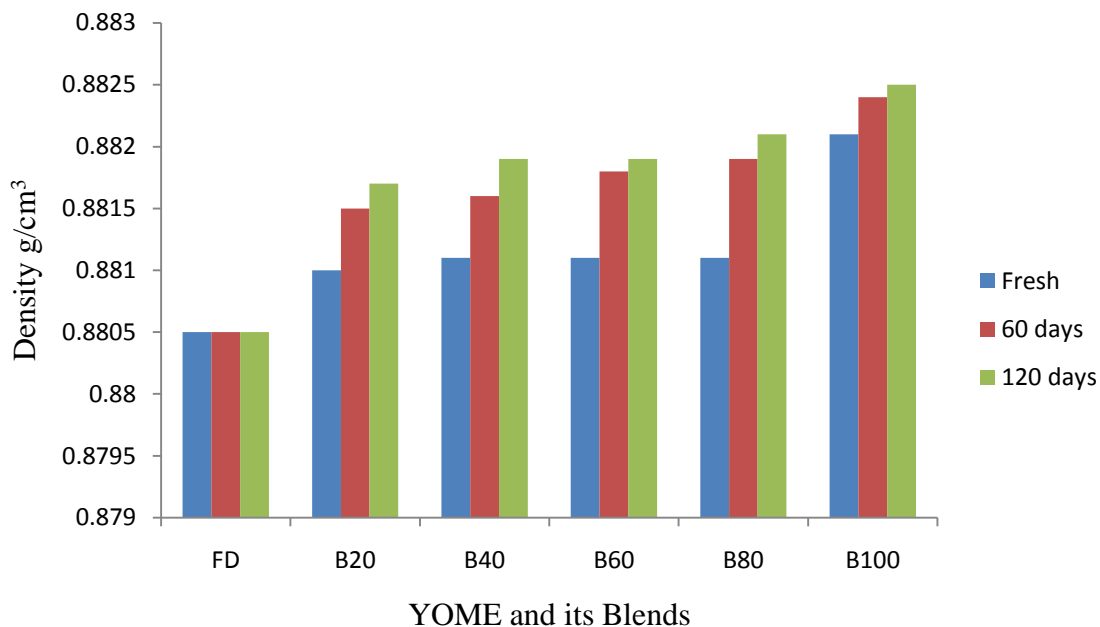


Figure 4.35: Effect of storage on the density of yellow oleander methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

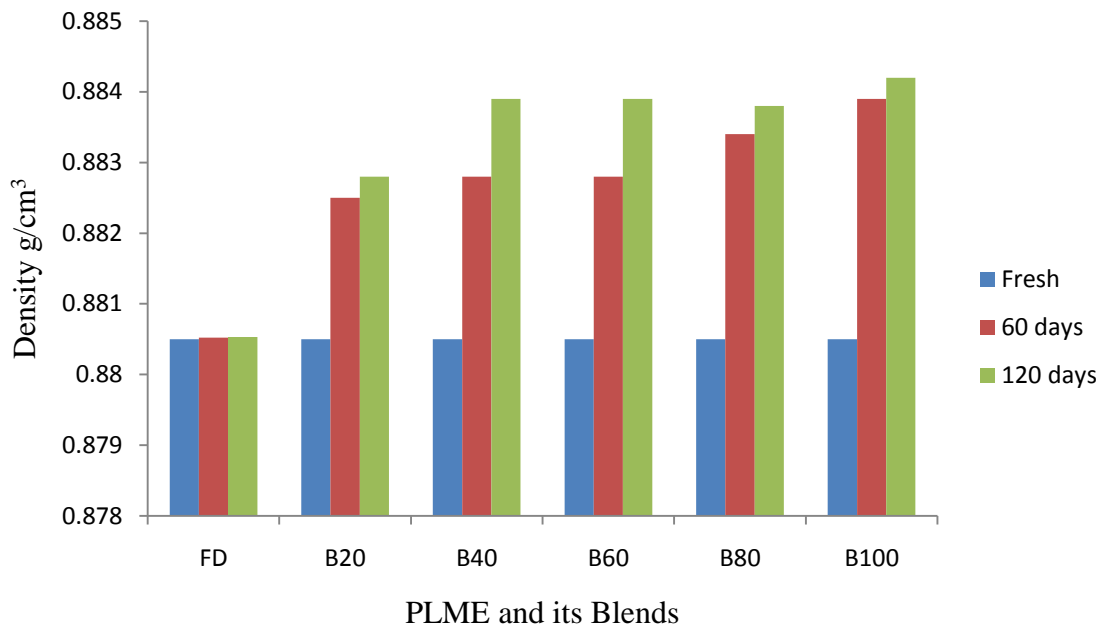


Figure 4.36: Effect of storage on the density of pig lard methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

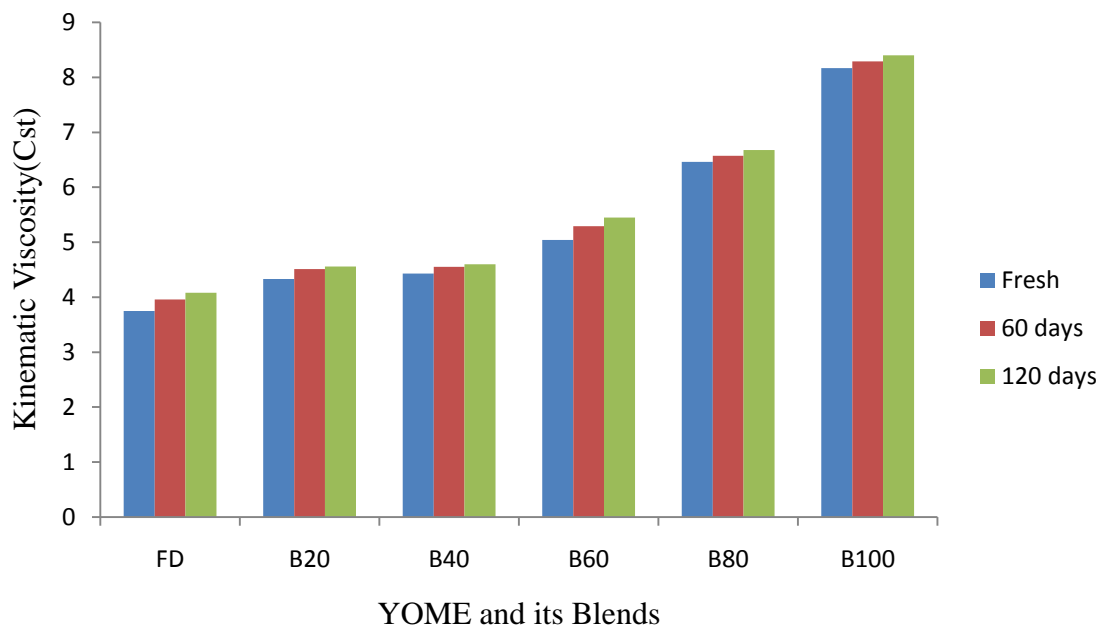


Figure 4.37: Effect of storage on the kinematic viscosity of yellow oleander methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

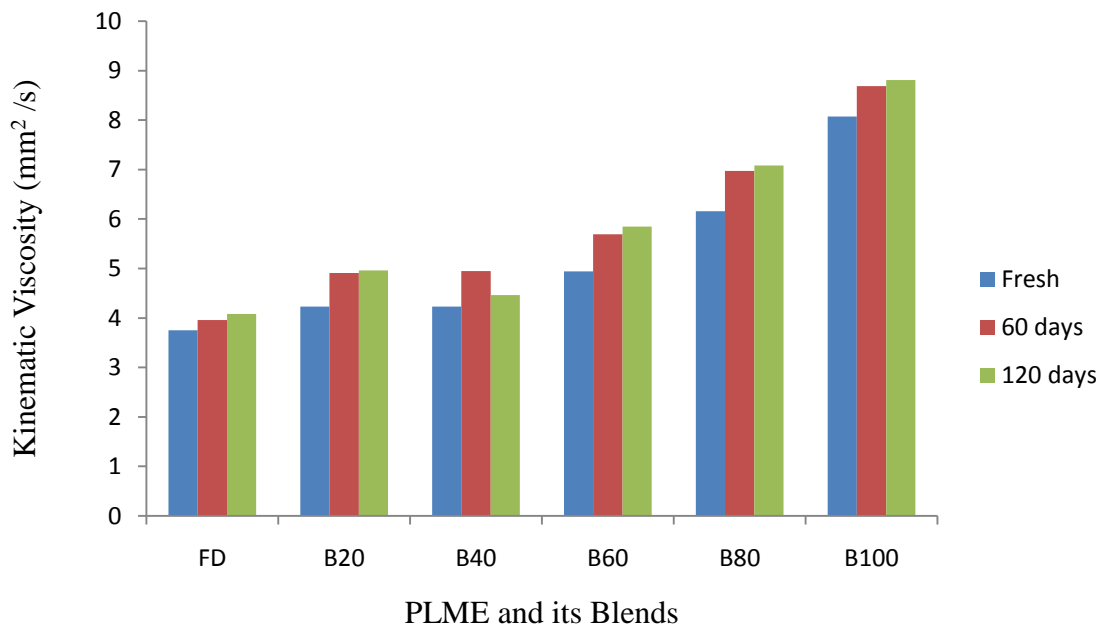


Figure 4.38: Effect of storage on the kinematic viscosity of pig lard methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

4.13 Effect of Elevated Temperatures on the Properties of Methyl Ester Blends

The specific gravities of fossil diesel, yellow oleander methyl ester, pig lard methyl ester and their blends were measured after heating to different temperatures and the effect of heat on each shown in Figures 4.39- 4.42.

It was observed that biodiesels and their blends experienced a decrease in specific gravity values with increase in temperature from 100°C to 250°C (Figure 4.39 and 4.40).

Figures 4.41 and 4.42 show the effect of blending pig lard methyl ester at elevated temperatures on specific gravity. The specific gravity increased with increase in volume of biodiesel in the blend at all test temperatures.

The viscosities of the fossil diesel, yellow oleander methyl ester, pig lard methyl ester and methyl ester blends decreased with increase in temperature, however, there was an increase in kinematic viscosity with increase in blending ratios at all temperatures (Figure 4.43 – 4.46).

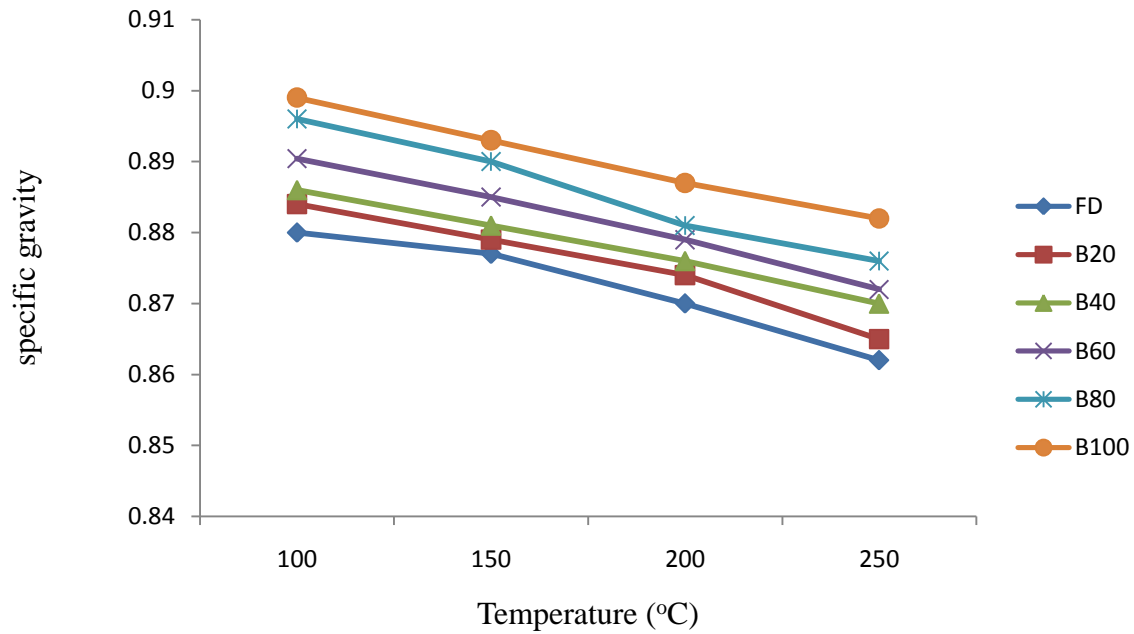


Figure 4.39: Effect of temperature on specific gravity of pig lard methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

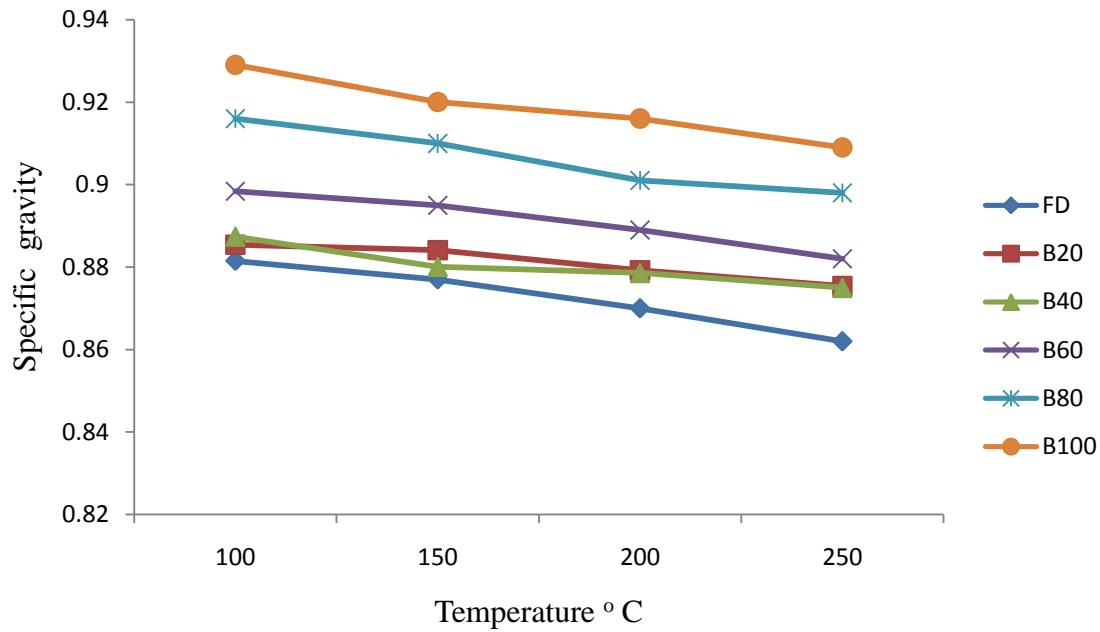


Figure 4.40: Effect of temperature on the specific gravity of yellow oleander methyl ester –fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

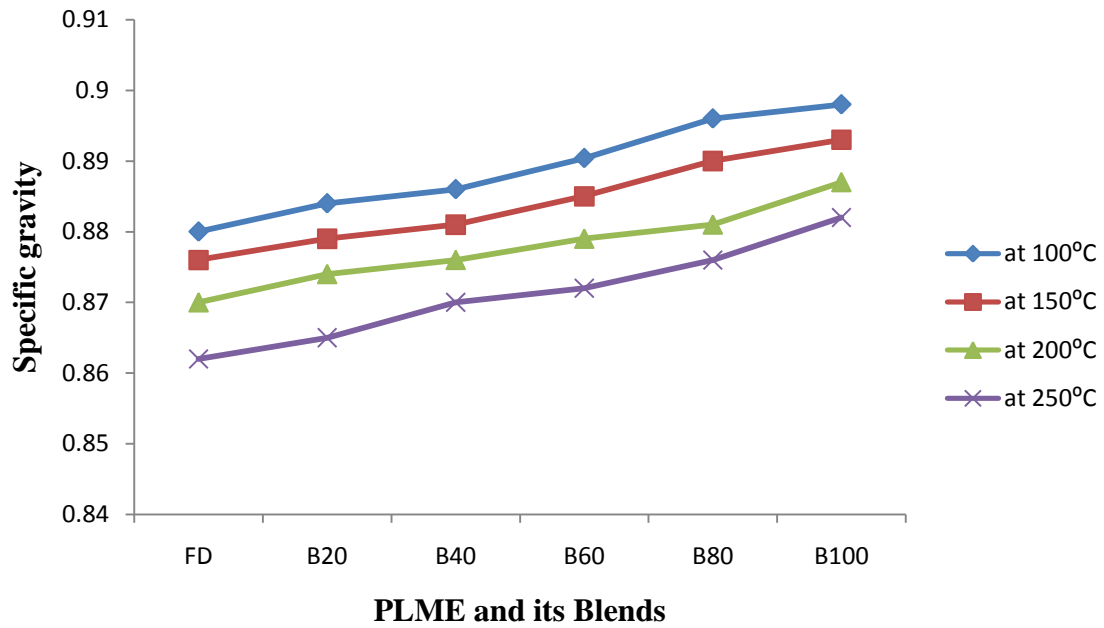


Figure 4.41: Variation of specific gravity of pig lard methyl ester- fossil diesel blends with temperature

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

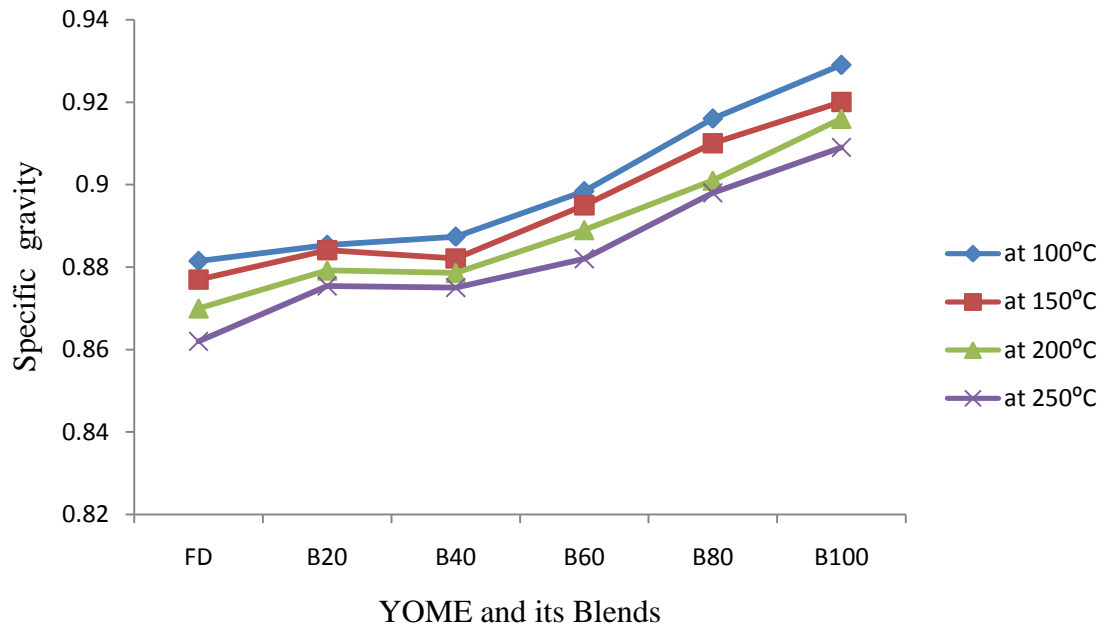


Figure 4.42: Variation of specific gravity of yellow oleander methyl ester-fossil diesel blends with temperature

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

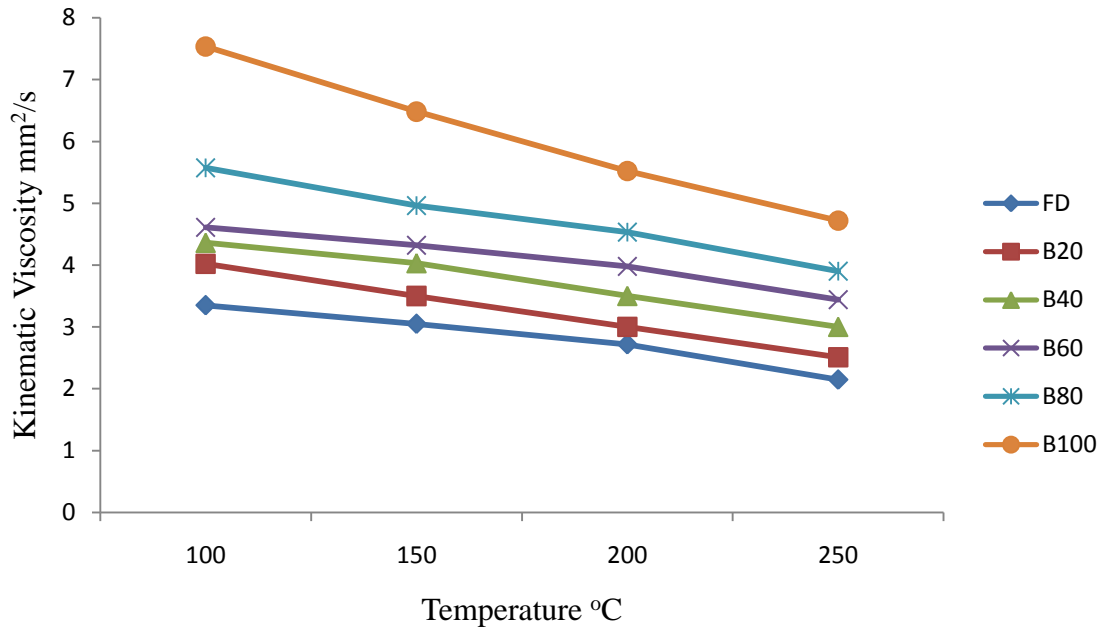


Figure 4.43: Effect of temperature on kinematic viscosity of pig lard methyl ester-fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

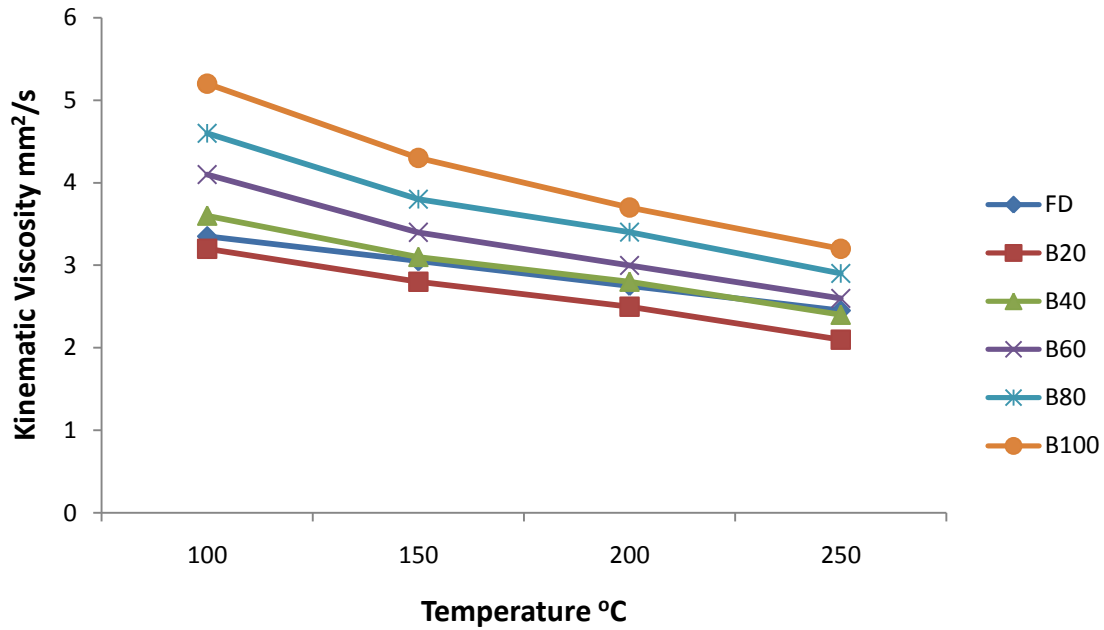


Figure 4.44: Effect of temperature on kinematic viscosity of yellow oleander methyl ester- fossil diesel blends

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

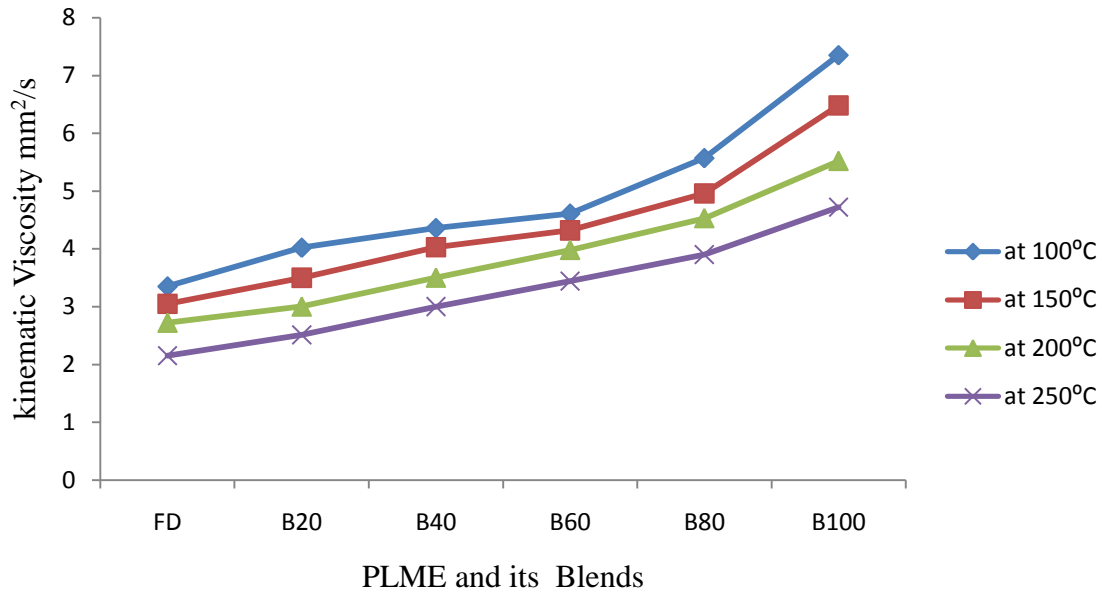


Figure 4.45: Variation of kinematic viscosity of pig lard methyl ester- fossil diesel blends with temperature

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 PLME = pig lard methyl ester

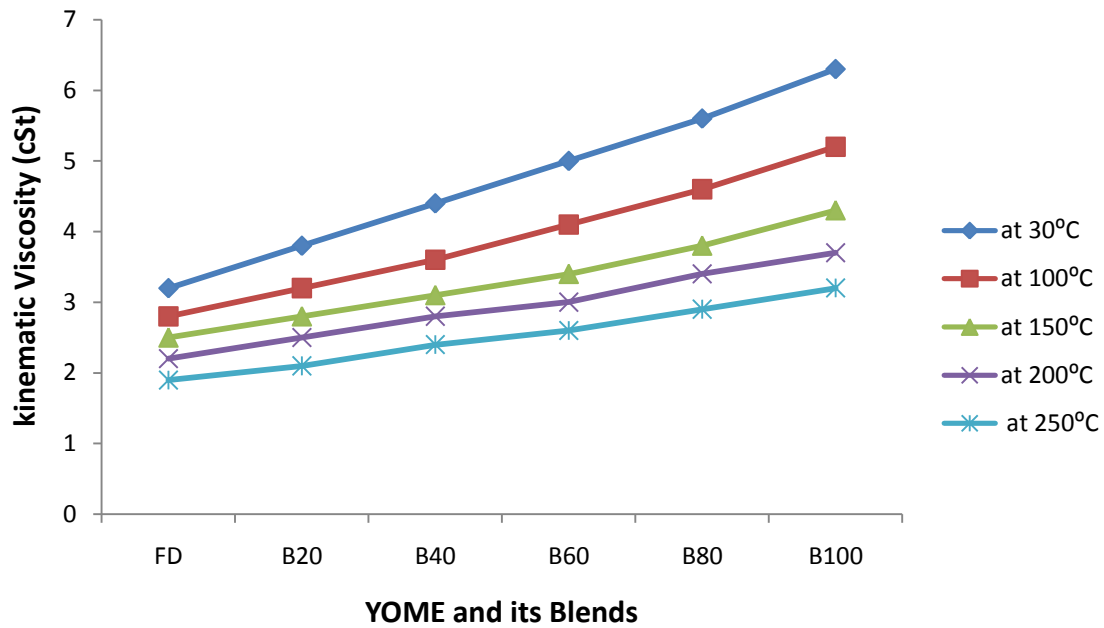


Figure 4.46: Variation of kinematic viscosity of yellow oleander methyl ester- fossil diesel blends with temperature

FD = fossil diesel
 B20 = 20% biodiesel + 80% diesel
 B40 = 40% biodiesel + 60% diesel
 B60 = 60% biodiesel + 40% diesel
 B80 = 80% biodiesel + 20% diesel
 B100 = 100% biodiesel
 YOME = yellow oleander methyl ester

4.14 Biodiesel from Mixed Yellow Oleander Seed Oil and Pig Lard

4.14.1 Properties of FAMES of mixed yellow oleander seed oil and pig Lard

The biodiesels prepared from mixtures of yellow oleander seed oil (YO) and pig lard (PL) were labeled as PL/YO (1:1) for a mixture of pig lard and yellow oleander seed oil in the ratio of 1:1, PL/YO (1:2) for a mixture of pig lard and yellow oleander seed oil in the ratio of 1:2 and PL/YO (2:1) for a mixture of pig lard and yellow oleander seed oil in the ratio of 2:1.

The fuel properties of the biodiesels prepared from the mixed oils show high concentration of sulphur in PL/YO (1:1) biodiesel, while the highest flash point value was recorded in the PL/YO (1:2) where a higher proportion of yellow seed oil was used in the formulation (Table 4.15). The cloud points of the biodiesel prepared from the mixed oils were all in a close range of 15- 16°C. The kinematic viscosity was observed to decrease with increase proportion of yellow oleander seed oil in the formulated biodiesels, but increased with increase proportion of pig lard. The cetane numbers were low in the formulated biodiesels compared to the methyl esters of pure yellow oleander seed oil or pig lard.

4.14.2 Effect of elevated temperature on biodiesels from mixed yellow oleander seed oil and pig lard

Tables 4.16 – 4.19 show the fuel properties of biodiesel samples of pig lard: yellow oleander seed oil (1:1), pig lard: yellow oleander seed oil (1:2) and pig lard: yellow oleander seed oil (2:1) from the oil mixtures after heating under a temperature range of 100– 250°C. The specific gravity, kinematic viscosity and cetane number of the biodiesels decreased with increase in temperature, however, the flash point and cloud point increased as the temperature increases.

Table 4.15: Fuel properties of biodiesels from mixed yellow oleander seed oil and pig lard at room temperature

	PLME	YOME	FD	PL:YO 1:1 FAME	PL:YO 1:2 FAME	PL:YO 2:1 FAME	*ASTM LIMIT Biodiesel
Sp.gr(15/14 ⁰ C)	0.881	0.882	0.881	0.876	0.878	0.878	0.860-.900
Sulphur(% w/w)	0.006	0.001	0.010	0.009	0.006	0.006	-
Flash point ⁰ C	86	96	88	90	92	88	Min 100
Cloud point ⁰ C	18	14	2	16	15	15	-1.0 – 4.0
ASTM colour	0.5	0.5	2.5	0.5	0.5	0.5	-
K. Viscosity at 40 ⁰ C(mm ² /s)	4.3	5.1	3.8	5.0	4.4	5.1	3.5 – 5.0
Diesel index	25.0	33.0	42.0	27.0	27.0	25.0	-
Cetane No.	56.0	60.0	41.0	30.0	32.0	31.0	-

*Source: Antolin *et al.*, 2002

FD = fossil diesel
 PL = pig lard
 YO = yellow oleander seed oil
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester
 ASTM = American society for testing and material
 FAME = Fatty acid methyl ester

Table 4.16: Fuel properties of biodiesels from mixed yellow oleander seed oil and pig lard at 100°C

	PLME	YOME	FD	PL:YO 1:1 FAME	PL:YO 1:2 FAME	PL:YO 2:1 FAME	*LIMIT Biodiesel
Sp.gr(15/14 ⁰ C)	0.876	0.878	0.881	0.875	0.876	0.876	0.860-.900
Sulphur(% w/w)	0.006	0.001	0.010	0.009	0.006	0.006	-
Flash point ⁰ C	87	98	88	95	94	91	Min 100
Cloud point ⁰ C	24	34	2	40	45	41	-1.0 – 4.0
ASTM colour	0.5	0.5	2.5	0.5	0.5	0.5	-
K. Viscosity at 40 ⁰ C(mm ² /s)	4.0	4.3	3.5	4.9	4.2	5.0	3.5 – 5.0
Diesel index	25.6	26.1	42.0	27.3	26.6	24.6	-
Cetane No.	50.6	48.8	41.0	29.6	29.1	29.7	-

*Source: Antolin *et al.*, 2002

FD = fossil diesel
 PL = pig lard
 YO = yellow oleander seed oil
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester
 ASTM = American society for testing and material
 FAME = Fatty acid methyl ester

Table 4.17: Fuel properties of biodiesels from mixed yellow oleander seed oil and pig lard at 150°C

	PLME	YOME	FD	PL:YO 1:1 FAME	PL:YO 1:2 FAME	PL:YO 2:1 FAME	*LIMIT Biodiesel
Sp.gr(15/14 ⁰ C)	0.876	0.875	0.881	0.870	0.872	0.872	0.860-.900
Sulphur(% w/w)	0.005	0.001	0.010	0.007	0.005	0.005	-
Flash point ⁰ C	89	99	88	97	98	95	Min 100
Cloud point ⁰ C	34	37	2	45	49	47	-1.0 – 4.0
ASTM colour	0.5	0.5	2.5	0.5	0.5	0.5	-
K. Viscosity at 40 ⁰ C (mm ² /s)	3.7	4.0	3.5	4.4	4.0	4.7	3.5 – 5.0
Diesel index	30.5	36.3	42.0	38.3	37.5	34.6	-
Cetane No.	40.1	42.8	41.0	24.5	25.3	24.6	-

*Source: Antolin *et al.*, 2002

FD = fossil diesel
 PL = pig lard
 YO = yellow oleander seed oil
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester
 ASTM = American society for testing and material
 FAME = Fatty acid methyl ester

Table 4.18: Fuel properties of biodiesels from mixed yellow oleander seed oil and pig lard at 200°C

	PLME	YOME	FD	PL:YO 1:1 FAME	PL:YO 1:2 FAME	PL:YO 2:1 FAME	*LIMIT Biodiesel
Sp.gr(15/14 ⁰ C)	0.870	0.874	0.881	0.870	0.871	0.871	0.860-.900
Sulphur(% w/w)	0.005	0.001	0.010	0.007	0.005	0.005	-
Flash point ⁰ C	93	103	88	101	102	99	Min 100
Cloud point ⁰ C	47	48	2	49	51	50	-1.0 – 4.0
ASTM colour	1.0	1.5	2.5	1.2	1.5	1.0	-
K. Viscosity at 40 ⁰ C (mm ² /s)	6.7	7.0	3.5	8.4	7.8	9.7	3.5 – 5.0
Diesel index	35.5	39.3	45.0	41.3	42.5	40.6	-
Cetane No.	38.1	40.8	41.0	21.6	22.5	21.8	-

*Source: Antolin *et al.*, 2002

FD = fossil diesel
 PL = pig lard
 YO = yellow oleander seed oil
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester
 ASTM = American society for testing and material
 FAME = Fatty acid methyl ester

Table 4.19: Fuel properties of biodiesels from mixed yellow oleander seed oil and pig lard at 250 °C

	PLME	YOME	FD	PL:YO 1:1 FAME	PL:YO 1:2 FAME	PL:YO 2:1 FAME	*LIMIT Biodiesel
Sp.gr(15/14 ⁰ C)	0.870	0.873	0.881	0.869	0.870	0.871	0.860-.900
Sulphur(% w/w)	0.006	0.001	0.010	0.006	0.005	0.005	-
Flash point ⁰ C	98	105	88	103	102	102	Min 100
Cloud point ⁰ C	49	50	2	50	52	53	-1.0 – 4.0
ASTM colour	1.0	1.5	2.5	1.2	1.5	1.0	-
K. Viscosity at 40 ⁰ C (mm ² /s)	8.5	8.9	3.5	15.8	17.2	14.9	3.5 – 5.0
Diesel index	30.8	34.7	45.0	38.1	34.5	35.4	-
Cetane No.	34.6	36.9	41.0	20.2	20.6	20.3	-

*Source: Antolin *et al.*, 2002

FD = fossil diesel
 PL = pig lard
 YO = yellow oleander seed oil
 PLME = pig lard methyl ester
 YOME = yellow oleander methyl ester
 ASTM = American society for testing and material
 FAME = Fatty acid methyl ester

CHAPTER FIVE

5.0 DISCUSSION

5.1 Oil Yield of Yellow Oleander Seed and Pig Lard

The oil contents of the Yellow Oleander seed (64.7%) and pig lard (85.4%) obtained in this work compare favourably with the oil yields of Yellow Oleander seeds (61.8%-64.7%) reported (Ibiyemi *et al.* 2002). These values also compare favourably with those from other oil bearing plants such as *Jatropha* kernel (63.16 %) as reported by Emil *et al.* (2009). The result is within the range of oil contents of 30 -65% from *Calophyllum inophyllum* reported (Azam *et al.* 2005). However, the oil yields are higher than those of *Azadirachta indica* (44.5%), *Pongamia pinnata* (33%) and *Ziziphus mauritiana* (33%) (Azam *et al.*, 2005). The pig lard yields of 70% to 93% reported by Clemen (1927) agree with the yield (85.4%) obtained in this work. These oils can be classified as commercially viable for production of biodiesel (Ikhuoria *et al.*, 2008; Emil *et al.*, 2009).

5.2 Physicochemical Properties of Yellow Oleander Seed Oil and Pig Lard

5.2.1 Specific gravity and density

Generally, plant oils with specific gravity of 0.820 to 1.071 at 30°C are considered good for use as biofuels (Bhattacharya *et al.*, 2013; Minzagi *et al.*, 2011). The specific gravity of the yellow oleander seed oil was found to be 0.884, and that of pig lard was 0.881 (Table 4.1). These values compare with other results found for *Tropical africana* samples (Dawodu, 2009; Minzagi *et al.*, 2011; Bhattacharya *et al.*, 2013).

5.2.2 Acid value

Acid value is an important property used to indicate the quality, age and suitability of oils for use in the biodiesel industry (Akubugwo *et al.*, 2008). The acid value of oils of yellow oleander seed oil and pig lard obtained are 1.26 mgKOH/g and 2.24 mg KOH/g respectively (Table 4.1). The lower acid value for yellow oleander seed oil implies that it contains less polyunsaturated fatty acids (that is linoleic acid and linolenic acid) (Khan *et al.*, 2001) than in pig lard. The higher acid value found in pig lard is an indication of higher level of free fatty acids which translates into decreased oil quality. Therefore, higher acid value in pig lard will make it more susceptible to lipase action and will decompose faster than yellow oleander seed oil. Acceptable levels for all oil samples should be below 0.6 mg KOH/g (AOCS Official Method Cd 8-53, 2003). However, these values were observed to be lower than those reported by Minzangi *et al.* (2011) and Zaku *et al.* (2012) for some non-edible oils of *Azadirachta indica* (17.40 mg KOH/g), *Ricinus communis* (12.48 mg KOH/g), *Moringa oleifera* (4.96 mg KOH/g) and *Jatropha curcas* (8.43 mg KOH/g) seeds.

The free fatty acid content of yellow oleander seed oil and pig lard are 0.63% and 1.12% respectively. The value of yellow oleander seed oil is close to the critical value (0.5%) required for alkaline transesterification. Therefore it may not need acid pretreatment for transesterification. The maximum acid value recommended by Canakci and Van Gerpen (2001) for alkaline transesterification is 2 mg KOH/ g oil; therefore, pig lard may also be considered for direct alkaline transesterification. The high free fatty acid content of pig lard suggests that pig lard is less economical for the production of biodiesel as it would require pretreatment before transesterification into biodiesel. This will invariably increase the cost of production of biodiesel, in addition to the excess soap formed which must be removed (Dorado *et al.*, 2002; Ma *et al.*,

1998). High oil acidity decreases yield of biodiesel by inhibiting the formation of methoxides thus neutralizing 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 (Meneghetti *et al.*, 2006).

5.2.3 Peroxide value

The peroxide value is an indication of the amount of hydroperoxides present in oil. These compounds arise from lipid oxidation; therefore, the peroxide value, expressed as milliequivalent oxygen per kilogram oil (meq/kg), is a measure of oil quality. The peroxide values of yellow oleander seed oil (3.00meq/kg) and pig lard (2.00meq/kg) are low but within the range of 0-10 meq/kg which is stipulated for freshly prepared oil (Cooks and Reds, 1996). These values bear a direct relationship to the level of unsaturated fatty acids in the oils. The low peroxide value implies high resistance to hydrolysis and oxidation, hence, may not deteriorate quickly. Therefore, storage for a long time may not affect the quality or lead to rancidity of the oil (Anyasor *et al.*, 2009; Atasié *et al.*, 2009).

5.2.4 Saponification value

The saponification values gives a measure of the average length of the fatty acid chains which make up the oil. The saponification values are relatively high in both yellow oleander seed oil and pig lard which can be attributed to the presence of high free fatty acid content (Hui, 1992). These values fall within the range of 182.5 – 260 mg/g reported by Minzangi *et al.* (2011) for oils obtained from plant species. The comparative lower saponification value in pig lard implies the presence of larger average molecular weight fatty acids (or long chain fatty acids) relative to yellow oleander seed oil (Denniston *et al.*, 2004). As a result of the high mass, the saponification value was low. Conversely, the higher saponification value recorded in yellow

oleander seed oil triglyceride is an indication of a larger number of short chain fatty acid molecules of low molecular weight, and accordingly consumes a larger number of moles of KOH.

5.2.5 Iodine value

The high percentages of unsaturated fatty acids obtained from yellow oleander seed oil (41.21%) and pig lard (35.9%) is supported by the iodine values (75.82g/g and 53.93g/g) obtained in this study. Since iodine value directly affects stability with regards to oxidation of oils, it suggests that the auto-oxidation of unsaturated fatty compounds proceeds at different rates depending on the number and position of double bonds. The species formed during the oxidation process cause the oil to eventually deteriorate. Small amounts of more highly unsaturated fatty compounds have a disproportionately strong effect (Knothe and Dunn, 2003). In this regard, yellow oleander seed oil and pig lard are relatively stable to oxidation and are likely to be stored for a long period without becoming rancid (Firestone, 1994). They are, therefore, likely to be good feedstock in biodiesel industry.

5.2.6 Refractive index

The refractive indices for yellow oleander seed oil and pig lard were found to be 1.479 and 1.472 respectively close to the value of 1.461 reported by Eshun *et al.* (2013) for peanut oil. These refractive indices tend to correlate with the degree of unsaturation or iodine value, and showed that both oils after extraction are clear and bright with no contamination or rancidity (Karabulut *et al.*, 2003).

5.2.7 Kinematic viscosity

The high viscosities of yellow oleander seed oil and pig lard imply low volatility which will reduce fuel atomization and cause the oils not to burn completely. This problem can be reduced by transesterification reaction (Atadashi *et al.*, 2011) which lowers the viscosity and enhances other physicochemical properties of the oil (Ferella *et al.*, 2010).

5.2.8 Calorific value

The calorific value of yellow oleander seed oil (13.7858 MJ/kg) will allow for more efficient combustion when used as fuel than pig lard with lower calorific value (12.0163MJ/Kg). The predominant fatty acids (palmitic, stearic, oleic) in yellow oleander seed oil might have contributed significantly to the calorific value of the oil. Stearic acid, a saturated fatty acid with 18 carbon atoms, a percentage composition of 10.78%, and heat of combustion of 39.422 MJ/kg was a major contributor to this calorific value. Another significant contributor to this calorific value of yellow oleander seed oil was palmitic acid, also a saturated acid, with composition of 23.61% and heat of combustion of 38.905 MJ/kg (Stacey, 2014). Most significantly will be the contribution of oleic acid (16.58%) and heat of combustion of 39.347 MJ/kg (Stacey, 2014). Yellow oleander methyl ester can therefore on this basis be a supplement to conventional fossil diesel in energy applications.

Following the fatty acid distribution observed in Tables 4.3, the percentage composition of stearic acid, oleic acid and palmitic acid which have higher heats of combustion are lower in pig lard, hence its lower calorific value, compared to that of yellow oleander seed oil. However, both yellow oleander seed oil and pig lard have good calorific values. They can therefore be considered good feed stocks for biodiesel production.

5.3 The FTIR Spectra of Yellow Oleander Seed Oil, Pig Lard, Yellow Oleander Methyl Ester and Pig Lard Methyl Ester

The IR spectra of the oils (Figures 4.3 and Figure 4.6) show strong absorbance around 2920 cm^{-1} due to the symmetric stretching vibration of the aliphatic CH_2 group. This may be due to the higher proportion of linolenic or linoleic acyl groups (26.10%) in pig lard compared to 20.26% in yellow oleander seed oil. This is similar to the observations made in chocolate containing lard by Che Man *et al.* (2005), Guillen and Cabo (1997), Suparman *et al.* (2015) and Vlachos *et al.* (2006).

A comparative analysis of the FTIR peaks of the functional groups of the oils and their respective biodiesels show significant differences which are due to the formation of biodiesels. Fatty acid methyl esters of YOME and PLME biodiesels have unique FTIR absorptions of their carbonyl ($\text{C}=\text{O}$) stretching vibrations near 1750 cm^{-1} and C-O bending vibrations in $1200\text{-}1170\text{ cm}^{-1}$ region, which are distinct from those of other components in biodiesel. The ester molecules in the raw oils (YO and PL), on the other hand, show a distinct C-O absorption near 1160 cm^{-1} . There are no such absorptions due to $\text{C}=\text{O}$ and C-O functional groups in fossil diesel. This spectral separation among the functional groups of vegetable oils, biodiesel and fossil diesel forms the basis of characterization and quantization of FAMES in biodiesel and in blended biodiesel-diesel fuel through IR spectroscopy.

The influence of the transesterification was indicated by the formation of a signal at 1448 cm^{-1} for the $(\text{CO})\text{-O-CH}_3$ group in the biodiesels spectra indicating the presence of a methyl ester group. Another visible transformation revealed by the IR spectra of the FAMES is a broad signal around 1170 cm^{-1} of C-O group in the ester controlled signal area.

5.4 Biodiesel Production from Yellow Oleander Seed Oil and Pig Lard

5.4.1 Effect of variation of reaction time on biodiesel yield

The time needed by the oil to react with the methanol to give the maximum biodiesel yield was 60 min with catalyst concentrations of 1% and 0.5%. This implies that 60 min was the optimal time with YOME yield of 96.89% (Figures 4.5 - 4.6). A similar pattern of conversion was observed for pig lard methyl ester using 1% and 0.5% (w/w) catalyst as shown in Figures 4.7 - 4.8. This can be explained that at the beginning of the reaction, transesterification was fast under the base catalyst and with the presence of excess methanol the overall reaction was maintained in the forward direction. However the reaction rate became slower with increasing reaction time since most of the reactants might have been converted to biodiesel. Similar explanations have been advanced for similar results by Encinar *et al.* (1999) on *Cynara cardunculus L.* oil; Okey and Okey (2013) on non-edible seed oil *Delonix regia* and on *karanja* oil by Ghosal and Pradhan (2014)

5.4.2 Effect of reaction temperature on biodiesel yield

The increase in biodiesel yield with increase in temperature as observed in Figures 4.9 – 4.12, was due to more effective collisions between the reacting molecules at higher temperatures which resulted in increase in rate for the reaction. Hence, the biodiesel yield increased with increasing temperature. Optimum yields were observed at reaction temperatures of 60°C and 70°C. Further increase in temperature lowered the biodiesel yield due to increased evaporation of methanol (boiling point is 67°C at atmospheric pressure). A Similar result was also observed by Leung *et al.* (2010); Pati and Deng (2009). Other researchers (Meher *et al.*, 2006) also studied the transesterification of refined oil using methanol with the molar ratio of alcohol to oil (6:1) and NaOH (1% w/w of oil) in three different temperatures. The temperature requirement for

yellow oleander methyl ester and pig lard methyl ester production were almost the same. This could be due to the similarity in composition of fatty acid (Table 2).

5.4.3 Effect of catalyst concentration on biodiesel yield.

The methyl ester yield increases with increased catalyst concentration at lower methanol:oil mass ratio. It was probably due to the lack of methyl ester production because of the mass transfer limitation at the lower mass ratio of reactants as suggested by Boocock *et al.* (1998); Darnoko *et al.* (2000); Jagadale and Jugulkar (2012). The increase in biodiesel yield by adding a catalyst to the reaction mixture is an indication that the reaction pathway has been altered so that the energy needed for reaction to occur was lowered. The higher the amount of catalyst in the reaction mixture the higher was the biodiesel yield (Akhiero *et al.*, 2013). However, with excessive amount of catalyst used in the reaction mixture, the biodiesel yield decreased (Figure 4.13), which is possibly due to the effect of saponification of the oil and the KOH catalyst. The rise in soap formation made the methyl ester dissolution in glycerol layer greater (Vincente *et al.*, 1998). Accordingly, only biodiesel yields of 89.65% and 88.65% were obtained for yellow oleander and pig lard biodiesels respectively when a catalyst concentration of 1.50% was used.

5.5 Fatty Acid Profile of Yellow Oleander Seed Oil, Pig Lard, Yellow Oleander Methyl Ester and Pig Lard Methyl Ester

The major fatty acid in yellow oleander seed oil and pig lard are palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), elaidic (18:1) acid and linoleic acid (18:2) (Table 4.3). The fatty acid composition is similar to those of yellow oleander reported by Usman *et al.* (2009). The high percentage of the saturated and monounsaturated fatty acid of yellow oleander seed oil contain high heat of combustion (Oseni *et al.*, 2012) which would be readily released

during combustion; this property compliments other properties such as specific gravity, peroxide value and iodine value to make it a good potential for biodiesel production (Gerpen *et al.*, 2004).

The relatively low percentage of polyunsaturated fatty acids in yellow oleander seed oil reduces its risk of undergoing auto-oxidation and rancidity, thereby making it suitable for storage and for further processing into biodiesel. The higher degree of polyunsaturated fatty acids in pig lard might produce pig lard methyl ester with high cloud point and other poor cold point properties. The pig lard itself has high viscosity and poor flow characteristics, hence usually become solid at room temperature though it may perform satisfactorily in hot climates.

Knothe (2009) reported on oleic acid as the desirable fatty acid among the other common fatty acids to enrich the fuel properties of biodiesel. The quality of the fuel is therefore a reflection of the composition of the oleic acid in the oil. Oleic acid, a monounsaturated fatty acid with high heat of combustion of 39.35 MJ/kg was a significant contributor to the energy value of yellow oleander methyl ester and pig lard methyl ester. The fatty acid profiles of both yellow oleander methyl ester and pig lard methyl ester are identical and contain as high as 57.84% and 57.82% oleic acid respectively. Another significant contribution to the heat of combustion of the oil and biodiesel comes from palmitic acid (38.905 MJ/kg). The fatty acid composition of yellow oleander methyl ester (99.76 %) and pig lard methyl ester (98.27 %) are good indicators that they can serve as fossil diesel substitute (World Watch Institute, 2008; Manuel, 2007; Vairavan *et al.*, 2010).

5.6 Comparison of Fuel Properties of Biodiesels of Yellow Oleander Seed Oil and Pig Lard

5.6.1 Specific gravity and density

The specific gravity of the methyl esters of yellow oleander seed oil and pig lard (Table 4.8 and 4.9) are within the stipulated limits of 0.90 for fuel grade biodiesel and conventional diesel. On transesterification, the specific gravity was reduced by 0.23% (from 0.8841 to 0.8821) in yellow oleander methyl ester and by 0.003% (from 0.8808 to 0.8805) in pig lard. Biodiesel with high density means more mass per unit volume of fuel which makes more energy available for work output.

5.6.2 Flash point

The flash point of yellow oleander methyl ester (98°C) was higher than that of fossil diesel (88°C) however, the flash point of pig lard methyl ester (86 °C) was slightly lower than that of fossil diesel. The decrease in flash point observed after transesterification indicated an improvement in the volatile characteristics of the biodiesel. Yellow oleander biodiesel whose flash point is higher has the advantage of increased safety, ease to transport and safe storage compared to fossil diesel; it also has lower fire risk and reduced chances of uncontrolled detonation (Sanjay, 2013).

5.6.3 Cloud point

The Cloud point of yellow oleander seed oil rose from 10°C on transesterification to 14 °C in the methyl ester (Table 4.8). In pig lard the cloud point was 15°C but increased to 18°C on transesterification to the methyl ester (Table 4.9). The cloud points observed in both biodiesels are expected because of the high composition of oleic acid in the biodiesels which enhances cloud point (Sharma *et al.*, 2008). In general, a fuel with high cloud point often limits its use as

fuel in cold climates. In Nigeria the oils and the FAME of yellow oleander will tend to retain their flow properties, but lard biodiesel would tend to precipitate wax under the condition where the ambient temperature is just a little above the cloud point.

5.6.4 Acid value

The acid value of yellow oleander methyl ester (0.63 mg KOH/g) and that for pig lard methyl ester (0.81 mg KOH/g) were slightly higher than the ASTM D6751 and EN 14214 specified maximum limit of 0.5 mg KOH/g for biodiesel. The acid number of biodiesel depends on the fatty acid content of the feedstock used. Pure yellow oleander seed oil contained 41.21% mono-unsaturated fatty acids while pig lard contains 35.97%, which may be responsible for the high acid number in their biodiesels. The low acid values in these fuels will not pose any threat to the engine's operating components, especially the fuel injection equipment.

There was appreciable reduction in percentage free fatty acid of the biodiesels compared to their oils, as high proportion of the FFA was neutralized by potassium hydroxide during transesterification (Vairavan *et al.*, 2010).

5.6.5 Kinematic viscosity

The difference in viscosities of the two biodiesels may be attributed to their different fatty acid compositions (Xu *et al.*, 2007). It was observed that the transesterification of the yellow oleander seed oil and pig lard sharply reduced the values of their kinematic viscosity by 64.65% and 39.68% respectively. The reduction in viscosity is expected in biodiesel production, since transesterification reduces viscosity and improves other fuel properties (Xu and Hanna, 2009). The viscosity of YOME (5.17 mm²/s) was higher than that of PLME (4.32 mm²/s) suggesting that YOME contains more of high amount of fatty acid. This reduction in viscosity in the biodiesel adds quality to the biodiesel, as high viscosity is a major problem in diesel engines.

Biodiesel having high viscosity does not burn completely and often leads to operational problems including deposit formation in the fuel injector of diesel engines (Li and Rudolph, 2008).

5.6.6 Cetane number

The cetane numbers of the biodiesels which are in the medium range indicates fuels with good ignition and combustion quality of the fuels. These values are close to the minimum limits of 47 and 51 prescribed in ASTM D6751 and EN 14214 respectively. The cetane number of yellow oleander methyl ester exceeds the minimum value of 47 prescribed by ASTM D6751 and is higher than that of fossil diesel (41). The Cetane numbers of these methyl esters are an indication of the presence of high percentage of mono-unsaturated fatty acids (58-63%) in the biodiesels (Knothe *et al.*, 2003). Bangboye and Hansen (2008), observed that feedstocks with high saturated fatty acids will have high cetane number, while those high in unsaturated fatty acid have lower cetane number (20-40).

5.6.8 Sulphur content in fatty acid methyl esters

The sulphur content was approximately 0.003% in all the samples. This is lower than the ASTM approved limit of 0.05% for biodiesels (Monteiroa *et al*, 2008). The average sulphur content measured in fossil-diesel was as high as 0.010%, this was approximately 70% more than the value obtained in the biodiesels which will make its combustion products to contain high oxides of sulphur, which has the potential to dissolve to form sulphuric acid and eventually cause corrosion of metals (Singal and Pundir (1996). On the other hand, the combustion of yellow oleander methyl ester and pig lard methyl ester will therefore yield products with low oxides of sulphur making it more environmentally friendly than fossil diesel.

5.7 Effect of Blending on Biodiesel Properties

In general, the blended fuels presented properties that satisfied most ASTM specifications for biodiesel. The blended samples of yellow oleander methyl ester and pig lard methyl ester had their specific gravities, cloud points, flash points and the cetane numbers within the acceptable limits.

Kinematic viscosity is increased with the carbon chain length in biodiesel containing free fatty acids and hydrocarbons; hence an increase in biodiesel fraction in the fuel mixture resulted in an increase in viscosity. The kinematic viscosities of Yellow oleander methyl ester and pig lard methyl ester blends were within the ASTM D6751 allowable limits of 3.5 - 5.0 mm²/s, similar to the reports of Chen *et al.* (2012) on microalgae biodiesel for blends B10 – B50. However, the kinematic viscosity of blends with higher biodiesel fractions (B60, B70, B80 and B90), exceeded the standard limit. A highly viscous fuel would take longer time to mix with air since the quality of the vaporization and atomization of the fuel is reduced. Sarin *et al.*, (2009) stated that blending of biodiesel is a simple but effective method to improve the flow properties at low temperatures.

The effect of blending on the specific gravity of yellow oleander methyl ester – fossil diesel blends was minimal, all within a close range of 0.881-0.882. Blending a high density yellow oleander biodiesel with a less density fossil diesel resulted to increase in density with increase ratio of the biodiesel in the blend (Kimilu *et al.* 2011). Pig lard methyl ester blends did not show any effect on specific gravity because the densities of pig lard methyl ester and fossil diesel are similar.

The increase in flash points with increased volume of biodiesel in the blends will result in inefficiencies in ignition quality of the biodiesel as depicted by the results of the flash point

which were higher than the 60°C recommended by ASTM D93 in blends of B60 to B90 (Bamgboye and Oniya , 2012; Mosesane *et al.* 2015). Generally, all the blends are safer for storage and easier for transportation compared to fossil diesel that have lower flash point.

All cloud point values recorded in the blends (Figure 4.21) were higher than the standard limit of 4°C (except for B10 and B20 blends of yellow oleander methyl ester which were 3°C and 4°C respectively). These values will limit the beneficial use of the blends in cold climates (Haiying *et al.*, 2008).

An increase in cloud point from 2°C in fossil diesel to 7°C in blends was observed in pig lard methyl ester-fossil diesel blend of B10 (Figure 4.28), while the yellow oleander methyl ester-blend of B10 was only 1°C higher than that of fossil diesel. Blends of both biodiesels with fractions greater than B10 had higher cloud points than fossil diesel, which means; they will gel in cold climates and may therefore require the use of cold flow improving additives in order to operate in winter. The cloud point of biodiesel is very important for its use in a cold-climate country. This is because when a blended fossil diesel is used at a low temperature, the biodiesel portion of the blend crystallizes and separates out from fossil diesel (Lang *et al.*, 2001), creating problems for the engine flow system, which eventually cause the engine to stop running. Therefore, a satisfactory attribute of biodiesel cloud point should be warranted prior to its use.

A steady rise in cetane number with increasing biodiesel content of the blends was observed. However, yellow oleander methyl ester – blends recorded higher increase in cetane number compared to pig lard methyl ester- blends. The cetane numbers of all the biodiesel blends were higher than the pure fossil diesel and above the minimum limit of 47 specified by ASTM D6751. The pure yellow oleander methyl ester has the highest cetane number of 59.82.

The amount of heat released from burning the neat yellow oleander methyl ester and pig lard methyl ester were lower than the heat released by fossil diesel, which is a hydrocarbon fuel. This means that favourable energy efficiency can be attained with a small fossil diesel fuel mass. This is in agreement with previously published results (Balat, 2010). This may be due to the lower elemental carbon content and higher oxygen content of the biodiesels compared to fossil diesel (Lin, 2013).

Also, the increase in ratio of biodiesel in blend samples lowered the calorific value continuously towards that for the pure biodiesel, suggesting an inverse relationship between the calorific value and the blending proportions. The difference in the calorific values between biodiesel and fossil diesel may be due to presence of unsaturated bonds in the biodiesels which are absent in fossil diesel. The lower calorific value of the biodiesels and their blends would lead to higher fuel consumption.

The IBM SPSS 20 statistical analysis of the properties of the biodiesel blends showed perfect positive correlation coefficients between sulphur content and ASTM colour at 99% confidence limit. Therefore, as values of sulphur increase there is a perfectly predictable increase in values on the ASTM Colour. In other words, as sulphur content goes up in the blends so does the colour of the blend. However, negative correlation coefficients were observed for fuel properties of ASTM Colour and calorific value at 95% confidence limit. The cetane number also showed negative correlation coefficients with sulphur content and ASTM Colour in yellow oleander blends.

5.8 Effect of Elevated Temperatures on Biodiesel Properties

From Figure 4.28, the kinematic viscosity of yellow oleander methyl ester and pig lard methyl ester decreased as the temperature of the reaction was increased up to 150°C. Further

increase in temperature resulted to an increase in kinematic viscosity up to 250°C, with pig lard methyl ester having higher viscosity at each temperature increase. The possible reason for this behavior may be due to Diels Alder reaction which leads to the formation of polymers at higher temperatures (200 – 300°C), as reported by Jain and Sharma, (2011). At lower temperatures of below 200°C polymers were not formed hence the decrease in viscosity with temperature increase. The formation of more stable conjugated structures called dimers or cyclohexene ring through the binding of a methyl ester conjugate (two double bonds) from one fatty acid chain with monounsaturated methyl ester from another fatty acid chain using the Diels Alder reaction at high temperatures have been reported by Jain and Sharma, (2012).

Thus, biodiesels produced from an oil with high content of unsaturated and polyunsaturated fatty acids (e.g., sunflower oil and soy oil) would be prone to form polymers at high temperatures between 250 and 300°C or more (Waynick *et al.*, 2005). The generation of asphaltene by biodiesels when exposed to high temperatures can result to increase in viscosity of the biodiesels, thus affecting their quality (Schober and Mittelbach, 2005).

Figure 4.29 indicates that both yellow oleander seed oil methyl ester and pig lard methyl ester experienced high rate of oxidation at elevated temperatures, resulting in acid values that exceeded the biodiesel standard limit of 0.80 mg KOH/g. Thermal degradation of the biodiesels may be responsible for the increase in acid value with increasing temperature as reported by Dunn, (2009) for methyl soyate biodiesel.

The acid value increases with increasing temperature for both biodiesels. The increment in acid value with increase in temperature is a negative effect of oxidation stability for both biodiesels. The yellow oleander seed oil methyl ester shows lower acid values compared to pig lard biodiesel because of its lower unsaturated fatty acid content at studied temperatures.

However, pigs lard biodiesel because of its high unsaturated fatty acid with long chain hydrocarbon, showed more susceptibility to oxidation. At high temperatures, biodiesel becomes oxidised as the fuel molecules react with oxygen in the air to form hydroperoxides, which may be further oxidised into acids, hence causing the acid value to increase. The esters first oxidise to form peroxides, which then turn into complex reactions, including a split into more reactive aldehydes, which further oxidise into acids.

At the initial temperatures, the peroxide values for both methyl esters increased following oxidation up to 100°C, after which the peroxide values for the biodiesels were consistently decreasing with respect to increasing temperature with the least value at 250°C. During oxidation of fatty derivatives at lower temperatures, primary products such as hydroperoxides increase in concentration, causing peroxide value to increase. Soon after this, at higher temperatures, the hydroperoxides began to decompose yielding a mixture of secondary products including short-chain carboxylic acids, ketones, epoxides, and mono- and dihydroxy compounds. As the temperature increases, the rate of disappearance of the hydroperoxides exceeds its formation; hence, the peroxide value began to decrease from the maximum value. This may be due to the reduction of oxygen content of the biodiesels as a result of acceleration of decomposition of hydroperoxides with increase in temperature. In their work on palm biodiesel, Lin and Chiu (2010), reported that the formation of oxidation products such as hydroperoxides, polymers and conjugated dienes causes the peroxide value to decrease.

5.9 Effect of Storage Period on Properties of Biodiesel Blends

During storage, the calorific value steadily decreased with increase storage time for both yellow oleander methyl ester-fossil diesel and pig lard methyl ester-fossil diesel blends (Figures

4.31 and 4.32). The calorific value of the fossil diesel remained relatively stable compared to that of the methyl esters and their blends. The decrease in calorific value was found to be higher in yellow oleander methyl ester blends than in pig lard methyl ester blends. By 120 days storage, the biodiesel blends recorded higher decrease rate in calorific values, implying that, oxidative instability increase in biodiesels with extension of oxidative period. This resulted in lower calorific values.

The flash points increased for all samples with increase in storage period (Figures 4.33 and 4.34). The flash point temperature is an important property for a fuel, especially in terms of handling, storage and forming of a combustible mixture. The flash point indicates the difference between a highly flammable, volatile and a relatively non-flammable nonvolatile material. Even though a good fuel is expected to have a low auto-ignition temperature, especially in a diesel engine (Kumaran *et al.*, 2011), the increased flash point of the biodiesel blends, at the end of the storage period was much lower than the ASTM D93 limiting value of 130°C for biodiesel as quoted by Igbum *et al.*(2013).The highest flash point over the entire storage period for the biodiesels was found to be 98°C, an increase of 10°C over that of fossil diesel. This may be as a result of the oxidative degradation of the biodiesels which converts unsaturated fatty acids to primary and secondary oxidation products such as free fatty acids, hydroperoxides and polymers of high molecular weight.

The flash points of the biodiesel blends reported for the storage period of 120 days places them under relatively non-flammable non-volatile materials (Pretsch *et al.*, 2009), hence they are safe to handle, store and transport (Shahabuddin *et al.*, 2012).

An increase in density over the storage period was observed for the biodiesels and their blends. The increase in density was caused by the formation of oxidation products, including

insoluble sediments caused by the presence of unsaturated fatty acids which are significantly more reactive to oxidation than saturated compounds. The increase in density of pig lard methyl ester and its blends with storage period was due to the presence of more unsaturated fatty acids in the fuel. Also, the fuels contain short chain hydrocarbons and more saturated fatty acids which are prone to crystallize and cause a reduction of its volume and consequently increase the density. Simultaneously the mass of the fuel is increased as the consequence of oxidation products as well (Ndana, 2012).

The changes in Kinematic viscosity with storage time of 60 days and 120 days at room temperature show that the viscosity of all the blends in both biodiesels increased with storage time but at different rates. The increasing trend in viscosity was due to the effect of oxidation. Fossil diesel fuel showed good characteristics in terms of viscosity as oxidation did not affect its viscosity very much over the storage period. This is because fossil diesel is less oxygenated than biodiesel (Knothe and Steidley, 2005). An increase in density of biodiesels increases their viscosity which is an important fuel property. This makes the fuel unsuitable for use in an ignition engine; especially at low temperature the fuel atomization characteristics become very poor in the fuel injector due to the high viscosity (Demirbas, 2008).

Approximately similar results have been previously observed by other researchers, who noted that the oxidation process leads to the formation of free fatty acids, double bond isomerisation (usually cis to trans), saturation and the production of higher molecular weight molecules (Knothe and Steidley, 2005; Jain and Sharma, 2011), and that kinematic viscosity increases with increasing oxidation with a longer storage period as the fatty acids polymerise and clump together to form more sediments (Jain and Sharma, 2011).

5.10 Effect of Elevated Temperatures on Biodiesel Blends

The specific gravity of the biodiesel blends generally increases with increasing molecular weight of the fuel molecules, hence the increase in specific gravities of the blends were correlated as a function of percentage biodiesel in the blend. Similarly, the thermal instability of biodiesel is the major contributor to the increase of density. With increase in temperature there was increase in oxidation rate which in turn, increased the mass of the biodiesel, due to the formation of insoluble sediments. Hence, as the mass increases, the density also increases. This finding is similar to those of Kimilu *et al.*(2011) in *Jatropha* methyl ester blends and Yoon *et al.*, (2008) as reported by Fahd *et al.*(2014) in waste cooking palm biodiesel and its diesel blends at elevated temperatures.

The kinematic viscosities decreased with increase in temperature (Figure 4. 47 and 4.48) and also increased as the percentage of methyl esters increased in the blends (Park *et al.*2008). The viscosities of the blends B20, B40, B60, and B80 were found to be higher than that of the fossil diesel at all temperatures, but are still within the ASTM D 975 standard limit (1.9-6.0 mm² /s at 40°C). This suggests that the fuels under study would give normal performance in a diesel engine within temperature range of 100°C to 250°C. However, kinematic viscosity increased as the percentage of methyl ester increases in the blends (Figures 4. 45 and 4.46) at all temperatures investigated. The higher blends had rapid increase in viscosity at higher temperatures due to high rate of oxidation.

5.11 Fuel Properties of Biodiesels Obtained from Mixed Yellow Oleander Seed Oil and Pig Lard

It can be seen from Table 4.11 that the fuel properties of biodiesel produced from mixtures of pig lard and yellow oleander seed oil are comparable to those of individual yellow oleander seed oil and pig lard.

The flash points, kinematic viscosity and specific gravity were all within the ASTM standard limits for biodiesel. The flash points of PL/YO (1:1) and PL/YO (1:2) were higher than that of fossil diesel but similar to those of the individual methyl esters. Their cloud points, like those of pig lard methyl ester and yellow oleander methyl ester were higher than the biodiesel limits (-1 to 4°C) making them less effective in winter conditions (NREL, 2003) . The cetane numbers recorded in the formulated biodiesels were lower than those of the pure methyl esters (Ferdous *et al.* 2013). This can result to poor ignition of the fuel in Diesel- engine.

5.12 Effect of Temperature on Fuel Properties of Biodiesels Obtained from Mixed Yellow Oleander Seed Oil and Pig Lard

The specific gravity of the biodiesels from mixed oils were minimally reduced by the increment in temperature and were found to be within the ASTM limits of biodiesel. The ASTM colour of the biodiesels was also accommodated within the limits except at higher temperatures of 200°C and 250°C where all the fuels indicated high colour values of between 1 and 2.5. The high colour values are indication of fuel deterioration at high temperature. The poor cloud points observed in the entire PL/YO methyl esters continue to increase at all treatment temperatures (Table 4.12 – 4.15. However, their flash points and cetane numbers under the treated temperatures were within the ASTM limits for biodiesels.

Flash point, kinematic viscosity and specific gravity of biodiesels from mixed oils were within ASTM limits for biodiesel, hence, the biodiesel can serve as alternative or supplement to fossil diesel in diesel engine.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

- i. The yield of yellow oleander seed oil was 64.7% and the rendered pig fat yielded 85.4% lard.
- ii. The physicochemical parameters of yellow oleander seed oil and pig lard were assessed following the ASTM standard methods, and the oils were found to have high flash points of 192°C and 165°C, calorific values of 13.79 MJ/Kg and 12.02 MJ/kg respectively.
- iii. The FTIR analyses of the yellow oleander seed oil and pig lard showed the carbonyl functional group of the triglycerides and FAMES at 1739 cm^{-1} to 1745 cm^{-1} as the most intense and prominent bands in the IR spectra, indicating the presence of fatty acids methyl esters.
- iv. The GC-MS result showed about 80% saturated/ monounsaturated fatty acids in both yellow oleander seed oil and pig lard, signifying high potential for biodiesel production. There were similarities in fatty acid compositions of both yellow oleander methyl ester and pig lard methyl ester, with oleic acid as high as 57.84%, palmitic acid (15.56% to 18.07%), stearic acid was in the range of 15.65 % to 15.98%, which placed them as good substitutes for fossil diesel.
- v. Biodiesels prepared from the yellow oleander seed oil and pig lard using the base-catalyzed transesterification yielded about 96% yellow oleander methyl ester and 85% pig lard methyl ester at the optimal conditions of 60°C, for 45 minutes with 1% (w/w) KOH catalyst.

- vi. Fuel properties of yellow oleander methyl ester-fossil diesel and pig lard methyl ester-fossil diesel blends (B10 to B50) agreed with most ASTM specifications for biodiesels. The Kinematic viscosities of pig lard methyl ester-fossil diesel blends (from 3.76 mm²/s in B10 to 4.84 mm²/s in B90) fall within the allowable limits of 3.5 - 5.0 centistokes specified by ASTM D6751, yellow oleander methyl ester –fossil diesel blends had viscosities of 5.04 in B60 to 6.53 in B90 above the ASTM limit. The specific gravity values of pig lard methyl ester-fossil diesel blends were not affected by the increasing biodiesel portion in the blends. All cloud points recorded in the blends were higher than the standard limit of 4°C, (except for B10 and B20 blends of yellow oleander methyl ester which were 3°C and 4°C respectively).
- vii. At elevated temperatures of 100°C – 250°C there was a decrease in specific gravities and kinematic viscosities of all the blends with increase in treatment temperature. Long time storage of biodiesel fuels showed a steady increase in flash point, density, kinematic viscosity and acid value, with a decrease in peroxide and calorific value over the storage period of 120 days. The rates of decrease in calorific value with increase fraction of yellow oleander methyl ester in blends were 1.10% in B20, 2.43% in B40 and 2.63% in B80 and were higher with storage time.
- viii. Biodiesels from mixtures of yellow oleander seed oil and pig lard (ratio of 1:1, 1:2, and 2:1) gave poor cloud point properties and low cetane numbers, however, their flash points (83°C - 91°C), specific gravity values (0.876 – 0.878) and kinematic viscosities (4.4 -5.1) were all within the ASTM limits of biodiesel. The specific gravity values of the pig lard: yellow oleander seed oil FAMES were minimally affected by high temperatures (100°C to 250°C) and were found to be within the ASTM limits for biodiesel. High ASTM colour

values (between 1 and 2.5) were recorded in all the pig lard: yellow oleander seed oil FAMES at 250°C indicating fuel deterioration at high temperatures. Biodiesels from yellow oleander seed oil were found to be better substitute of conventional diesels than biodiesel from pig lard.

6.2 Conclusion

- i. The oil content of the YO (64.7%) and PL (85.4%) were high enough to be classified as commercially viable sources of oil for the production of biodiesel.
- ii. From the physicochemical properties, the high calorific values and densities of the oils are indications of higher energy content which can be considered good for use as biodiesels. YO showed low acid value with FFA close to the critical value of 0.5% required for alkaline transesterification without acid pretreatment makes it economical for the production of biodiesel.
- iii. Biodiesel yields were found to be as high as 96% for YOME and 85% for PLME at optimal conditions of 60°C at 45minutes with 1% (w/w) KOH for base catalysed transesterification.
- iv. The FTIR spectra of the fatty acid methyl esters of YOME and PLME showed unique carbonyl (C=O) stretching vibrations near 1750 cm⁻¹. The influence of the transesterification was demonstrated by the formation of a signal at 1448cm⁻¹ for the (CO)-O-CH₃ group (a methyl ester group) in the biodiesels spectra. There are no such absorptions due to C=O functional groups in fossil diesel.
- v. The GC-MS result showed about 80% saturated/ monounsaturated fatty acids in both yellow oleander seed oil and pig lard, signifying high potential for biodiesel production. The fatty acid methyl esters show fatty acid profiles rich in palmitic, stearic and oleic

acids with high heats of combustion indicating that these FAMES can serve as fossil diesel substitute

- vi. The biodiesel quality parameters such as specific gravity, flash point, Kinematic viscosity, cetane number and acid values of the biodiesels produced were within the stipulated ASTM limits for fuel grade biodiesels with low sulphur content. However, high cloud points were observed that can cause the biodiesels to gel in cold climates creating problem to engine operation.
- vii. Blending of biodiesels improves their fuel properties. Fuel properties of lower YOME and PLME blends agreed with the ASTM specifications for biodiesels. Higher biodiesel fractions in blends lowered calorific value due to the presence of unsaturated bonds in the biodiesels which are absent in fossil diesel.
- viii. At elevated temperatures biodiesels and their blends experienced high rate of oxidation to form oxidative products which altered the quality of the fuel.
- ix. During storage the biodiesels undergo oxidative degradation converting unsaturated fatty acids to primary and secondary oxidative products of high molecular weight which steady lead to increase in flash point density kinematic viscosity and acid value of the fuel.
- x. Biodiesels from mixtures of YO and PL gave fuel properties similar to those of YOME and PLME and within the ASTM limits of biodiesel. However, low cetane numbers were recorded which can cause poor ignition of fuel in diesel engine.

6.3 Recommendations

- i. Considering the similarities in fuel properties of YOME to the ASTM standard for biodiesel, it is hereby recommended that the production of biodiesels from other non-

edible seed oils of Nigerian origin such as *Jatropha curcas*, neem, castor and rubber oils be investigated.

- ii. In this work the biodiesels produced and their blends recorded poor cold flow properties. Hence, in order to improve on the cloud points, the effect of application of some anti-gelling additives such as opti-lube, Dee-Zol, power service , ethanol and stanadyne additives to the biodiesels and blends should be investigated.
- iii. One of the problems detected in this study was the instability of biodiesels and blends with storage period. It is therefore recommended that suitable additives be tested on the biodiesels and their blends with the aim of enhancing their oxidative and storage stability.

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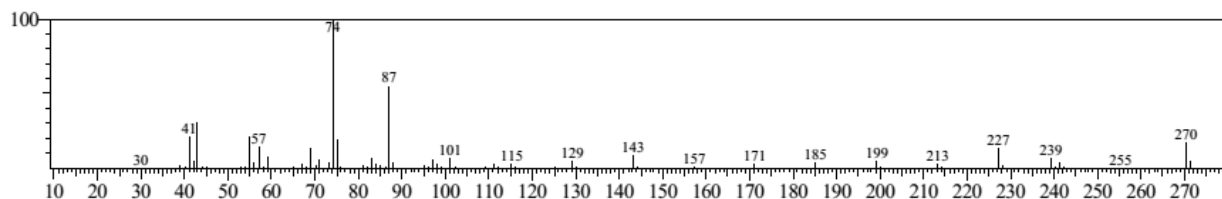
APPENDICES

Appendix i : Mass spectra of the fatty acids of yellow oleander seed oil

Line 7

Compound Name: Hexadecanoic acid, methyl ester / Palmitic acid

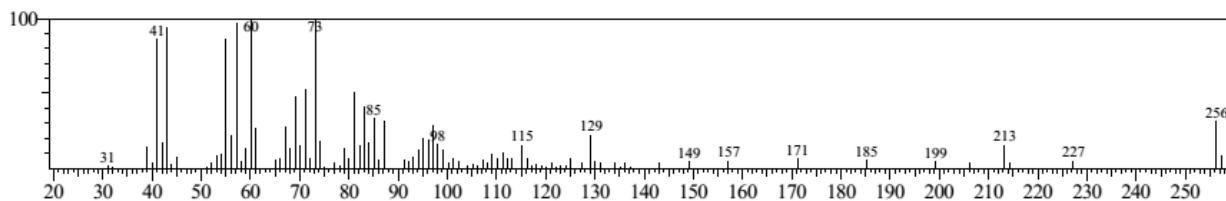
Retention time: 19.06; **Mass peaks:**145 ; **Formula:** C₁₇H₃₄O₂; **Molecular weight:** 270



Line 8

Compound Name: n- Hexadecanoic acid, methyl ester / Palmitic acid

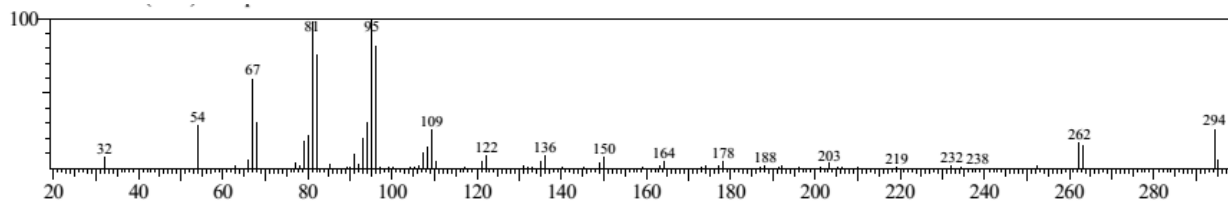
Retention time: 19.63; **Mass peaks:**99 ; **Formula:** C₁₆H₃₂O₂; **Molecular weight:** 256



Line 11

Compound Name: 9,11- Octadecadienoic acid, methyl ester.

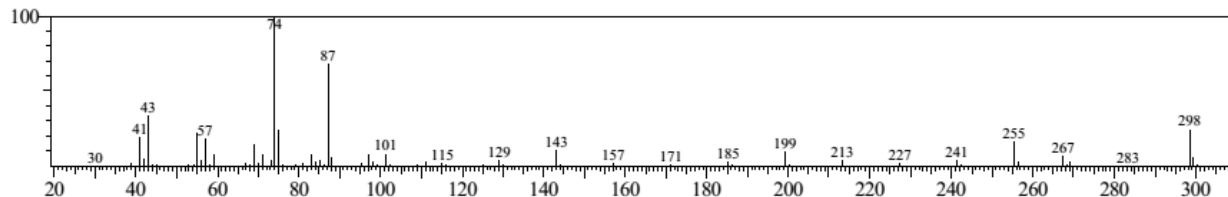
Retention time: 20.90; **Mass peaks:**96 ; **Formula:** C₁₉H₃₄O₂; **Molecular weight:** 294



Line 12

Compound Name: Octadecanoic acid, methyl ester/Stearic acid.

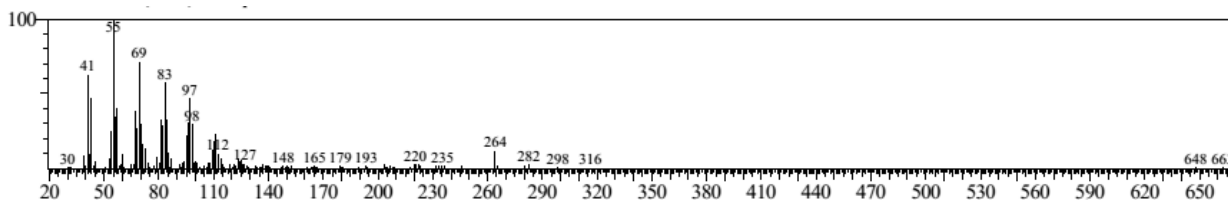
Retention time: 21.17; **Mass peaks:**158 ; **Formula:** C₁₉H₃₈O₂; **Molecular weight:** 298



Line 13

Compound Name:9- Octadecenoic acid, methyl ester/Oleic acid.

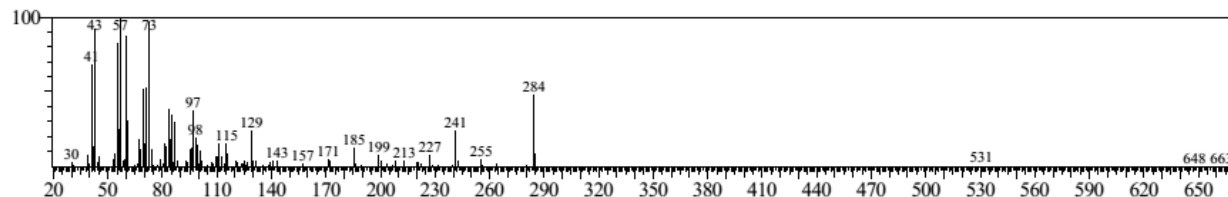
Retention time: 21.45; **Mass peaks:**141 ; **Formula:** C₁₈H₃₄O₂; **Molecular weight:** 282



Line 14

Compound Name: Octadecanoic acid, methyl ester/Stearic acid.

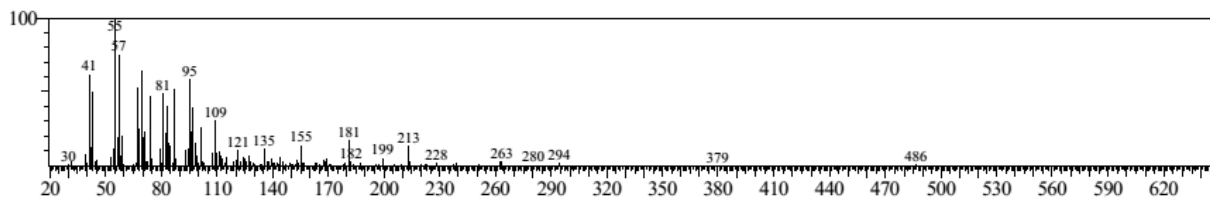
Retention time: 21.63; **Mass peaks:**115 ; **Formula:** C₁₈H₃₆O₂; **Molecular weight:** 284



Line 15

Compound Name:Oxiranooctanoic acid, methyl ester/Oleic acid.

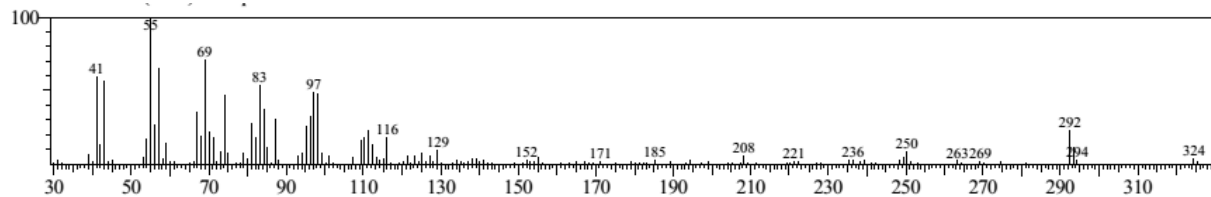
Retention time: 22.65; **Mass peaks:**154 ; **Formula:** C₁₉H₃₆O₃; **Molecular weight:** 312



Line 16

Compound Name: 11- Eicosenoic acid, methyl ester/Oleic acid.

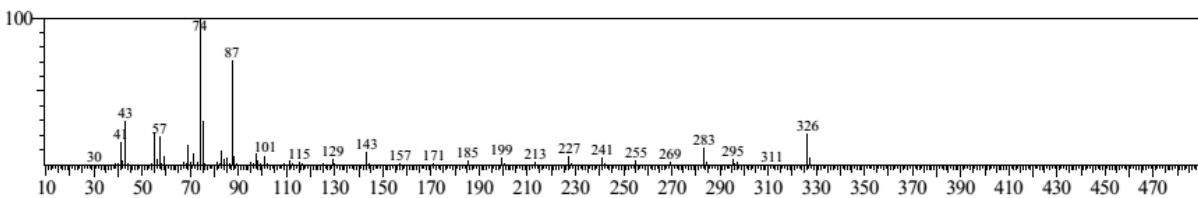
Retention time: 22.79; **Mass peaks:**167 ; **Formula:** C₂₁H₄₀O₂; **Molecular weight:** 324



Line 18

Compound Name:Eicosanoic acid, methyl ester/Arachidic acid.

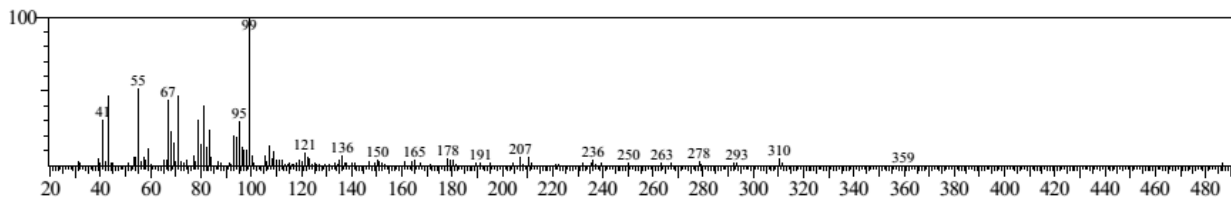
Retention time: 23.00; **Mass peaks:**174 ; **Formula:** C₂₁H₄₂O₂; **Molecular weight:** 326



Line 19

Compound Name:14- Oxononadec-10-einoic acid, methyl ester.

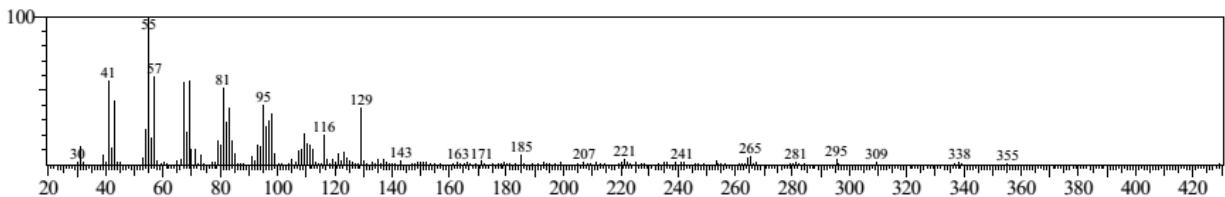
Retention time: 23.17; **Mass peaks:**139 ; **Formula:** C₂₀H₃₆O₃; **Molecular weight:** 324



Line 23

Compound Name: 9- Octadecenoic acid, methyl ester.

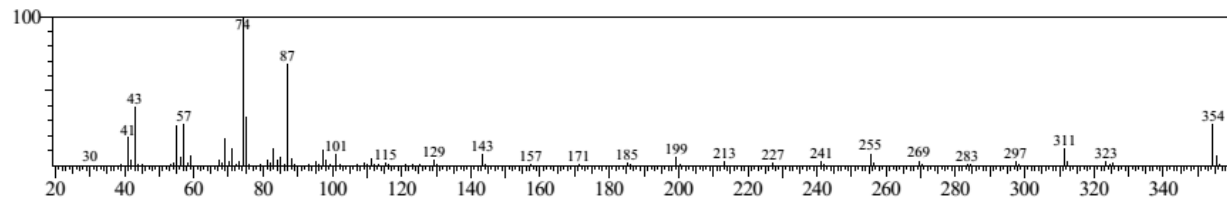
Retention time: 24.44; **Mass peaks:**177 ; **Formula:** C₁₉H₃₄O₂; **Molecular weight:** 310



Line 24

Compound Name: Docosanoic acid, methyl ester/ Behenic acid.

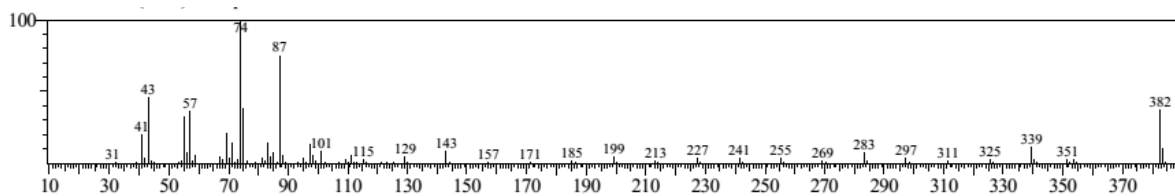
Retention time: 24.76; **Mass peaks:**152 ; **Formula:** C₂₃H₄₆O₂; **Molecular weight:** 354



Line 25

Compound Name: Tetracosanoic acid, methyl ester/Lignoceric acid.

Retention time: 26.49; **Mass peaks:**160 ; **Formula:** C₂₅H₅₀O₂; **Molecular weight:** 382

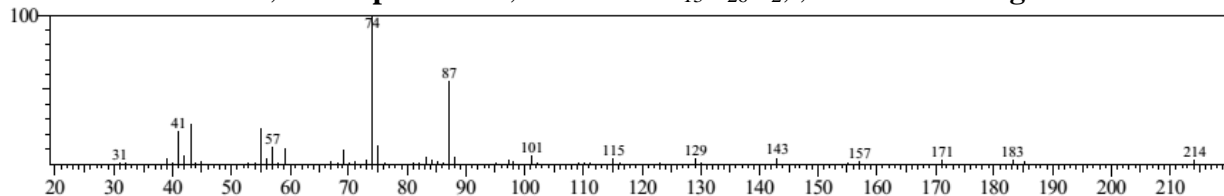


Appendix ii: Mass spectra of the fatty acids of pig lard

Line 11

Compound Name: Dodecanoic acid, methyl ester /Lauric acid.

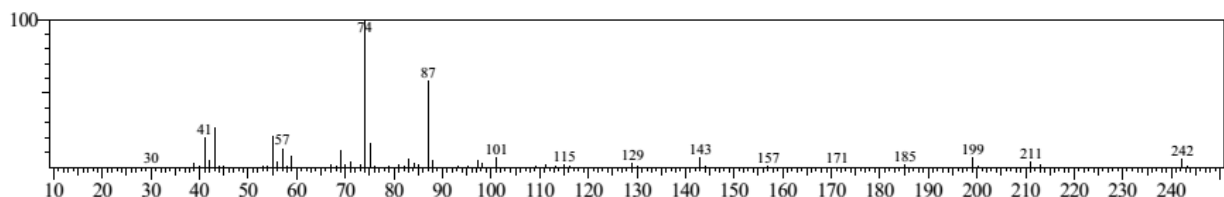
Retention time 13.97; **Mass peaks:** 77.; **Formula:** C₁₃H₂₆O₂; **Molecular weight:**214



Line 15

Compound Name: Tetradecanoic acid, methyl ester /Myristic acid.

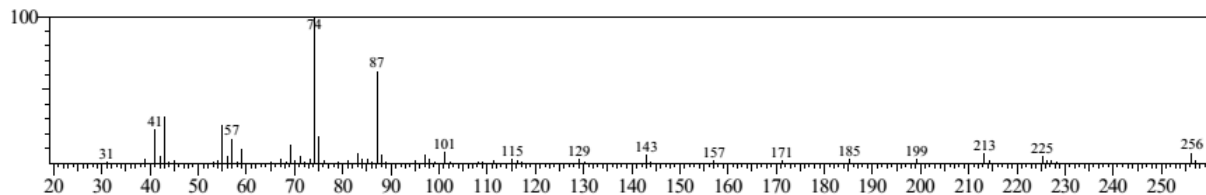
Retention time: 16.55; **Mass peaks:** 123; **Formula:** C₁₅H₃₀O₂; **Molecular weight:** 242



Line 17

Compound Name: Pentadecanoic acid, methyl ester.

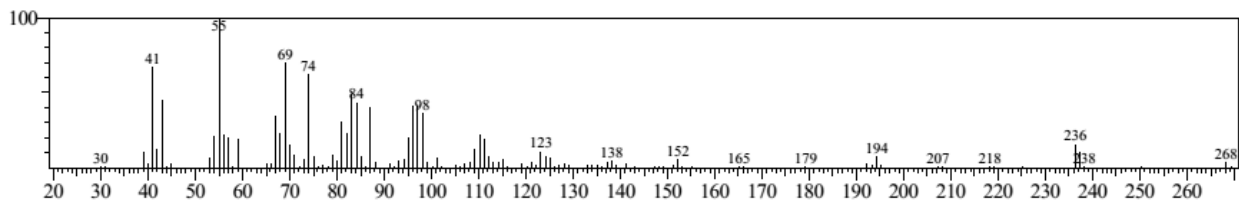
Retention time: 17.73; **Mass peaks:** 81; **Formula:** C₁₆H₃₂O₂; **Molecular weight:** 256



Line 19

Compound Name: 9-Hexadecenoic acid, methyl ester /Palmitoleic acid

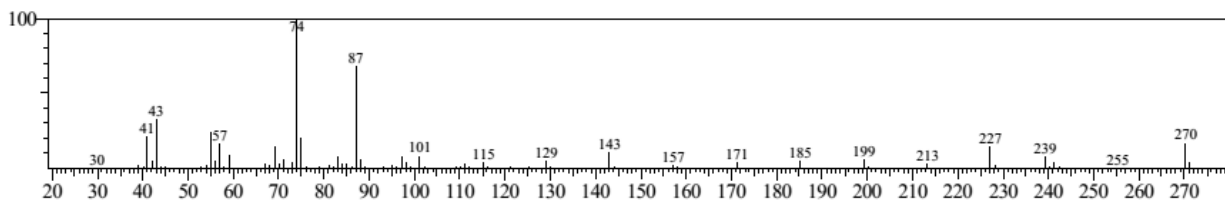
Retention time: 18.68; **Mass peaks:** 165; **Formula:** C₁₇H₃₂O₂; **Molecular weight:** 268



Line 20

Compound Name: Hexadecanoic acid,methyl ester/Palmitic acid.

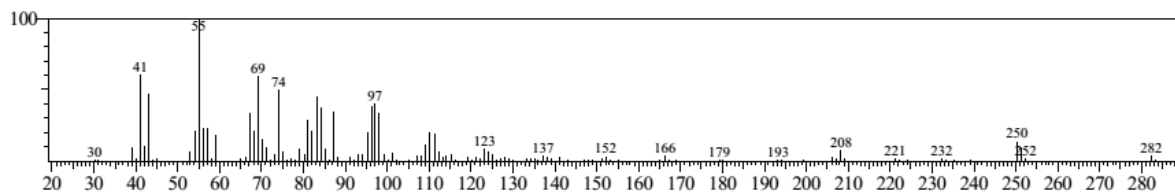
Retention time: 18.91; **Mass peaks:** 158; **Formula:** C₁₇H₃₄O₂; **Molecular weight:** 270



Line 22

Compound Name: Cyclopropaneoctanoic acid,2-hexyl-,methyl ester.

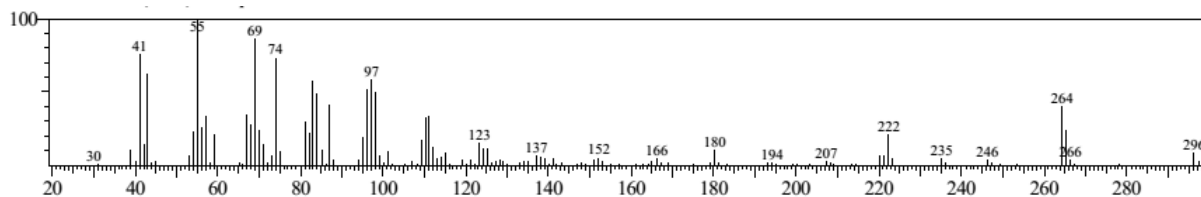
Retention time: 19.73; **Mass peaks:** 136; **Formula:** C₁₈H₃₄O₂; **Molecular weight:** 282



Line 23

Compound Name: 9- octadecenoic acid, methyl ester.

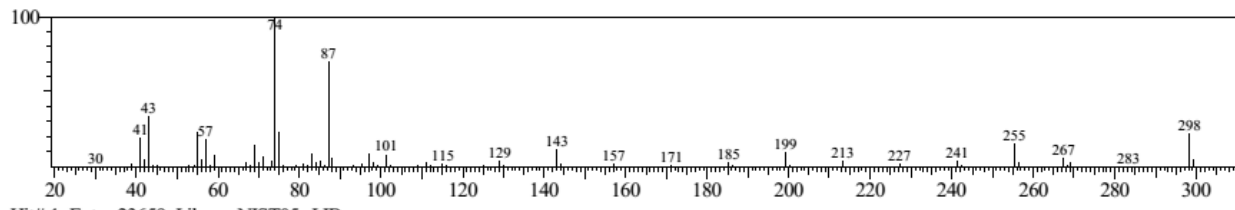
Retention time: 20.90; **Mass peaks:** 201; **Formula:** C₁₉H₃₆O₂; **Molecular weight:** 296



Line 24

Compound Name: Octadecanoic acid, methyl ester/Stearic acid.

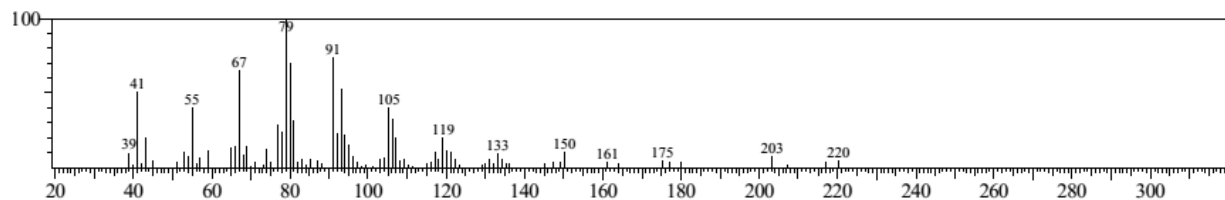
Retention time: 21.04; **Mass peaks:** 169; **Formula:** C₁₉H₃₈O₂; **Molecular weight:** 298



Line 26

Compound Name: 5,8,11,14-Eicosatetraenoic acid, methyl ester/Arachidonic acid.

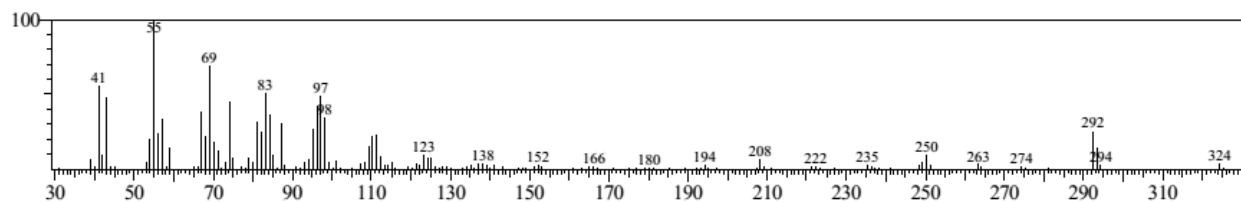
Retention time: 22.37; **Mass peaks:** 85; **Formula:** C₂₁H₃₄O₂; **Molecular weight:** 318



Line 27

Compound Name: 11-Eicosenoic acid, methyl ester.

Retention time: 22.69; **Mass peaks:** 184; **Formula:** C₂₁H₄₀O₂; **Molecular weight:** 324

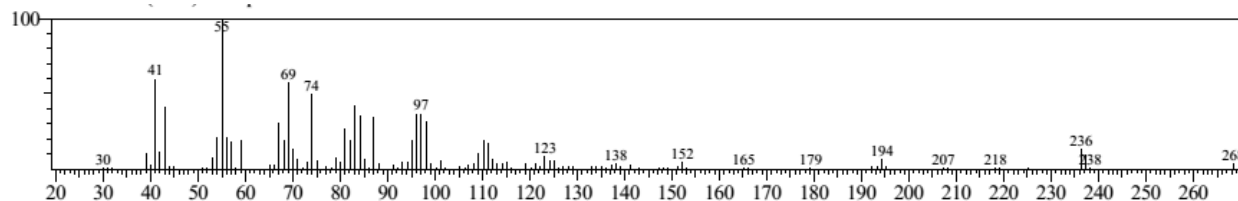


Appendix iii: Mass spectra of fatty acids of yellow oleander methyl ester

Line 9

Compound Name:Hexadecenoic acid, methyl ester/palmitoleic acid.

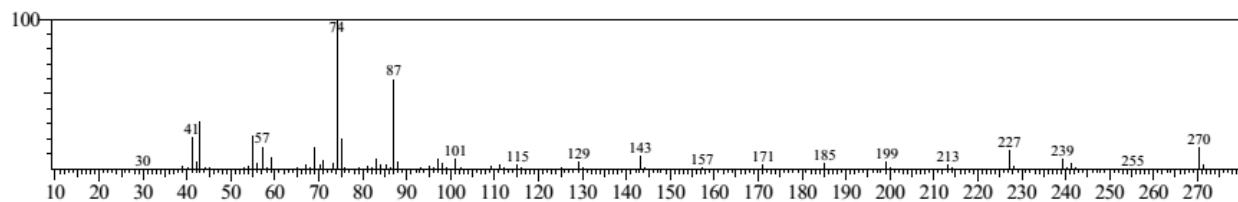
Retention time: 18.66; **Mass peaks:** 109; **Formula:** C₁₇H₃₂O₂; **Molecular weight:** 268



Line 10

Compound Name:Hexadecanoic acid, methyl ester/palmitic acid.

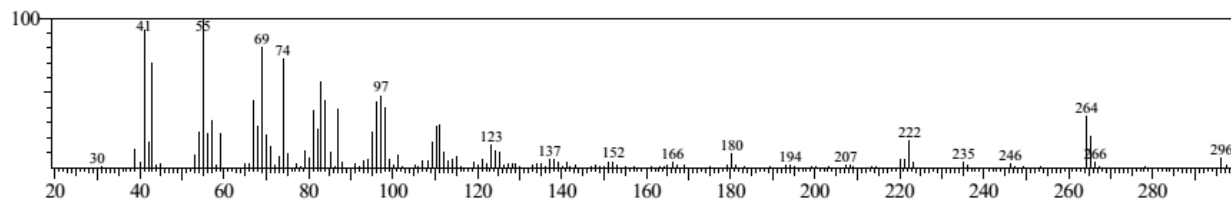
Retention time: 18.92; **Mass peaks:** 157; **Formula:** C₁₇H₃₄O₂; **Molecular weight:** 270



Line 13

Compound Name: 7-Octadecenoic acid, methyl ester.

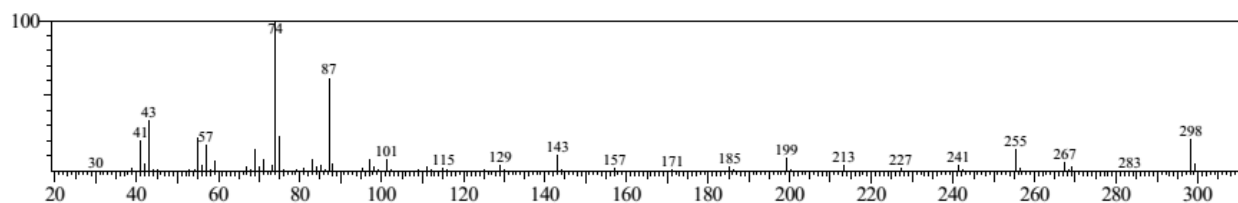
Retention time: 20.92; **Mass peaks:**206; **Formula:** C₁₉H₃₆O₂; **Molecular weight:** 296



Line 14

Compound Name: Octadecanoic acid, methyl ester/stearic acid.

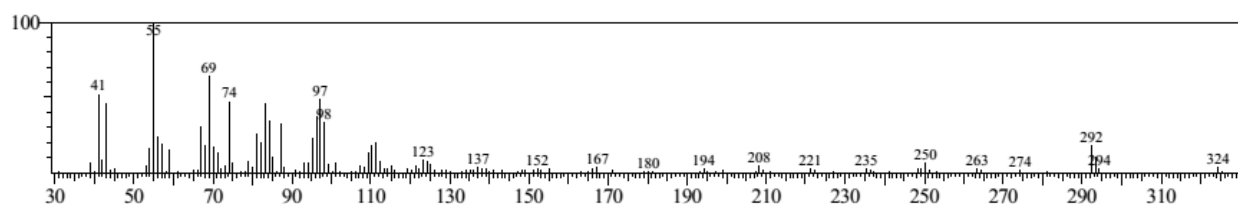
Retention time: 21.06; **Mass peaks:** 169; **Formula:** C₁₉H₃₈O₂; **Molecular weight:** 298



Line 17

Compound Name: 11- Eicosenoic acid, methyl ester.

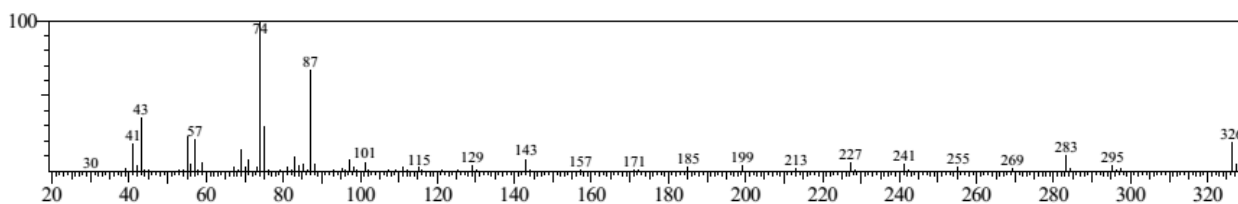
Retention time: 22.69; **Mass peaks:** 133; **Formula:** C₂₁H₄₀O₂; **Molecular weight:** 324



Line 19

Compound Name: Eicosenoic acid, methyl ester/ Arachidic acid

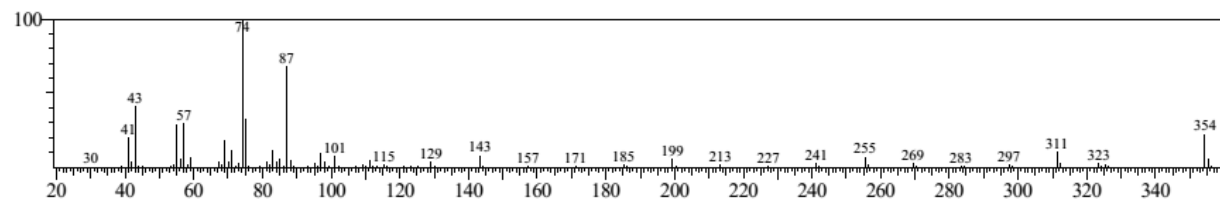
Retention time: 22.91; **Mass peaks:** 162; **Formula:** C₂₁H₄₂O₂; **Molecular weight:** 326



Line 23

Compound Name: Docosanoic acid, methyl ester / Behenic acid

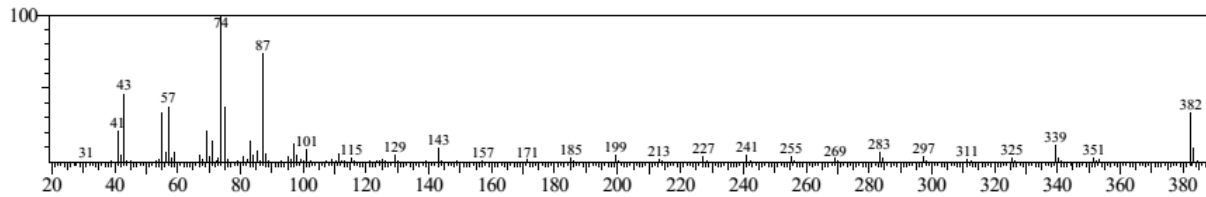
Retention time: 24.66; **Mass peaks:** 141 ; **Formula:** C₂₃H₄₆O₂; **Molecular weight:** 354



Line 25

Compound Name: Tetracosanoic acid, methyl ester.

Retention time: 26.37; **Mass peaks:** 133 ; **Formula:** C₂₅H₅₀O₂; **Molecular weight:** 382

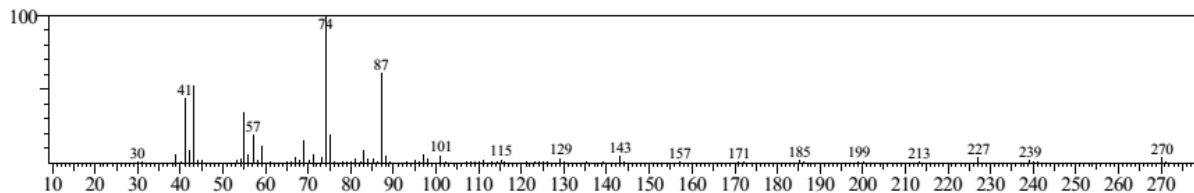


Appendix iv: Mass spectra of the fatty acid of pig lard methyl ester.

Line 1

Compound Name: Pentadecanoic acid, methyl ester.

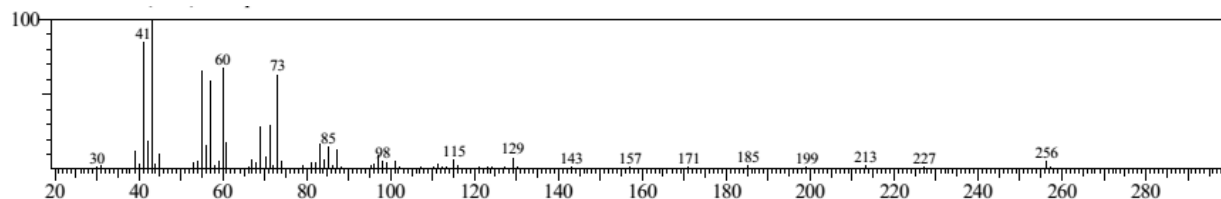
Retention time: 19.08; **Mass peaks:** 97; **Formula:** C₁₇H₃₄O₂; **Molecular weight:** 270



Line 2

Compound Name: n-Hexadecanoic acid/palmitic acid.

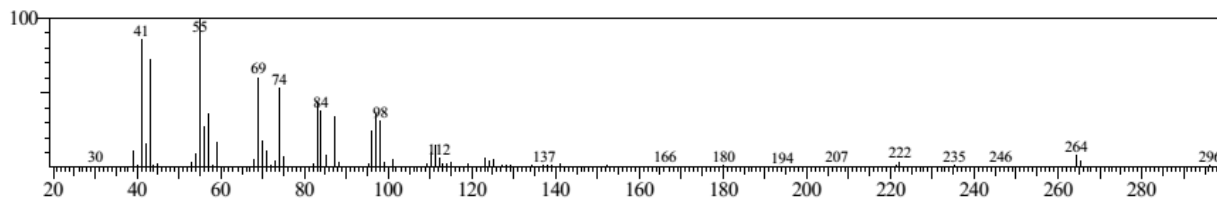
Retention time: 19.90; **Mass peaks:** 77; **Formula:** C₁₆H₃₂O₂; **Molecular weight:** 256



Line 3

Compound Name: n-Octadecenoic acid, methyl ester.

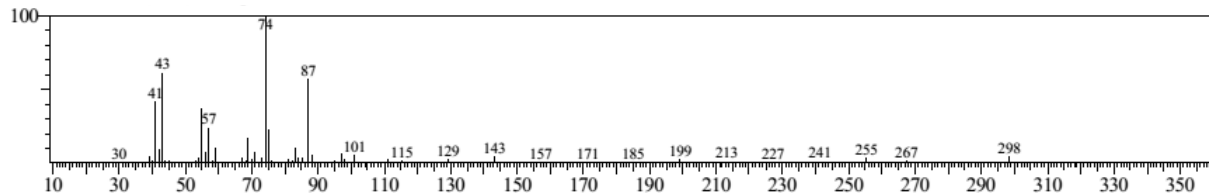
Retention time: 21.00; **Mass peaks:** 115; **Formula:** C₁₉H₃₆O₂; **Molecular weight:** 296



Line 4

Compound Name: Octadecanoic acid, methyl ester/ Stearic acid.

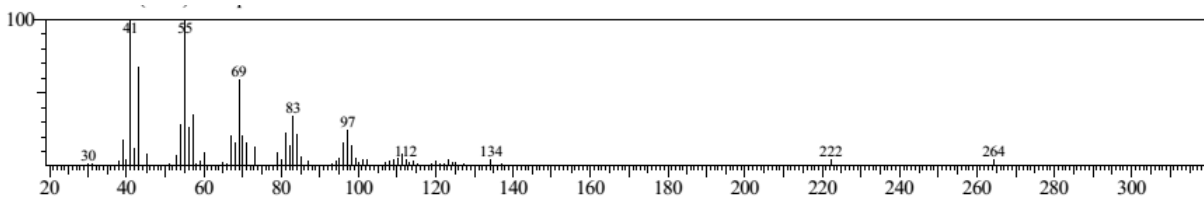
Retention time: 21.20; **Mass peaks:** 99; **Formula:** C₁₉H₃₈O₂; **Molecular weight:** 298



Line 5

Compound Name: Oleic acid.

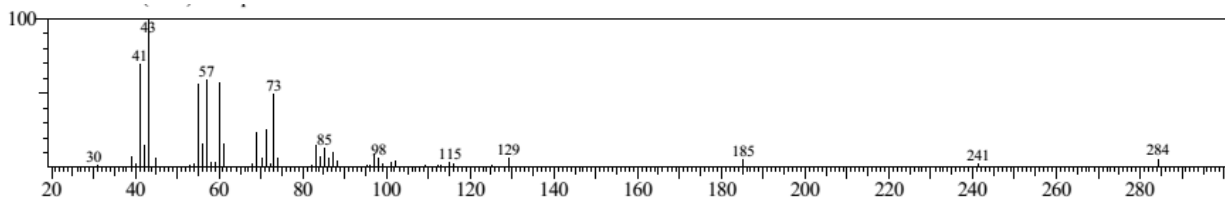
Retention time: 21.77; **Mass peaks:** 82; **Formula:** C₁₈H₃₄O₂; **Molecular weight:** 282



Line 6

Compound Name: Hexadecanoic acid/ palmitic acid.

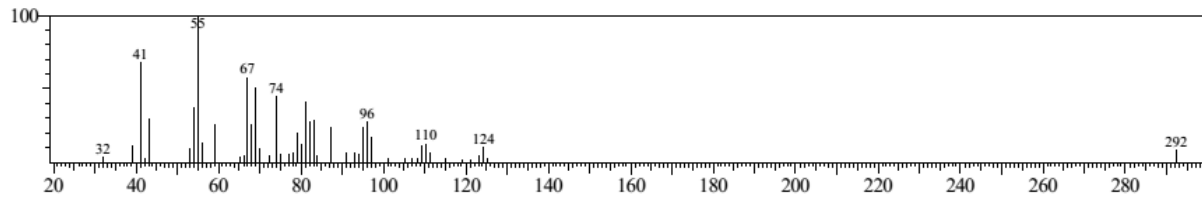
Retention time: 21.93; **Mass peaks:** 61; **Formula:** C₁₆H₃₂O₂; **Molecular weight:** 256



Line 7

Compound Name: 13,16-Octadecadienoic acid.

Retention time: 22.91; **Mass peaks:** 49; **Formula:** C₁₉H₃₄O₂; **Molecular weight:** 294



Appendix v: Effect of variation of reaction time, temperature and catalyst concentration on biodiesel yields

Effects of reaction time on yellow oleander biodiesel yield with 0.5% (w/w) catalyst at different temperatures.

Time(s)	at 30°C	at 40°C	at 50°C	at 60°C	at 70°C
30	41.32	53.56	65.06	74.73	80.94
45	71.41	77.1	80.92	86.35	89.83
60	73.39	79.58	84.67	89.41	91.77
75	78.51	85.09	87.89	90.98	93.36
90	81.5	87.86	90.92	92.89	94.45

Effects of reaction time on yellow oleander biodiesel yield with 1%(w/w) catalyst at different temperatures.

Time(s)	at 30°C	at 40°C	at 50°C	at 60°C	at 70°C
30	41.32	58.56	72.06	77.73	78.94
45	67.41	77.1	86.92	90.35	89.83
60	71.39	80.58	92.67	96.89	96.07
75	74.51	83.79	94.79	96.82	96.55
90	75.5	83.86	94.92	96.8	96.15

Effects of reaction time on pig lard biodiesel yield with 0.5 % (w/w) catalyst at different temperatures.

Time(s)	at 30°C	at 40°C	at 50°C	at 60°C	at 70°C
30	42.44	58.61	68.76	78.45	81.04
45	63.85	72.67	82.54	88.42	89.67
60	69.13	78.3	83.4	90.52	90.85
75	72.07	79.6	86.88	90.76	91.98
90	75.4	82.25	89.08	91.18	92.45

Effects of reaction time on pig lard biodiesel yield with 1% (w/w) catalyst at different temperatures.

Time(s)	at 30 ^o C	at 40 ^o C	at 50 ^o C	at 60 ^o C	at 70 ^o C
30	44.24	48.16	60.32	72.04	71.26
45	65.25	75.46	85.56	90.72	89.93
60	70.54	78.79	86.55	95.39	94.12
75	74.53	80.85	90.07	94.31	93.91
90	75.26	83.5	92.5	94.04	93.3

Effects of reaction temperature on yellow oleander biodiesel yield with 0.5 % (w/w) catalyst at different time.

Temp(^o C)	at 30 min	at 45 min	at 60 min	at 75 min	at 90 min
30	41.32	55.41	63.39	71.51	75.5
40	65.56	72.1	82.58	85.79	87.86
50	69.06	77.92	84.67	87.79	89.92
60	74.73	80.35	87.41	89.95	90.89
70	75.04	80.55	87.07	90.06	90.55

Effects of reaction temperature on yellow oleander biodiesel yield with 1% (w/w) catalyst at different time.

Temp(^o C)	at 30 min	at 45 min	at 60 min	at 75 min	at 90min
30	60.4	67.5	72.15	78.49	80.95
40	78.19	83.15	87.03	89.15	89.94
50	83.5	85.64	88.03	90.74	91.82
60	86.26	88.3	89.69	90.95	92.36
70	87.89	90.04	90.48	91.93	92.45

Effects of reaction temperature on pig lard biodiesel yield with 0.5%(w/w) catalyst at different time.

Temp(°C)	at 30 min	at 45 min	at 60 min	at 75 min	at 90 min
30	52.44	63.85	69.13	77.07	80
40	68.61	78.67	85.3	89.6	91.25
50	76	82.54	90.1	91.88	93.08
60	78.45	87.74	91.45	93.76	95.18
70	83.04	90.22	92.05	93.98	95.45

Effect of reaction temperature on pig lard biodiesel yield with 1% (w/w) catalyst at different time.

Temp(°C)	at 30 min	at 45 min	at 60 min	at 75 min	at 90 min
30	54.24	65.25	70.54	78.53	83.26
40	70.16	80.46	88.79	90.85	93.5
50	76.32	85.56	91.55	92.7	94.5
60	80.26	90.93	94.42	95.71	96.9
70	82.04	90.72	93.89	95.31	96.04

Effect of catalyst concentration (% w/w) on yellow oleander biodiesel and pig lard biodiesel yield at different time.

Time(s)	0.50% withYO	1.00% withYO	1.50% with YO	0.5% with PL	1.00% with PL	1.50% with PL
30	73.39	84.73	78.26	78.45	80.26	75.38
45	82.58	92.35	86.5	87.74	90.93	83.9
60	88.67	97.41	89.65	91.45	95.12	88.65
75	92.41	97.98	90.05	93.76	95.71	89.13
90	94.02	97.89	90.15	95.18	96.5	89.12

Appendix vi: Properties of YOME and YOME blends

Properties	YOME	B10	B20	B30	B40	B50	B60	B70	B80	B90
SG@15/14 °C	0.882	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.882
Sulphur(% wt)	0.001	0.090	0.080	0.066	0.056	0.043	0.034	0.025	0.015	0.005
Flash point °C	86	54	68	70	72	78	82	85	86	88
Cloud point °C	10	3	4	6	6	6	6	10	11	12
ASTM colour	>0.5	2.5	2.5	2.5	2.0	1.5	1.5	1.0	1.0	0.5
Viscosity @40 °C	8.17	4.19	4.33	4.39	4.43	4.97	5.04	5.94	6.46	6.53
Diesel index	33	36	33	29	34	28	34	29	29	38
Calorific value (MJ/Kg)	39.78	44.98	44.50	44.32	44.00	43.75	43.36	42.88	42.54	42.25
Cetane No.	60	44	48	50	53	55	56	58	58	59

Appendix vii: Properties of PLME and PLME blends

	PLME	AGO	B10	B20	B30	B40	B50	B60	B70	B80	B90
SG@15/14 ⁰ c	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881
Sulphur(%wt)	0.006	0.010	0.091	0.076	0.065	0.053	0.044	0.036	0.024	0.015	0.004
Flash point ⁰ c	98	88	75	78	80	80	82	84	85	86	105
Cloud point ⁰ c	13	2	7	8	9	9	9	9	10	10	11
ASTM colour	0.5	2.5	2.5	2.5	2.5	2.0	1.5	2.0	1.0	1.0	0.5
Viscosity @40 ⁰ c	7.32	3.75	3.76	4.04	4.09	4.14	4.14	4.16	4.73	4.78	4.84
Diesel index	25	42	37	24	26	22	34	26	25	24	25
Calorific Value (MJ/kg)	40.36	45.87	45.56	45.08	44.74	44.30	43.81	42.65	42.12	41.84	41.44
Cetane No.	56	41	42	45	47	49	51	52	53	54	55

Appendix viii: Kinematic viscosity of FD, YOME and PLME biodiesels and their blends at various temperatures.

Viscosity of FD, PLME and their Blends.

Temp. °C	AGO	B20	B40	B60	B80	B100
100	3.35	4.02	4.36	4.61	5.57	7.35
150	3.05	3.5	4.03	4.32	4.96	6.48
200	2.72	3.00	3.50	3.98	4.53	5.52
250	2.15	2.51	3.00	3.44	3.9	4.72

Viscosity of FD, YOME and their Blends.

Temp. °C	AGO	B20	B40	B60	B80	B100
100	3.35	3.2	3.6	4.1	4.6	5.2
150	3.05	2.8	3.1	3.4	3.8	4.3
200	2.8	2.5	2.8	3.0	3.4	3.7
250	2.45	2.1	2.4	2.6	2.9	3.2

Appendix ix: Kinematic Viscosity with % YOME and %PLME in blends under various temperatures

Viscosity with % PLME in blends under various temperatures.

Fuel	at 100 °C	at 150 °C	at 200 °C	at 250 °C
AGO	3.35	3.05	2.72	2.15
B20	4.02	3.5	3	2.51
B40	4.36	4.03	3.5	3
B60	4.61	4.32	3.98	3.44
B80	5.57	4.96	4.53	3.9
B100	7.35	6.48	5.52	4.72

Viscosity with % YOME in blends under various temperatures

Fuel	at 30 °C	at 100 °C	at 150 °C	at 200 °C	at 250 °C
AGO	3.2	2.8	2.5	2.2	1.9
B20	3.8	3.2	2.8	2.5	2.1
B40	4.4	3.6	3.1	2.8	2.4
B60	5.0	4.1	3.4	3.0	2.6
B80	5.6	4.6	3.8	3.4	2.9
B100	6.3	5.2	4.3	3.7	3.2

Appendix x: Kinematic Viscosity, Acid Value, and Peroxide Value of YOME and PLME Before and After Oxidation at 100, 150, 200 and 250°C.

Temp(°C)	Kinematic Viscosity (cSt)		Acid Value (mg KOH/g)		Peroxide Value (meq/kg)	
	YOME	PLME	YOME	PLME	YOME	PLME
30	8.17	7.32	1.30	1.92	5.90	7.67
100	11.00	12.30	1.80	2.60	13.4	16.43
150	13.50	14.80	2.64	3.20	9.70	11.40
200	18.60	20.00	3.95	4.52	1.51	3.60
250	23.00	24.00	5.76	6.40	0.67	1.23

Appendix xi: Calorific value of YOME and PLME and their blends after storage.

Calorific Value (MJ/Kg) of Yellow Oleander Biodiesel after storage

Fuel	Storage period (days)				
	0	60	% decrease	120	% decrease
AGO	45.87	45.72	0.33	45.72	0.33
B20	44.5	44.01	1.10	43.62	1.3
B40	44	42.93	2.43	42.01	4.52
B60	43.36	42.57	1.82	41.12	5.52
B80	42.54	41.42	2.63	40.22	5.50
B100	39.78	38.51	3.19	37.96	4.58

Calorific Value (MJ/Kg) of Pork Lard Biodiesel after storage

Fuel	Storage period (days)				
	0	60	% decrease	120	% decrease
AGO	45.87	45.72	0.33	45.72	0.33
B20	44.08	43.51	1.30	42.92	2.64
B40	43.30	42.73	1.32	42.01	3.0
B60	42.81	42.0	1.90	41.42	3.25
B80	41.84	40.82	2.44	40.52	3.15
B100	40.36	39.34	2.52	39.16	3.0

Appendix xii : Flash Points of YOME and PLME Biodiesels and their Blends after Storage.

Flash point(^oC) of Oleander Biodiesel after Storage

Fuel	Storage period (days)		
	0	60	120
AGO	88	88	88
B20	68	78	82
B40	72	75	86
B60	82	88	94
B80	86	90	96
B100	86	92	98

Flash point (^oC) of pork lard Biodiesel after storage

Fuel	Storage period (days)		
	0	60	120
AGO	88	88	88
B20	78	90	95
B40	80	89	97
B60	84	90	98
B80	86	92	98
B100	48	62	80

Appendix xiii: Densities of YOME and PLME Biodiesels and their Blends after Storage.

Density (g/cm^3) of Oleander Biodiesel on storage

Fuel	Storage period (days)		
	0	60	120
AGO	0.881	0.881	0.881
B20	0.881	0.882	0.882
B40	0.881	0.882	0.882
B60	0.881	0.882	0.882
B80	0.881	0.882	0.882
B100	0.882	0.882	0.883

Density (g/cm^3) of pig lard Biodiesel on storage

Fuel	Storage period (days)		
	0	60	120
AGO	0.881	0.881	0.881
B20	0.881	0.883	0.883
B40	0.881	0.883	0.884
B60	0.881	0.883	0.884
B80	0.881	0.883	0.884
B100	0.881	0.884	0.884

Appendix xiv: Kinematic Viscosity of YOME and PLME Biodiesels and their Blends after Storage.

Kinematic viscosity (cst) of Oleander Biodiesel after storage

Fuel	Storage period (days)		
	0	60	120
AGO	3.75	3.96	4.08
B20	4.33	4.51	4.56
B40	4.43	4.55	4.60
B60	5.04	5.29	5.45
B80	6.46	6.57	6.68
B100	8.17	8.29	8.40

Kinematic viscosity (cst) of lard Biodiesel after storage

Fuel	Storage period (days)			
	0	60	% decrease	120
AGO	3.75	3.96	4.08	4.08
B20	4.33	4.51	4.56	4.56
B40	4.43	4.55	4.60	4.60
B60	5.04	5.29	5.45	5.45
B80	6.46	6.57	6.68	6.68
B100	8.17	8.29	8.40	8.40

Appendix xv: Specific Gravities of YOME and PLME Biodiesels and their Blends after Storage.

Specific Gravities of PLME and Biodiesel Blends at Various Temperatures

Temp. °C	AGO	B20	B40	B60	B80	B100
100	0.880	0.884	0.886	0.890	0.896	0.899
150	0.877	0.879	0.881	0.885	0.89	0.893
200	0.870	0.874	0.876	0.879	0.881	0.887
250	0.862	0.865	0.870	0.872	0.876	0.882

Specific Gravities of YOME and Biodiesel Blends at Various Temperatures

Temp. °C	AGO	B20	B40	B60	B80	B100
100	0.882	0.885	0.887	0.898	0.916	0.929
150	0.877	0.8841	0.8801	0.895	0.910	0.920
200	0.870	0.879	0.879	0.889	0.901	0.916
250	0.862	0.875	0.875	0.882	0.898	0.909

Appendix vi: Properties of YOME Blends

Properties	YOME	B10	B20	B30	B40	B50	B60	B70	B80	B90
SG-Y	0.882	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.882
	0.881	0.880	0.883	0.880	0.881	0.882	0.881	0.882	0.881	0.882
S-Y	0.001	0.090	0.080	0.066	0.056	0.043	0.034	0.025	0.015	0.005
	0.002	0.088	0.082	0.068	0.057	0.045	0.033	0.026	0.013	0.006
FP-Y	86	54	68	70	72	78	82	85	86	88
	87	55	67	72	71	79	81	84	88	87
CP-Y	10	3	4	6	6	6	6	10	11	12
	11	2	5	7	5	6	7	9	9	10
ASTMC-Y	0.5	2.5	2.5	2.5	2.0	1.5	1.5	1.0	1.0	0.5
	0,5	2.0	2.2	2.4	2.3	1.8	1.8	1.2	1.3	0.7
KV-Y	8.17	4.19	4.33	4.39	4.43	4.97	5.04	5.94	6.46	6.53
	8.10	4.16	4.35	4.40	4.45	5.01	5.00	6.00	6.50	6.50
DI-Y	33	36	33	29	34	28	34	29	29	38
	35	35	34	30	32	30	35	30	31	37
CV-Y	39.78	44.98	44.50	44.32	44.00	43.75	43.36	42.88	42.54	42.25
	40.12	45.14	44.55	44.36	44.08	44.00	43.66	43.05	42.89	42.36
CN-Y	60	44	48	50	53	55	56	58	58	59
	59	46	47	51	52	56	54	59	58	57

Appendix vii: Properties of PLME and PLME Blends

Properties	PLME	B10	B20	B30	B40	B50	B60	B70	B80	B90
SG-P	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881	0.881
	0.883	0.879	0.880	0.884	0.882	0.880	0.883	0.880	0.880	0.880
S-P	0.006	0.091	0.076	0.065	0.053	0.044	0.036	0.024	0.015	0.004
	0.008	0.015	0.092	0.078	0.070	0.051	0.040	0.030	0.014	0.005
FP-P	98	75	78	80	80	82	84	85	86	105
	87	75	67	72	71	79	81	84	88	107
CP-P	13	7	8	9	9	9	9	10	10	11
	11	8	9	7	10	8	9	9	9	10
ASTMC-P	0.5	2.5	2.5	2.5	2.0	1.5	2.0	1.0	1.0	0.5
	0.5	2.3	2.4	2.6	2.3	1.7	1.9	1.1	1.2	0.7
KV-P	7.32	3.76	4.04	4.09	4.14	4.14	4.16	4.73	4.78	4.84
	7.50	3.79	4.08	4.10	4.15	4.18	4.14	4.76	4.75	4.90
DI-P	25	37	24	26	22	34	26	25	24	25
	26	35	24	28	23	30	25	27	25	27
CV-P	40.36	45.56	45.08	44.74	44.30	43.81	42.65	42.12	41.84	41.44
	40.40	45.54	45.15	44.66	44.34	43.92	42.66	42.15	41.89	41.46
CN-P	56	42	45	47	49	51	52	53	54	55
	57	43	47	48	50	50	51	52	55	54