PRODUCTION AND CHARACTERIZATION OF BIODIESEL AND BIODIESEL – DIESEL BLEND FROM *TERMINALIA CATAPPA* SEED OIL

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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY ZARIA
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DEPARTMENT OF CHEMISTRY,
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DECLARATION

I declare that this work titled **“Production and Characterization of Biodiesel and Biodiesel-Diesel blend from *Terminalia Catappa* seed oil**” has been performed by me in the Department of Chemistry, under the supervision of Profession V. O Ajibola and Dr. S. E. Abechi. The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this research was previously presented for another degree or diploma at any University or Institution.

Lawal SANI	________________	________________
Name of Student	Signature	Date

CERTIFICATION

This Dissertation titled **PRODUCTION AND CHARACTERIZATION OF BIODIESEL AND BIODIESEL-DIESEL BLEND FROM *TERMINALIA CATAPPA* SEED OIL** by Lawal **SANI** meets the regulation governing the award of the degree of MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Prof. V. O. Ajibola
Chairman Supervisory Committee
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Member Supervisory Committee
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DEDICATION

This Dissertation is dedicated to God and members of the armed forces Federal Republic of Nigeria.

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ABSTRACT

Terminalia Catappa seed oil was explored as a potential feedstock for biodiesel production. The oil was extracted via mechanical pressing and solvent extraction method. The percentage oil yield was 56.30 ± 1.60% w/w. The oil was degummed using 5% citric acid in amount of 10% by volume of the oil to determine the effect of degumming on physicochemical and biodiesel properties of the oil. The acid value of raw and degummed oil is7.57 mgKOH/g and 3.82 mgKOH/g respectively. The oil was esterified to reduce the acid value to less than 2mgKOH/g for base-catalyzed transesterification. The fatty acid composition of *Terminalia Catappa* seed oil revealed predominance of oleic acid, palmitic acid and linoleic acid with decrease in level of unsaturation in the degummed oil. Transesterification was carried out with NaOH catalyst for both raw and degummed oil. The degummed oil was further catalyzed with KOH and CaO/Al_2O_3 catalyst. Physicochemical properties of the biodiesel obtained were carried out using American Standard for Testing and Material (ASTM) methods. Results obtained shows that degummed oil gave high biodiesel yield and reduced the acid and iodine value compared to the raw oil. The effect of blending on biodiesel properties of NaOH catalyzed biodiesel was studied. The result showed that B10-B20 biodiesel-diesel blend of *Terminalia Catappa* methylester agreed with ASTM specification for B6-B20 biodiesel-diesel blend and can therefore be used as blended fuel in diesel engines.

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LIST OF ABBREVIATIONS

ASTM	American Standard for Testing and Material
CTC	Crude *Terminalia Cattapa*oil
DTC	Degummed *Terminalia catappa* oil
FAAE	Fatty Acid Alkyl ester
FAME	Fatty Acid Methyl ester
FFA	Free fatty acid
FTIR	Fourier transforms infrared
GC-MS	Gas Chromatography mass spectroscopy
IV	Iodine value
NARICT	National Research Institute for Chemical Technology
SV	Saponification value
TCME	*Terminalia Cattapa* Methyl ester

CHAPTER ONE

1.0 INTRODUCTION

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 (Dallatu, 2015).

Going by the present rate of global fossil fuel consumption, crude oil reserves could be depleted in 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.*, 2007). 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 (Dallatu, 2015).

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.

Another important factor that necessitated 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 greenhouse gases (Munack *et al.,* 2001; Saravanan *et al.,*2007). The emitted gases such as CO_2, CO, NO_2, NO, SO_2 and SO_3 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). The environmental concerns regarding greenhouse gas emissions and commitment of the International Community to significantly reduce emissions as formalized by the Kyoto Protocol adopted in December, 1997 also triggered the need to find more sustainable alternatives to fossil fuels (Dallatu, 2015).

Biodiesel is considered as a “direct-pour” alternative fuel to petroleum diesel, as it requires almost no modification to most modern diesel engines. Biodiesel can be produced locally and therefore reduces foreign oil dependence. It has been reported that biodiesel combustion can result in less air pollutant emissions, such as carbon monoxide, sulphur dioxide, particulate matter, hydrocarbons, but with slightly higher nitrogen oxides (Graboski 1998; Nwaiwu *et al.,* 2017). Since the feedstock of biodiesel is mostly renewable, it significantly reduces carbon dioxide emission during its whole life cycle (Sheehan *et al.,* 1998; De jong *et al.,* 2017)**.** According to the American Standard Testing Methods (ASTM), biodiesel is defined as a fuel comprising mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat (Knothe, 2009; Zahan and Kano, 2018).As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel as an alternative fuel has many merits. It is derived from a renewable resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission.

1.1 Renewable Energy

Renewable energy is the energy produce from sources that can be replenished within a human’s life time. The most common examples include wind, solar, biomass etc. this is contrast to non-renewable sources such as fossils fuels.

Biodiesel is a renewable energy source whuch, 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 (Dallatu, 2015). 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 biodiesel 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 than fossil diesel (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 (Ndana *et al.*, 2011). 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 (Canakci *et al.*, 2001; Veljkovic *et al.*, 2006). 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

The ever-increasing competing demand for energy sources, coupled with the fact that fossil fuel is non-renewable, has led to the prediction that the world‘s reserves of fossil fuel would be expended before the end of the 21st century (Shahriar and Erkan, 2009). Petroleum crises, which include 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 meet an increasing energy demand (Dallatu, 2015).

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 (non-edible oil) 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 centered 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; Giwa and Ogunbona 2014; Dallatu, 2015; Adekunle *et al*., 2016).

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 unstable oil supply and unpredictable prices. Use of fossil fuels leads to increase in greenhouse gases (SO_2, NO_2, CO_2 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.

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 developing countries. It is therefore inevitable to look for non-edible but economically viable feedstocks as an alternative to edible vegetable oils.

1.4 Aim and Objectives

The aim of this work is to produce biodiesel and biodiesel-diesel blends from *Terminaliacatappa*seed oil and to evaluate their quality.

The objective of this research include to;

(i) Extract oil from *Terminaliacatappa* seed
(ii) Degum the oil obtained
(iii) Determine the physicochemical properties of the raw oil and degummed oil.
(iv) Produce biodiesel through transesterification of the oil.
(v) Determine the fuel properties of biodiesel and biodiesel-diesel blends produced.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Biodiesel

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters (Ibrahim, 2015). It is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines (NBB, 2009). It can be used alone, or blended with petro diesel and can also be used as a low carbon alternative to heating oil. It can be made from new or used vegetable oils and animal fats, which are nontoxic, biodegradable, and renewable. It is always produced by means of transesterification of vegetable oil or animal fat (Yun *et al.*, 2011) with monohydric alcohol into fatty acid methyl esters (FAME). Glycerin (used in pharmaceuticals and cosmetics, among other markets) is produced as a co-productof transesterification (Ibrahim, 2015).

Biodiesel can be produced using a variety of transesterification technologies. The oils and fats are filtered and preprocessed to remove water and contaminants. If free fatty acids are present, they can be removed or transformed into biodiesel using special pretreatment technologies (esterification). The pretreated oils and fats are then mixed with an alcohol (usually methanol) and a catalyst. The oil molecules (triglycerides) are broken apart and reformed into alkyl esters and glycerin, which are then separated from each other and purified.

2.2 HistoricalDevelopment ofBiodiesel

It is generally known that vegetable oils were tested as diesel fuels well before the energycrises 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 (Dallatu, 2015).

Several other European countries took up the idea after the Exhibition, which resulted in a number of articles in different European Countries. Subsequently, 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 during the 1920s and 1930s and later during World War II (Dallatu, 2015).

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 (Ibrahim, 2015)

2.3 Biodiesel Feedstocks

Biodiesel can be produced from a variety of renewable lipid sources, including Jatropha, soybeans, rapeseed, sunflower, wild mango, yellow oleander and peanut seed oil (Bajaj, *et al.*, 2010; Dallatu, 2015; Ibrahim, 2015; Adekunle, *et al.*, 2016*).*

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, CO_2 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.

2.3.1 *Terminalia Catappa*

Terminalia Catappa is a large tropical tree in the Leadwood tree family combretaceac (Pate I) that grows mainly in the tropical region of Asia, Africa and Australia. It grows principally in freely drained, well-aerated sandy soils. It is widely planted for shade and ornamental purposes, and is easily propagated from seed, if is fast growing and flourishes with minimal maintenance in suitable environments. Its fruits that are produced from about three years of age, feature an ellipsoidal format and a colouration that ranges between yellow and purple when ripe and contain a very hard kernel as shown in plate II (Thomson and Evans, 2006)

Plate I: *Terminalia catappa* tree

Plate II: *Terminalia catappa* fruits

Terminaliacatappa is a source of non-edible vegetable oil which is underutilized in Nigeria. The tree is grown commonly as a shade tree in towns, villages and cities. The tree is found in most residential and public quarters in Nigeria. (Adewuyi, *et al.*, 2011). The outer flesh which contains 95.9 ± 5.8 mg ascorbic acid/100g fruit (Keshinro, 1985), is usually consumed by children in the tropics. Vast quantities lie on the ground and the flesh is consumed by land crabs, scavenger beetles, birds or other animals. Eventually, the fruits are raked up and discarded as waste. Several species of the genus *Terminalia* have long been used in traditional medicine in both East and West African countries to treat infectious diseases (Fabry *et al.*, 1996). The oil yield of the seed of T. catappa has been reported in the literature to be 55.05g/100g (Oderinde, 1998). Suggesting that it can be used as feedstock for production of biodiesel in Nigeria.

2.4 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 multispeed 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 discussedbelow.

2.4.1 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 (Dallatu, 2015). 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).

2.4.2 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, J*atropha* 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; Dallatu, 2015)

2.4.3 Mechanical extraction

Mechanical pressing is the oldest and simplest method for oil extraction. No chemical is used for oil extraction. It uses mechanical presses/expellers (Bhargavi *et al.*, 2018). Mechanical extraction of the oil is accomplished by exerting sufficient force on confined seed. Under this condition, pressure is high enough to rupture thecells 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; Bhargavi *et al.,* 2018).

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 ofoil, 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).

2.4.4 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 (Dallatu 2015).

2.4.5 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 to 60ºC 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 (Bhargavi*et al.,* 2018).

2.4.6 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, 2006). 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 ascompared 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; Bhargavi *et al.,* 2018).

2.5Pretreatment of Feedstock

Production of high quality biodiesel begins with the quality of the feedstock used. Hence, it is essential that the oil is purified before its processing for biodiesel. This is because the fuel is to be fed into engines which require the best quality possible. As such, careful steps must be taken to remove all undesirable constituents from the feedstock. In the case of vegetable oil extracted from plant seeds, the most recognizable impurities can be categorized into three (Ibrahim, 2015):

i. Solid (solute) content

ii. Water and volatile content

iii. Free fatty acid content

Vegetable oil extracted from seeds is regarded as crude and contains a lot of substances that are not required in a high quality biodiesel. Suspended particles are examples of these unwanted elements, and are categorized as solid contents or solute (Agbogun, 2014). Although it is required that oil bearing seeds are dried to remove water before extracting the oil from the seed, experience has shown that the oil usually contains water and other substances that can be removed by heating the oil. Those other substances that are not water are called the volatile contents. Free fatty acids do not fit directly into this category of impurities. But direct preparation of biodiesel without careful consideration of free fatty acid content of the oil can hamper theprocess.

2.5.1 Removal of Impurities from Feedstock

Solid contents can be removed by simple filtration. The filter used must be of very small pores like a filter paper in other to be able to trap all the solid materials. When the oil has been completely filtered, the next step is to remove the volatile content and water by heating the oil sample until the bubbling stop. Oil that has been subjected to filtration and heating can finally be put to the crucial free fatty acid removal process (Ibrahim, 2015).

2.5.2 Removal of Free Fatty Acid from Feedstock

There are two ways of removal of free fatty acid from vegetable oil. They are by:

i. Washing with soap and water

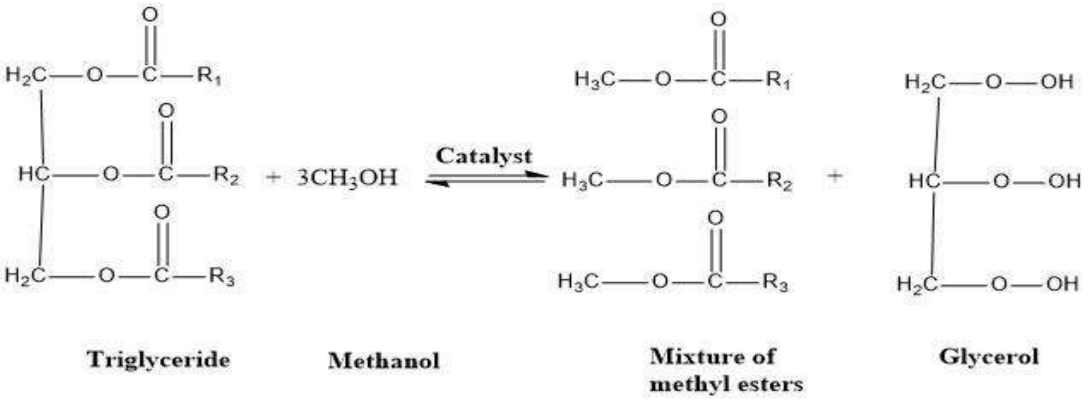
Washing under soap is the easier of the two methods. It can be carried out with minimum experience and risk. But the problem with this method is that, it results to wastage of usable free fatty acid; hence reduce the quantity of biodiesel. For example, free fatty acid content of rubber seed oil is said to be up to over 30% (Agbogun, 2014). Removal of this amount from the total oil can reduce the quantity of biodiesel obtained by that amount.

ii. Esterification with acid

Esterification on the other hand, does not remove the fatty acid. Instead, it helps to shield the fatty acids from the attack of alkaline and transform it into a constituent of the final product.Esterification of high free fatty acids feedstock is the better way of removing the free fatty acids from vegetable oil. It involves substituting an alkyl group (R) for the hydrogen of the carboxyl functional group of the acid. In this way, the fatty acid will transform into an ester which will allow almost all of the oil to be available for biodiesel. If the feedstock is confirmed from titration analysis to contain more than 1% free fatty acids, it is safer to esterify it before using it to produce biodiesel especially if base catalyst (either homogenous or heterogeneous) is employed. The amount of methanol required is 2.25 g x %FFAx mass of the oil and the amount of concentrated sulphuric acid is 0.05 g x %FFA x mass of the oil (Gerpen *et al.,* 2004) are added to the oil to be esterified after preheated to 60^0C. This mixture is stirred and heated at 60^oC for about 60 minutes. At the end of this reaction ester, water and the sulphuric acid are products which can be separated in the separating funnel. After settling in a separating funnel the ester is run off from the bottom of the funnel leaving behind water/acid mixture. The esterified oil can be tested for FFA and the process is repeated until the final %FFA is less than 1%.

2.6 Transesterification

Transesterification has been reported as the key and foremost important step in the production of cleaner and environmentally safe fuel from vegetable oils (Canoira *et al.,*2006; Shahid and Jamal, 2008; 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 stoichometry of methanolysis reaction (transesterification reaction) requires three moles of methanol and one mole of triglyceride to give a mixture of three fatty acid methyl ester and one mole of glycerol as shown in equation 2.1.



Equation 2.1: Transesterification reaction of vegetable oils or animal fats

The symbols R_1, R_2 and R_3 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.

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; Talha and Sulaiman, 2016).

2.6.1 Homogeneous base catalyze transesterification

Biodiesel is currently synthesized using homogeneous alkaline catalyst because the transesterification reaction by an acid catalyst is much slower than the base-catalyzed reaction. The most common basic catalystsare potassium hydroxide (KOH), Potassium methoxide($KOCH_3$), sodium hydroxide(NaOH), and sodium Methoxide($NaOCH_3$). These catalyst are commonly used because of several advantages such as ability to catalysed reaction at low reaction temperature and atmospheric pressure, high conversion in shorter time, and economically available (Lam *et al.,* 2010). 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; Ejikeme *et al.,* 2010; Nasreen *et al.,* 2018).

NaOH and KOH are the most common homogeneous base catalyst in biodiesel production. Table 2.1 Listed reports that used NaOH and KOH in their works. The highest biodiesel yield produce by *calophyllum inophyllum* was reported by silitonga *et al.,* (2014) with 98.53% by using 1 wt% KOH and 9:1 methanol to oil ratio. Silva *et al.,* (2011) reported 95% of biodiesel yield from soyabean oil using NaOH with 1.3 wt% catalyst loading and ethanol to oil ratio of 9:1

2.6.2 Heterogeneous base catalysed transesterification

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). Most of the heterogeneous catalysts developed for production of biodiesel are either alkaline oxide or alkaline earth metal oxide supported over large surface area. (Helwani,*et al.,* 2009). Table

2.1 List some of the reaction conditions for various types of heterogeneous base catalyst in transesterification reaction of lipid.

Table 2.1: Comparisons of reaction conditions for various types of catalyst

Catalyst	Reaction conditions					Biodiesel yield	Remark	Reference
	Temp. ^{0}C	Type of (alcohol to oil molar ratio	Catalyst loading wt%	Reaction time, h	Mixing rpm			
				Homogeneous base catalyst				
Sodium hydroxide (NaOH)	40	Ethanol (9.1)	1.3	1.33	-	Soybean oil 95%	Batch reactor	Silva *et al.*, 2011
Sodium hydroxide (NaOH)	60	Methanol (5:1)	0.12	1.30	-	*Citrullus vulgaris*70%	Shake flask	Efavi *et al.*, 2018
Sodium hydroxide (NaOH)	60	Methanol (475:1)	0.1	1	-	Rapeseed, 88.8%	Soxhlet	Zakariya and Harvey 2012
Potassium hydroxide (KOH)	60	Methanol (4:1)	0.1	1	550	Pongamia pinnata	-	Porwal *et al.*, 2012
Potassium hydroxide (KOH)	50	Methanol (6:1)	0.075	5	800	Jatropha seed, 87%	Three necked round bottom flask equipped with reflux system	Karkita *et al.*, 2013
Potassium hydroxide (KOH)	55	Methanol (9.1)	1	1	-	Calophyllum inophyllum 98.53%	-	Silitonga *et al.*, 2014
Potassium hydroxide (KOH)	60	Methanol (6:1)	1	1	-	Soybean oil, 88.73%	-	Adekunle *et al.*, 2016
				Heterogeneous base catalyst				

Bone	60	Methanol (20:1)	18	4	600	Rapeseed oil, 96% Peanut oil, 94%	Batch reactor	Bajaj *et al.*, 2010
Rice Husk	65	Methanol (24:1)	4	3	300	Soybean oil, 99.5%	Shake flask	Chen *et al.*, 2013
Snail shells	60	Methanol (6.03:1)	2	7	-	Waste frying oil, 99.58%	-	Birla *et al.*, 2012
-Eggshells -Snailshells -Venues shells	60	Methanol (15:1)	10	2	-	Palm olein oil, 94.1% Palm olein oil 93.2% Palm olein oil, 92.3%	-	Viriya *et al.*, 2012
Vegetable oil asphalt	220	Methanol (16.8:1)	0.2	4.5	-	Vegetable oil, 94.8%	-	Shu *et al.*, 2010
Oyster shells	65	Methanol (6:1)	25	5	-	Soybean oil, 96.5%	Magnetic stirrer	Nakatani *et al.*, 2009
NaOH/CaO	65	Methanol (6:1)	5	2	600	Waste cooking oil, 92.2%		Abatyough, 2016
				Homogeneous acid catalyst				
Hydrochloric acid (HCI)	100	Methanol	1.85	1	-	Sunflower oil, 95.2%	-	Sagiroglu *et al.*, 2011
Sulphuric acid (H_2SO_4)	120	Methanol (40:1)	0.5	3	-	Chlorella pyrenoidasa, 92.5%	-	Cao *et al.*, 2013
Sulphuric acid (H_2SO_4)	50	Methanol (6:1)	3	1	-	Vegetable oil by product, >90%	Reflux condenser reactor	Javidialesaadi and Raeissi 2013
				Heterogeneous acid catalyst				
Titanium-doped amorphous zirconia	245	Methanol (40:1)	11	-	-	Rapeseed oil, 65%	-	Brucato *et al.*, 2010
Sulphated zirconia	65	Methanol (9:1)	1	2	-	Neem oil, 95%	-	Muthu *et al.*, 2010
Carbon-based solid acid catalyst	220	Methanol (16.8:1)	0.2	4.5	-	Waste vegetable oil, 94.8%	-	Shu *et al.*, 2010

				Enzyme catalyst				
Lipase	52.1	Methanol (4:1)	-	-	-	Soybean oil, 83.31%	Continuous packed bed reactor	Chen *et al.*, 2011
Immobilised lipase on SiO_2	50	Methanol (12:1)	-	11	-	Babassu oil, 96.0%	Continuous packed bed reactor	Simoes *et al.*, 2015
Immobilised lipase on crystalline PVA	37	Methanol (6:1)	4	72	-	Soybean oil, 66.3%	-	Bergamasco *et al.*, 2013

2.6.3 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; Talha and Sulaiman, 2016). 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 Van Gerpen, 2001; Abatyough, 2016). The initial step for the transesterification is protonation of the carbonyl group of the ester by the acid to give (i) a carbocation intermediate which undergoes a nucleophilic addition reaction with the alcohol forming (ii) a tetrahedral intermediatewhich breakdown by proton migration and eliminates alcohol to form (iii) the new ester, 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). Acid-catalyzed transesterification therefore,shouldbe carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduces the yields of alkyl esters.

2.6.4 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. When the FFA level has been reduced to 0.5%, or lower, an alkali catalyst is added to convert the triglycerides to methyl esters (Dallatu, 2015). 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.

2.6.5 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; Talha and Sulaiman, 2016). 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.

2.6.6 Non-catalyzed System- Supercritical Process

According to Gerpen *et al.,*(2004) when a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. There is no longer a distinct liquid and vapor phase, but a single, fluid phase present. Solvents containing a hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids. Compared to the alkali catalyzed method, in which the mixing effect is significant in a heterogeneous two-phase system, the mixing is not necessary in supercritical methanol because the reactants are already in a homogeneous phase (Saka and Minami, 2006). The non-catalytic supercritical dimethyl carbonate had successfully been proven to produce biodiesel with non-glycerol by-products such as glycerol in one-step (Ilham and Saka, 2016). Figure 2.1 depicts one conception of a configuration for a supercritical transesterification process by Saka and Minami (2006).

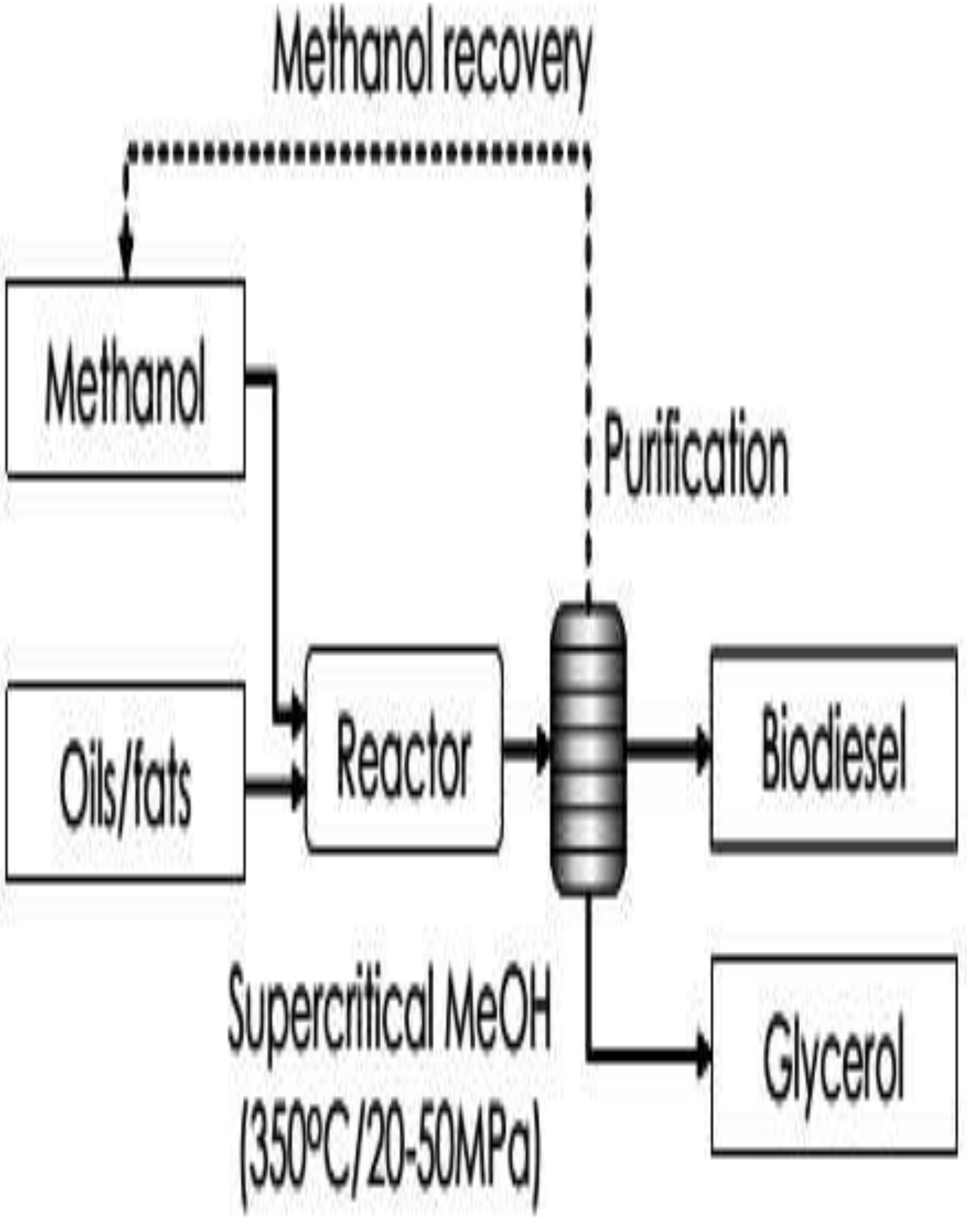


Figure 2.1: One-step supercritical methanol method (Saka and Minimi process) for biodieselproduction.

In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock; free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures transesterification by super critical method of 1 mole of spent fish oil with 41 moles of methanol at 525 K (252^{o}C) and 24 MPa took only 6 minutes and 100% yield was obtained (Ozcimen and Yucel 2011).

Energy consumption and excess amount of alcohol usage are the disadvantages of biodiesel production in supercritical conditions (Ozcimen and Yucel, 2011). Indeed, the high temperature and pressure requires both an expensive reactor and a sophisticated energy and safety management policy (Ngamprasertsith and Sawangkeaw, 2011).

2.6.7 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-ditertbutylpyridine 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 guanidine’s 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, 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).

Table 2.2: Advantage and disadvantage of different catalysts used in transesterification

Types of catalyst	Advantages	Disadvantages
Homogeneous base catalyst	▪ Do not form water during transesterification reaction ▪ 4000 times faster reaction rate than acid catalyzed transesterification. ▪ Two-step alkaline-catalyzed transesterification from used vegetable oil is an economic method for biodiesel production ▪ Reaction can occur at mild reaction condition and thus less energy required ▪ NaOH and KOH are economically feasible and widely available	▪ Sensitive to FFA content in the oil ▪ Saponification can occur if the FFA content in the oil is more than 2 wt.% ▪ Saponification will decrease the biodiesel yield and cause problem during product purification ▪ Produce more wastewater from purification
Heterogeneous base catalyst	▪ Reusable ▪ Easy to separate from product ▪ Relatively faster reaction rate than acid catalyzed transesterification ▪ Reaction can occur at mild reactioncondition and relatively lower energy ▪ - Long catalyst life times	▪ Poisoning of the catalyst when exposed to ambient air ▪ Sensitive to FFA content in the oil due to its basicity property ▪ Saponification can occur if the FFA content in the oil is more than 2 wt.% ▪ Saponification will decrease the biodiesel yield and cause problem during product purification ▪ Higher molar ratio of alcohol to oil ▪ Produce more wastewater from purification ▪ Diffusion limitation
Homogeneous acid catalyst	▪ Insensitive to FFA and water content in the oil ▪ Preferred-method if low-grade oil is used ▪ Esterification and transesterification occur simultaneously ▪ Saponification can be avoided ▪ Produce high yield of biodiesel	▪ Low reaction rate ▪ Can lead to equipment corrosion ▪ Harder separation of catalyst from product

Heterogeneous acid catalyst	▪ Insensitive to FFA and water content in the oil ▪ Preferred-method if low-grade oil is used ▪ Esterification and transesterification occur simultaneously ▪ Easy separation of catalyst from product ▪ High possibility to reuse and regenerate the catalyst ▪ Recyclable	▪ Low reaction rates ▪ Unfavorable side reaction ▪ Higher cost ▪ High reaction conditions and longer reaction times ▪ More energy requirement ▪ Leaching of catalyst active sites may result to product contamination
Enzyme catalyst	▪ Prevents saponification ▪ Only simple purification step is required ▪ Environmental friendly and nonpolluting	▪ Very slow reaction rate ▪ High cost ▪ Sensitive to alcohol, typically methanol that can deactivate the enzyme ▪ Inactivation and denaturation of enzyme can lead to decreasing yield of biodiesel

(Talha and Sulaiman, 2016)

2.7 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.

2.7.1 Effects of moisture and free fatty acids

The water and Free Fatty Acid (FFA) contents are critical factors fortransesterification. 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).

2.7.2 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).

Akhihiero *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 (Dallatu, 2015).

2.7.3 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; Talha and sulaiman, 2016). 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 catalyzed 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 reasons 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% $NaOCH_3$ were almost the same after 60 min (Freedman *et al.*, 1984; Aransiola *et al.*, 2010). 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).

2.7.4 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; Abatyough, 2016).

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.

2.7.5 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; Adewuyi *et al.*, 2011).

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).

2.7.6 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 (Dallatu, 2015). 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.

2.7.7 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 (Kansedo, 2009; Jagadale and Jugulkar, 2012).

In transeterification 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; Ajala *et al*., 2017).

2.8 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 (Lin, 2014). 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 (EPAct) of 1992 (Dallatu, 2015). 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 (Dallatu, 2015). 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 CO_2 accumulated in the atmosphere by 78% due to CO_2 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.D.E, 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).

2.9 Biodiesel Quality

The use of low-quality biodiesel due to incomplete reaction or contaminants in a diesel engine could result in several engine problems (Ma and Hanna 1999; Portillo *et al*., 2015). In order to protect consumers from unknowingly purchasing substandard fuel, several fuel standards have been adopted for quality control. Among these standards, the American Society for Testing and Materials (ASTM D6751) and European Committee for Standardization (EN 14214) are the most referred standards for pure biodiesel and are presented in Table 2.3 In addition, American Oil Chemists' Society (AOCS) has established official test methods for biodiesel quality and these methods are also listed in Table 2.3. It is reported that FAAEs can be added at a low ratio to petroleum diesel fuel without substantially changing fuel properties (Reaney *et al.,* 2005). The low-temperature flow properties of the blended fuel with lower than 30% FAAEs is not significantly changed from its parent petroleum diesel fuel. When FAAEs that meets standard specifications is properly blended into petroleum diesel fuel and is handled according to standard techniques, the resulting fuel is of high quality and should perform well in a diesel engine. In the United States, ASTM D7467 is adopted for quality control of blended fuel containing 6–20% FAAEs and is shown in Table 2.4 [ASTM 2008b). It is imperative that FAAEs must meet standards for pure biodiesel prior to blending. Blends up to 5% are allowed in ASTM D957 for diesel fuel and ASTM D396 for heating oil provided that FAAEs meets standards for pure biodiesel.

Table 2.3: U.S. and European specifications for biodiesel (B100)

Property	Biodiesel blend stock (B100)			
	U. S. (ASTM D6751-08)		Europe (EN 14214)	
	Limits	Method	Limits	Method
Water and sediment (vol.%, max)	0.05	D2709	0.05	EN 12937G
Total contamination (mg/kg, max.)			24	EN 12662
Kinematic viscosity @ 40 0C (mm^2/S)	1.9–6.0	D445	3.5-5.0	EN 3104/3105
Flash point, closed cup (^{0}C, min)	93	D 93	101	EN 3679
Methanol (wt% max.)	0.20[a]	EN 14110	0.20	EN 14110
Cetane no (min)	47	D 613	51	EN 5165
Cloud point (^{0}C)	Report[d]	D 2500	Country Specific[d]	
Sulphated ash (wt.%, max.)	p.020	D 874	0.020	EN 3987
Total ash (wt.%. max.)				
Gp I metals Na + K (mg/kg, max.)	5.0	EN 14538	5.0	EN
Gp II Metals Ca + Mg (mg/kg, max.)	5.0	EN 14538	5.0	14108/14109
Total Sulfur (ppm, max.)	15[b]	D 5453	10	EN 14538
Phosphorous (ppm, max.)	10	D 4951	4	EN 2846
Acid no. (mg KOH/g, max.)	0.50	D 664	0.50	EN 14107
Carbon residue (wt.%, max.)	0.50	D 4530	0.30[c]	EN 14104
Free glycerine (wt.%, max.)	0.02	D 6584	0.02	EN 10370
Total glycerine (wt.%, max.)	0.24	D 6584	0.25	EN
Mono glycerine (wt.%, max.)			0.80	14105/14106
Diglyceride (wt.%, max.)			0.20	EN 14105
Triglyceride (wt.%, max.)			0.20	EN 14105
Distillation (T_{90}^{0}C, max.)	36[c]	D 1160		EN 14105
Copper strip corrosion (3-h at 50^{0}C, max.)	No.3	D 130	No. 1	EN 14105
Oxidation Stability (h @ 110^{0}C, min)	3.0	EN 14112	6.0	
Linolenic acid methyl ester (wt.%, max.)			12.0	EN 2160
Polyunsaturated acid methyl esters (wt.%, max.)			1.0	EN 14112
Ester Content (wt.%, min)			96.5	EN 14103
Iodine Value (g 12/100g, max)			120	PrEN 15799
Density (kg/m3			860-900	EN 14103
Lubricity @ 600C, WSD, microns (max.)				EN 14111
Cold Soak Filterability (seconds, max.)	360[f]	D 7501		EN 3675

a. Alternative, flash point must be >130^{0}C.
b. For blending with ULSD. For other fuels, higher sulphur levels are allowed
c. Atmospheric equivalent T-90 point.
d. Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser.
e. This limit is based on the bottom 10% fraction of the fuel, not the either fuel.

Table 2.4:Fuel standard ASTM D7467 for B6 to B20 Blended biodiesel-petroleum diesel fuel.

Property	ASTM Method	ASTM Limits
Acid value	ASTM D664	0.3 max (mg KOH/g)
Water and sediment	ASTM D2709	0.05 max (vol%)
Ash content	ASTM D482	0.01 max (% mass)
Sulphur		
S15 grade	ASTM D5453	15 max (µg/g)
S500 grade	ASTM D2622	0.05 max (% mass)
Copper corrosion 3h 50 ^{0}C	ASTM D130	No. 3 max
Cetane number	ASTM D613	40.0 min
One of the following must be met		
(1) Cetane index	ASTM D976	40.0 min
(2) Aromaticity	ASTM D1319	35.0 max (vol%)
Cloud point		
	ASTM D2500	-
	ASTM D4539	
	ASTM D6371	
Electrical conductivity	ASTM D2624	-
Carbon residue, 10% bottoms	ASTM D524	0.35 max (% mass)
Oxidation stability	-	6.0 min (h)
Flash point	ASTM D93	52 min (^{0}C)
Kinematic viscosity, 40 ^{0}C	ASTM D445	1.9-41 (mm^2/S
Distillation temperature	ASTM D86	343 max (^{0}C)
Lubricity, HFRR 60 ^{0}C	ASTM D6079	520.0 mas (µ m)
Biodiesel content	ASTM D7371	6–20 (vol%)

2.10 Fuel Properties of Biodiesel

The following properties for biodiesel affect the performance of diesel engine, hence it is important to control the quality of biodiesel to meet the ASTM and EN standards shown in Table 2.4 and 2.5 before being used in a diesel engine.

2.10.1 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 (1998). 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, 1998). 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.

2.10.2 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^{o} 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) (Pramanik, 2002; Saed *et al.*, 2008). 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 *et al.*, 2007). The variation in densities and viscosities of methyl esters of some fatty acids has been studied and was observed to vary linearly with temperature (Liew *et al.*, 1992; Tate *et al.*, 2006).

2.10.3 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 (Raj and Sahayaraj, 2010; Dallatu, 2015). 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).

2.10.4 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 ASTMD-2500 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, 2003). 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 (Dallatu, 2015).

2.10.5 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, 2008a). All convectional diesel fuels have high flash points, 54^0C minimum and 71^oC typical. The flash point of neat biodiesel is typically greater than 93^{o}C and a flash point below 93°C is considered to be out of specification (ASTM, 2008a). The U.S. department of transportation considers a material with a flash point of 93°C and above to be nonhazardous. (Divya and Tyago, 2006). If the biodiesel has not flashed at 160°C, the test is finished and the result is reported as >160°C (ASTM, 2008a).

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.

2.10.6 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, 1997; Tutunea and Dumitru, 2017). 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.

2.10.7 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 grams 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.

2.10.8 Oxidation stability

The oxidation stability measures the ability of the oil to resist oxidation, this is important in the overall storage ability of the oil. Oxidative stability of biodiesel is determined through measurement of the oil stability index (OSI) by the Rancimat method (EN 14112). The Rancimat method indirectly measures oxidation by monitoring the gradual change in conductivity of a solution of water caused by volatile oxidative degradation products that have been transported via a stream of air (10 l/h) from the vessel (at 110°C) containing the biodiesel sample (Moser, 2009a). Stability can be improved with the addition of antioxidants. The EN and ASTM minimum standards at 110^0C are 6 hours and 3 hours respectively (Biodiesel standard, 2013). The standard methods for oxidation stability is EN 14112 (Moser, 2009a; Barabas and Todoruţ, 2011).

2.10.9 Heat of combustion

Heat of Combustion is the amount of heat energy released by the combustion of a unit volume of fuel (Dallatu, 2015). 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, 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).

2.10.10 Lubricity

Lubricity is the fuel quality that prevents or minimizes wear in diesel injection equipment (Zhiyou *et al.,*2006). According to Moser (2009b) Lubricity is determined at 60°C in accordance to ASTM D6079 using a high-frequency reciprocating rig instrument. During the course of the experiment, a ball and disk are submerged in a liquid sample and rubbed at 60°C against each other for 75 minutes at a rate of 50 Hz to generate a wear scar. At the conclusion of the experiment, the maximum length of the wear scar is determined, and this value represents the lubricity of the sample. Shorter wear scar values indicate that the sample has superior lubricity compared to another sample that resulted in a longer wear scar. Lubricity is not prescribed in ASTM D6751 or EN 14214. However, the petro-diesel standards, ASTM D975 and EN 590,contain maximum allowable wear scar limits of 520 and 460 μm, respectively. Biodiesel possesses inherently good lubricity, especially when compared to petro-diesel this gives it an advantage over fossil diesel. The maximum standard for lubricity at 60^0C is 520 μm with test method ASTM D6079 (Moser, 2009b).

2.10.11 Water content

Water is a constant problem both for producers and users. Excess water promotes bacterial growth and encourages the reversal of biodiesel into free fatty acids (Barabas and Todoruţ, 2011). The moisture accumulated in biodiesel leads to the increase of free fatty acid concentration, which can corrode metal parts of the engine's fuel system. Biodiesel is much more hygroscopic (it attracts water) than diesel oil (Barabas and Todorut, 2011). The biodiesel absorbs water during storage when the temperature is higher and the water absorbed is precipitated at lower temperatures. Following these repeated processes, the accumulated water is deposited on the bottom of the tank. The EN and ASTM maximum standards are 500 mg/kg (Burton, 2008; Barabas and Todoruţ, 2011). The standard test methods for water content are EN ISO 12937 and ASTM D2708/P40 (Barabas and Todorut, 2011).

2.10.12 Total contamination

This measures the insoluble material; if the values are high the solids will cause filter and injector blockages. The EN maximum standard is 24 mg/kg (Moser, 2009a; Barabas and Todoruţ, 2011). The European Union test method for total contaminant is EN 12662 (Barabas andTodoruţ, 2011).

2.10.13 Glycerides

These must be kept low as they are a measure of low conversion yield high value can lead to deposits on valves and injectors. The EN maximum standard for diglycerides and triglycerides is 0.2% by mass (Biodiesel standard, 2013). The standard test method for glycerides is EN 14105 (Moser, 2009a; Barabas and Todoruţ, 2011).

2.11 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, 2009a; 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 Sample Collection

Fully matured almond fruits (*Terminalia catappa)* were collected from the department of Microbiology and faculty of Agricultural science within the premises of Ahmadu Bello University main Campus, Zaria, Kaduna State, Nigeria. The edible portion (flesh) was manually removed, leaving the stony shell containing the seed. The stony shell was carefully cracked to remove the groundnut-like seed. 5 kg of almond seeds were gathered and sun-dried for two weeks before being milled using a domestic blender. The resulting powder was preserved in airtight sample bottles under cool condition in preparation for oil extraction (Giwa and Ogunbona, 2014). The seeds and fruits of almond (*Terminalia catappa)* are shown in Plate III

Plate III: Seed and fruits of *Terminalia catappa*

3.2 Reagents and Equipment

3.2.1 Reagents

All chemicals used are of analytical grade and are used without further purification.

Methanol

Sulphuric acid

Potassium hydroxide

Sodium hydroxide

Ethanol

Wijjis reagent

Hydrochloric acid

Calcium hydroxide

Aluminium oxide

Citric acid

3.2.2 Equipment

Gas Chromatography-Mass Spectrometry

Fourier Transform Infrared Spectrophotometer

Muffle Furnace

Electric Blender

Cetane Analyzer tool; KD R3034

Thermometer

Pensky-Mertens closed up tester

Kinematic Viscosity recognizer tool; KD R0515

Stanhope-Seta

3.3 Oil Extraction

3 kilogram of the powdered seed was used for oil extraction. The oil was extracted by a mechanical pressing machine at the National Research Institute for Chemical Technology Zaria. The expelled oil was filtered using a cloth sieve into a beaker. The pulp was then dissolved in cyclohexane to extract the remaining oil. The pulp was filtered out from the solution. The remaining oil and cyclohexane are separated by means of distillation.

The percentage oil yield was then calculated as in equation 3.1

$$\%\,Oil\,Yield = \frac{weight\ of\ oil\ \ (g)}{weight\ of\ ground\ seed\ (g)}\ x\ 100 \tag{3.1}$$

3.4 Degumming of oil

The procedure of Zufarov *et al.,* (2008) was modified. 1000g of the oil was preheated to 80 ^{o}C, water solution of citric acid (5%) was then added in amount of 10% (by volume of oil). The mixture was stirred for 20 minutes. The oil/acid mixture was transferred to a holding vessel to settle for 60 minutes after which the degummed oil was separated from its by-products. The same procedure was repeated for the degummed oil.

3. 5 Determination of physicochemical properties

3.5.1 Preparation of reagents.

Potassium hydroxide (0.1 M) solution: Potassium hydroxide (56g), was dissolved in 20cm^3 distilled water in a 250cm^3 beaker and transferred to a 1000 cm^3 volumetric flask and made to mark with distilled water, to give a concentration of 1.0 M. Working solution of 0.1 M was prepared by diluting 100 cm^3 of stock solution with distilled water to 1000 cm^3 mark in a volumetric flask.

Alcoholic KOH (0.5 M) solution: KOH (7.00 g) pellet was dissolved in 20 cm^3 ethanol and the solution transferred into a volumetric flask (250 cm^3) and made up to the mark with ethanol.

Hydrochloric acid (0.5 M) solution: From concentrated hydrochloric acid, 42cm^3 was accurately measured and dissolved in a 1000cm^3 volumetric flask and made up to the mark with distilled water.

Potassium iodide KI (10% w/v) solution: Potassium iodide, (10g) was dissolved in 20 cm^3 distilled water in a beaker and was transferred to a volumetric flask and made to 100 cm^3 mark with distilled water to make 10 % solution.

Sodium thiosulphate $Na_2S_2O_3$ (0.1M) solution: Sodium thiosulphate, (24.82 g) was dissolved in 20 cm^3 distilled water in a beaker and transferred to a volumetric flask and made to 1000 cm^3 with distilled water making 0.1 M solution.

Starch indicator (1% w/v): Starch powder (1 g) was dissolved in warm distilled water in a beaker and the clear fraction was transferred into 100cm^3 volumetric flask and made up to the mark with distilled water.

Phenolphthalein indicator: Phenolphthalein (0.25 g) was dissolved in a 250 cm^3 volumetric flask and made up to the mark with ethanol.

Wijs' reagent: Wijs' solution was prepared by dissolving 8 g iodine trichloride in 200cm^3 glacial acetic acid. Iodine (9 g) was also dissolved in 300 cm^3 carbon tetrachloride and the two solutions mixed and diluted to 1000cm^3 with glacial acetic acid. The Wijs' reagent was stored in a glass-stoppered amber bottle.

Preparation of CaO/Al_2O_3: Hydrated lime (15 g) was dissolve in 500 cm^3 beaker with distilled water. After thorough mixing, 85 g of Alumina was added and stirred. The mixture was dried over a magnetic stirrer. The dried mixture was loaded into crucible and was calcined in a muffle furnance at 700 ^{o}C for 90 minutes. The calcined catalyst was grounded into powder.

3.5.2 Acid Value

Acid value was determined according to ASTM method (ASTM D974). 0.5g of the Oil sample (Crude and Degummed), was weighed into 250 cm^3 conical flask and 50 cm^3 of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was allowed to cool and titrated against 0.1M KOH using phenolphthalein as indicator until a pink coloration persisted for at least 15 seconds. The volume of KOH solution used was recorded and the acid value and free fatty acid were determined as shown in equation 3.2

$$Acid\ value = \frac{A\ x\ M\ x\ 56.1}{W} \tag{3.2}$$

Where;

A = volume of KOH solution used (in cm^3)

M = Molarity of KOH

W = weight in grams of the oil sample

56.1= Relative molar mass of KOH

The Free fatty acid (%FFA) was determined as:

% Free fatty acid (FFA) = Acid value x 0.503

3.5.3 Saponification Value

Saponification value analysis was carried out in accordance to ASTM D5558. The oil sample (2.0 g) was weighed accurately into a 250 cm^3 conical flask containing 25 cm^3 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. Two drops of phenolphthalein were added to the mixture and was titrated against 0.5M HCl. A blank test was performed by titrating 25 ml of 0.5M alcoholic KOH solution without oil sample and also not heated under reflux against 0.5M HCl with two drops of phenolphthalein indicator. The Saponification value (SV) was then calculated using the expression in equation 3.3

$$Saponofication\ value = \frac{56.1\ x\ (B - S) x\ C}{M} \tag{3.3}$$

where;

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

S =Volume (cm^3) of the 0.5M HCl solution used oil sample

C=Molar concentration of HCl solution used

M = Mass in g of oil used and

56.1 = Relative molar mass of KOH

3.5.4 Iodine Value (AOCS Cd 1-25, 1998)

The oil sample (0.5 g) was weighed into conical flask and 20 cm^3 of carbon tetrachloride was added to dissolve the oil. 25 cm^3 of Wijj"s Reagent was added in a fume chamber. The flask was plugged with stopper, and left for 35 minutes in a dark room at room temperature. At the end of this period, 20 cm^3 of 10% aqueous potassium iodide and 100 cm^3 of water were added. The content was titrated with 0.1M sodium thiosulphate solution. Few drops of 1% starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorously shaking. The same procedure was used for the blank titration without the oil or biodiesel sample. The Iodine Value (I.V) is given by the expression in equation 3.4.

$$Iodine\ value = \frac{12.96C\ (V1 - V2)}{M} \tag{3.4}$$

where;

C = Concentration of Sodium thiosulphate used

V1 = Volume of Sodium thiosulphate used for blank

V2 = Volume of Sodium thiosulphate used for sample

M = Mass of sample (g)

12.69= Constant

3.5.5 Water and Sediment

The sample 30g was placed in a test tube and its content was stoppered and allowed to attain the laboratory temperature. The tube was placed in a trunnion cup opposite another filled tube to establish a balanced condition of the mechanical shaker. The samples were whirled for agitation at a speed of 1800 rpm for 10 minutes to ensure homogeneity. The combined water and sediment at the bottom of the tube was then reported as percentage of sample (ASTM D2709 – 96) as shown in equation 3.5

$$Water\ and\ sediment = \frac{(W1 - W2)}{W1}\ x\ 100 \tag{3.5}$$

3.5.6 Density

A 25 cm^3 density bottle with a FA2004N digital precision electronic analytical weighing balance was used for density determination at 15 °C according to the method ASTM D4052. The density bottle was first weighed empty, then with water in it and finally with the biodiesel sample. the density was then calculated as in equation 3.6

$$Density = \frac{W3 - W1}{W2 - W1}\ x\ density\ of\ water \tag{3.6}$$

where;

w_3 = weight of bottle with biodiesel sample

w_2= weight of bottle with water

w_1= weight of empty density bottle

3.5.7 Kinematic Viscosity

The viscosity was determined using kinematic viscosity recognizer item tool: KD R0515. A sample holder carried the sample and a calibrated thermometer was held in upright position and inserted into the bath by a holder. at set temperature of 40 ^{0}C, The biodiesel was then allowed to freely flow and the time required for the meniscus to pass from the first to the second timing marks was noted. The viscosity reading was taken and compared to ASTM standards.

3.5.8 Ash Content

For the determination of ash content furnace was used at a temperature of 500^{o}C. 15 g of oil was added in a burning cup and placed in a furnace. The furnace was heated to a temperature of 500 ^{o}C for 1 hour and after burning the residue sample was weighted and ash content was calculated. The experiment was done in triplicate. The ash content was calculated using equation 3.7.

$$Ash\ content = \frac{Final\ mass\ of\ oil\ after\ burning}{Initial\ mass\ of\ sample}\ x\ 100 \tag{3.7}$$

3.6 Determination of Fatty Acid Composition

The gas chromatographic analysis of Degummed and crude *Terminalia catappa* seed oil and the biodiesel was made using GCMS-QP2010 PLUS SHIMADZU, JAPAN. 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 100ºC for 20 min, and then increased to 180ºC at the rate of 10ºC/min, for 10 min and then increased to 290ºC. The inlet temperature was set at 300ºC. 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 5.0cm^3 of n-hexane. The methylated sample was diluted in hexane and 1µl of this solution was injected into the column at a temperature of 230ºC, and a detector temperature of 240 ºC, 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).

3.7 Esterification of Oil

The %FFA was too high for transesterification; hence acid esterification was employed to reduce the free fatty acid value to less than 1.0%. The oil (100g) in a 250 cm^3 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 cm^3 conical flask containing the oil followed by the addition of methanol (20.0g) and stirred (800 rpm) for 1 hour at 60^oC 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 3.4.2, in order to ensure it was less than 1.0% before base transesterification of the oil.

3.8 Transesterification of Oil

The method of laboratory scale biodiesel production employed by Maher *et al.,* (2006) was adopted. Exactly 20g of methanol was poured into a plastic container. 1g of the catalyst (NaOH) was carefully added to the plastic container and secured tightly. The container was placed on a shaker for about 5 minutes until the NaOH completely dissolved in the methanol, forming sodium methoxide. 100 g of *Terminaliacatappa* seed oil pre heated to 60^oC was poured into an electric blender. 80% of the prepared sodium methoxide from the plastic container was carefully poured into the blender. The blender was secured tightly, switch on at full agitation speed and the agitation was maintain for 15 minutes. The resulting product was poured into a separating funnel mounted on a clamp stand and was allowed to settle down. The biodiesel was separated from the glycerine and poured into the electric blender and the remaining 20% of sodium methoxide was added, the blender was switched on at full agitation for 15 minutes. The resulting product was poured into a separating funnel and allowed to stand. The glycerine was tap off, leaving the biodiesel in the separating funnel. The biodiesel was washed with warm distilled water to remove traces of catalyst and glycerol in the methyl ester. The same procedure was repeated for KOH and CaO/Al_2O_3 catalyst.

The percentage yield of biodiesel (fatty acid methyl ester) was calculated as in equation 3.8

$$\%\,Biodiesel\;yield = \frac{weight\;of\;biodiesel}{weight\;of\;oil\,used}\;x\;100 \qquad (3.8)$$

3.9 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 *Terminalia catappa* oil methyl ester and fossil diesel were prepared as B10 (10%vol. TCME + 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 to obtain blends of B10, B20, B30, up to B90.The blends were centrifuged for homogeneity before proceeding with fuel analysis using ASTM standards.

3.10 Determination of Physicochemical Properties of Biodiesel and Blends

3.10.1 Flash point determination (ASTM D93)

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 biodiesel.

3.10.2 Cloud point analysis (ASTM D2500)

The sample was filtered and about $50cm^3$ 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 set of 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.

3.10.3 Pour point

The sample tube was filled to the mark with the prepared biodiesel fuel, corked with thermometer. The tubes were inserted into STANHOPE-SETA Cloud and Pour point tester. The sample was checked from time to time until it could no longer flow, the temperature was read and recorded as pour point. This test was carried out in the Quality control department of Kaduna Refinery and Petrochemical Company, Kaduna.

3.10.4 Calorific value determination (ASTMD2015)

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.

3.10.5 Cetane number

The cetane number was determined using automatic cetane analyzer tool; KD R3034, the prepared biodiesel sample (50 cm^3) was placed in the inner sample holder and inserted into the outer sample holder, at room temperature the machine gives the cetane reading of the sample.

CHAPTER FOUR

4.0 RESULTS

4.1 Extraction and Physicochemical Properties of *Terminalia Catappa* seed oil

The result of the extraction of *T. catappa* seed oil revealed an oil yield of 56.30±1.60%, the high yield suggest an economical viability of the seed. The values obtain for characterization of the crude and Degummed*Terminalia Catappa* seed oil are presented in Table 4.1. The following paramaters: Acid value, Density, Free Fatty Acid (FFA), Viscosity, Moisture Content, Iodine Value, Saponification Value and Ash Content were determined and presented in table 4.1.

4.2 Fatty Acid Profile of *T.Catappa* Seed Oil

The fatty acid composition of the oil as analyzed by GC-MS (appendix I and II) and identified using NIST05 Library search is given in Table 4.2. The fatty Acids are Myristic, Palmitic, Palmetoleic, Stearic, Oleic, Linoleic, and Arachidic. The level of saturation and unsaturation of the oil was found to be 45.35% and 54.65% respectively for the crude oil and 49.15 and 50.85 respectively for the degummed oil.

4.3 FTIR Analysis of Crude and Degummed*Terminalia Catappa* Seed oil

Figure 4.1-4.2 are the FTIR spectra of crude and Degum *Terminalia Catappa* seed oil. The assignments of functional groups in the FTIR of the seed oil are shown in Table 4.3. The peaks observed include – CH stretch at 3008 cm^{-1}, stretching vibration band of $–CH_2$ at 2852 – 2922 cm^{-1}.The double bond of ester carbonyl functional group at 1743 cm^{-1}, -CH bending vibration at 1461cm^{-1}, CH_3 and CH bending vibration at 1370-1390 cm^{-1}, the symmetric and Asymmetric stretching of C-CO-O at 1200-1270 cm^{-1}, C-O stretching vibration of ester group at 1159 cm^{-1}, $-CH_2$ wagging in RCOCO- at 964 cm^{-1} and –

CH_2rocking at 723 cm^{-1}, were observed in both oil. At 913 cm^{-1}, a peak is observed in crude oil and absence in the degummed oil.

Table 4.1: Physicochemical properties of crude and degummed*Terminalia Catappa*Seed oil

Properties	**Crude oil**	**Degummed oil**
Density gcm^{-3}	0.881	0.881
Acid value mgKOH/g	7.57	3.82
FFA %	3.79	1.91
Viscosity at 40^0C mm^2/s	46	46
Water and sediment % w/w	2.48	2.40
Iodine value $gI_2/100g$ of oil	82.42	78.80
Saponification value mgKOH/g	195.37	192.57
Ash content% w/w	0.86	0.65

Table 4.2: Fatty acid profile of *Terminalia Catappa* seed oil

	wt% of seed oil	
Fatty acids	**Crude**	**Degummed**
Mynstic (14:0)	1.62	1.32
Palmitic (16:0)	33.65	37.50
Palmitoleic (16:1)	0.66	0.74
Stearic (18:0)	7.26	8.23
Oleic (18:1)	40.16	40.16
Linoleic (18;2)	13.83	9.95
Arachidic (20:0)	2.82	2.10
Saturated	45.35	49.15
Mono – unsaturated	40.82	40.92
Poly – unsaturated	13.83	9.95
Total unsaturated	54.65	50.85

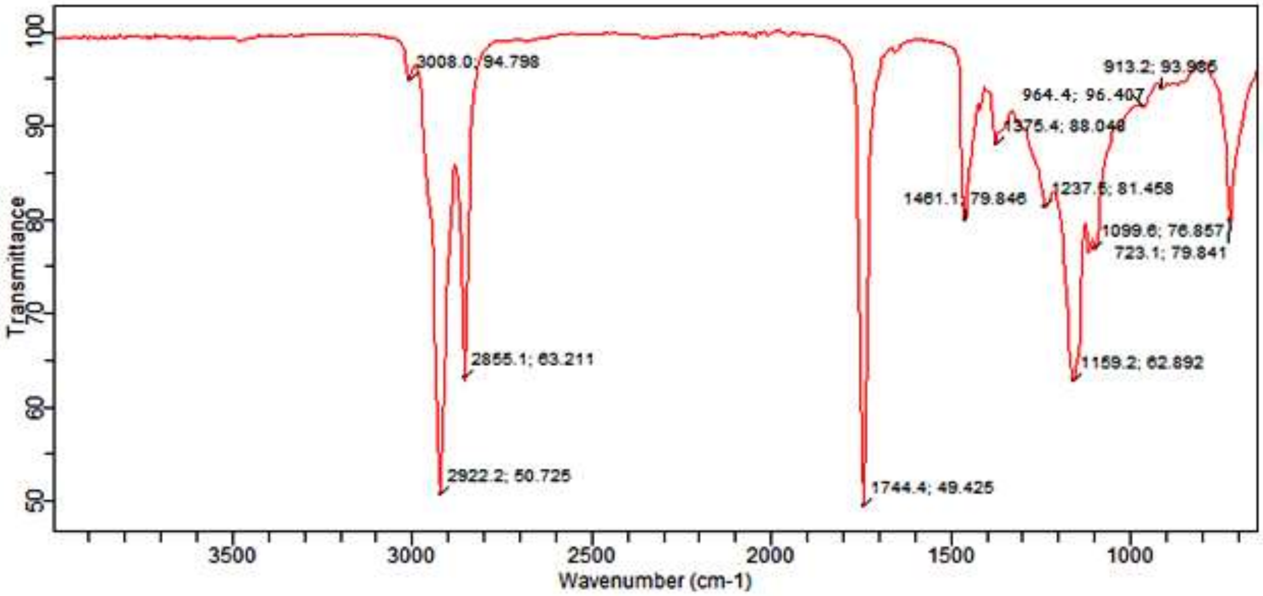


Figure 4.1: FTIR Spectra of Crude *Terminalia Catappa* seed oil

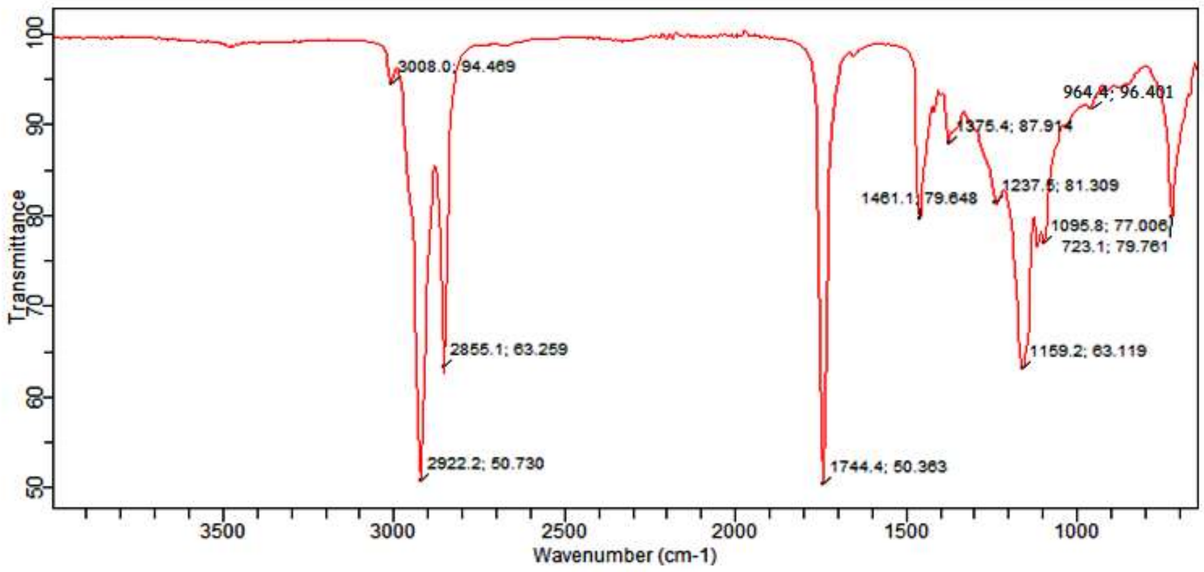


Figure 4.2: FTIR Spectra of Degummed *Terminalia Catappa* Seed Oil

Table 4.3: Assignment of FTIR peaks (cm^{-1}) of Crude and Degum *Terminalia Catappa*seed oil

CRUDE	DEGUM	ASSIGNMENT
3008.00	3008.00	- CH stretch
2922.20	2922.20	Symmetric and asymmetric stretching vibration of the aliphatic –CH_2 and CH_3 group
2855.10	2855.10	-CH_2
1744.40	1744.40	C = 0, Ester carbonyl functional group of triglycerides
1461.10	1461.10	C-H bend
1375.40	1375.40	CH_3 bending
1237.50	1237.50	=C-O-C stretch
1159.20	1159.20	O=C-O-C stretching vibration of Ester group
1099.6	1095.80	C-O-C stretching of Ester group
913	-	P-O-C stretch
964.41	964.41	CH_2 wagging in $RCOCO^-$
723.10	723.10	-CH_2 rocking vibrations

4.4 Effect of Different Catalyst on the Yield of Biodiesel

Figure 4.3 – 4.4 show the effect of different catalyst on the yield of *Terminalia Catappa* methylesters (Biodiesel) in base catalysed – transesterification.. With NaOH catalyst a yield of 86.64% and 92.68% *Terminalia Catappa* methylester were obtain from crude and degum *Terminalia Catappa* seed oil respectively. The degum *Terminalia Catappa* seed oil transesterified with KOH and CaO/Al_2O_3 produce a yield of 95.50% and 97.20% *Terminalia Catappa* methylester respectively.

4.5 FTIR Analysis of *Terminalia Catappa* Methylester

FTIR spectra of *Terminaliacatappa* methylester and fossil diesel are shown in fig. 4.5 – 4.7. A summary of the FTIR spectra are compared with that of *Terminalia Catappa* seed oil in Table 4.4. *Terminalia Catappa* methylester shows C-O stretching of $–O-CH_2-C$ at 1017 cm^{-1} and $O-CH_3$ of methylester group at 1438 cm^{-1}, while $–CH_2$ rocking at 723 cm^{-1}, -C=O stretch of Ester at 1159 – 1170cm^{-1}, $-CH_3$ bending at 1375-1379 cm^{-1}, and $–CH_2$ vibration at 2922 cm^{-1} were observed in the seed oil, T. catappa methylester and fossil diesel. The CH_2 wagging vibration of RCOCO- appears only in the seed oil.

4.6 Fatty acid Profile of *Terminalia Catappa* methylester

The fatty acid composition of the Biodiesel as analyzed by GC-MS (Appendix III) and identified using NIST05 library search is given in Table 4.5. The fatty acids are myristic acid methylester 1.17%, palmitic acid methylester 37.73%, palmitoleic acid methylester 0.85%, stearic acid methylester 8.26%, oleic acid methylester 39.89%, linoleic acid methylester 9.98% and Arachidic methylester 2.12%. The saturation and unsaturation level of the methylester was found to be 49.28% and 50.72% respectively

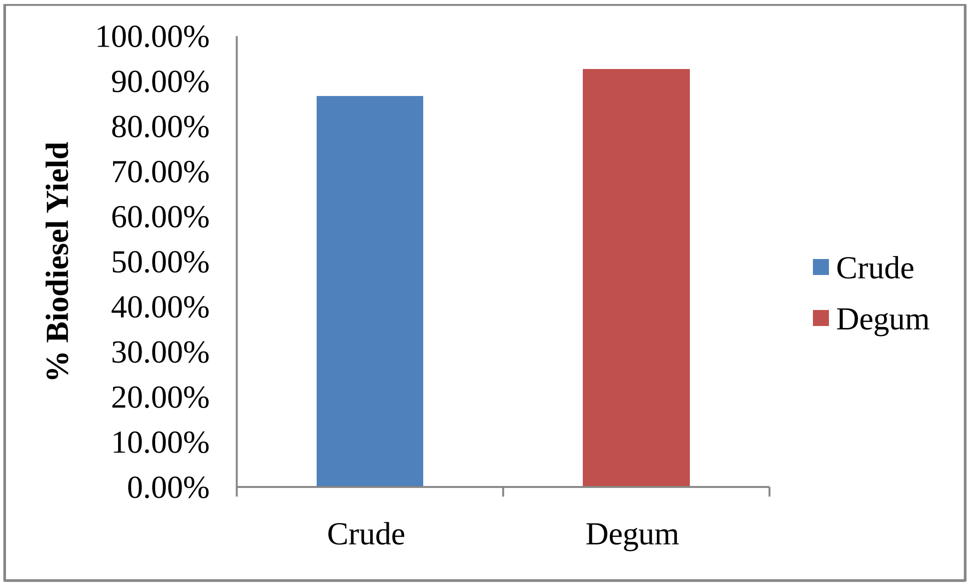


Figure 4.3 Effect of NaOH catalyst on Ester yield of *Terminalia Catappa* crude and degummed seed oil (reaction conditions: methanol: oil = 6:1, catalyst concentration = 1% w/w)

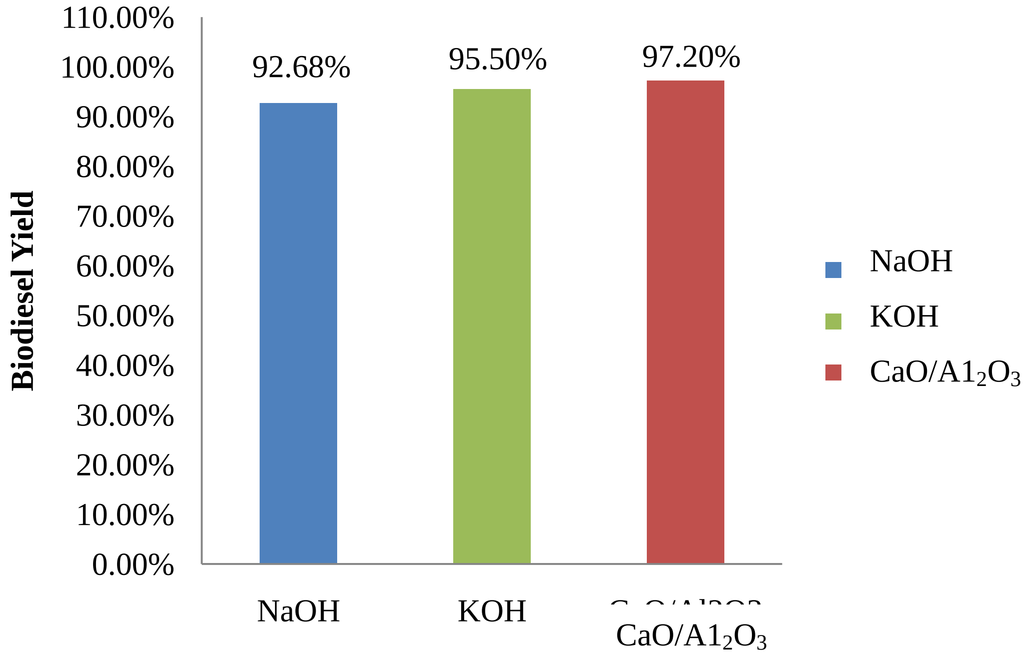


Figure 4.4 Effect of different catalyst on Ester yield of degummed termination catappa seed oil (reaction conditions; methanol:oil = 6:1, catalyst concentration = 1% w/w)

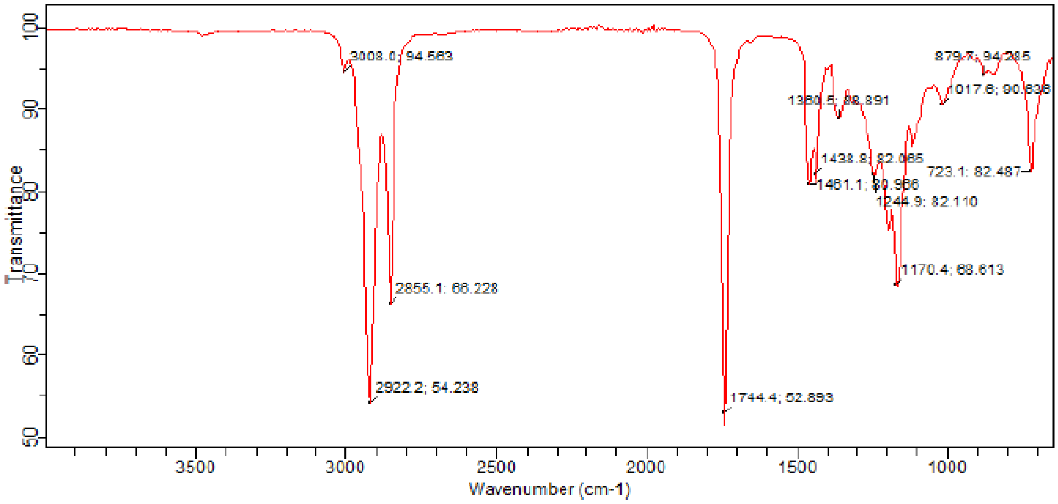


Figure 4.5: FTIR Spectra of CaO/Al_2O_3 catalyzed degummed*Terminalia Catappa* Methylesther

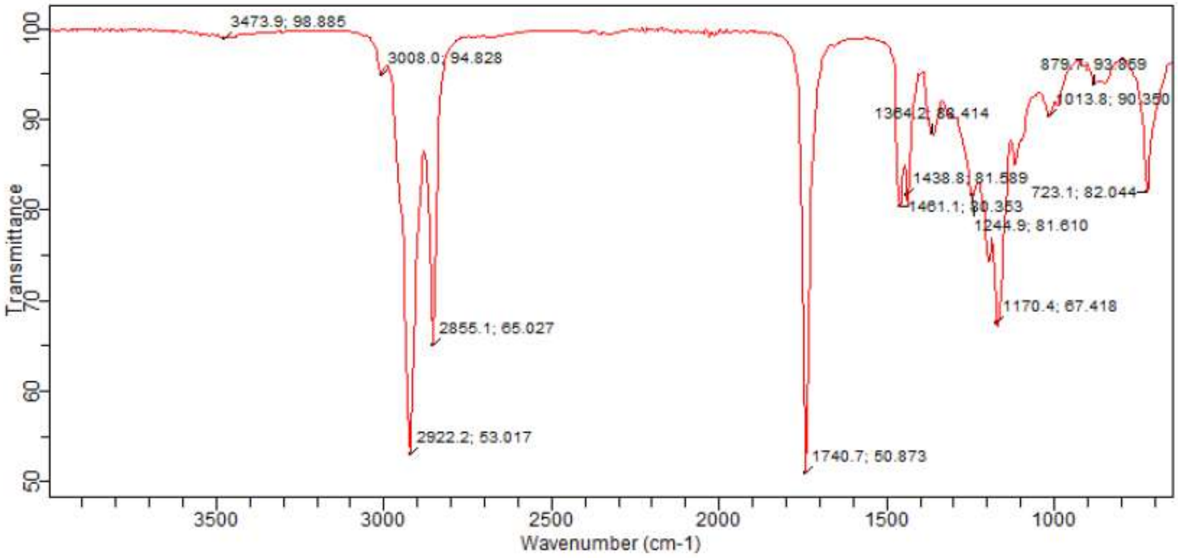


Figure 4.6: FTIR Spectra of KOH catalyzed Degummed *Terminalia Catappa*Methylesther

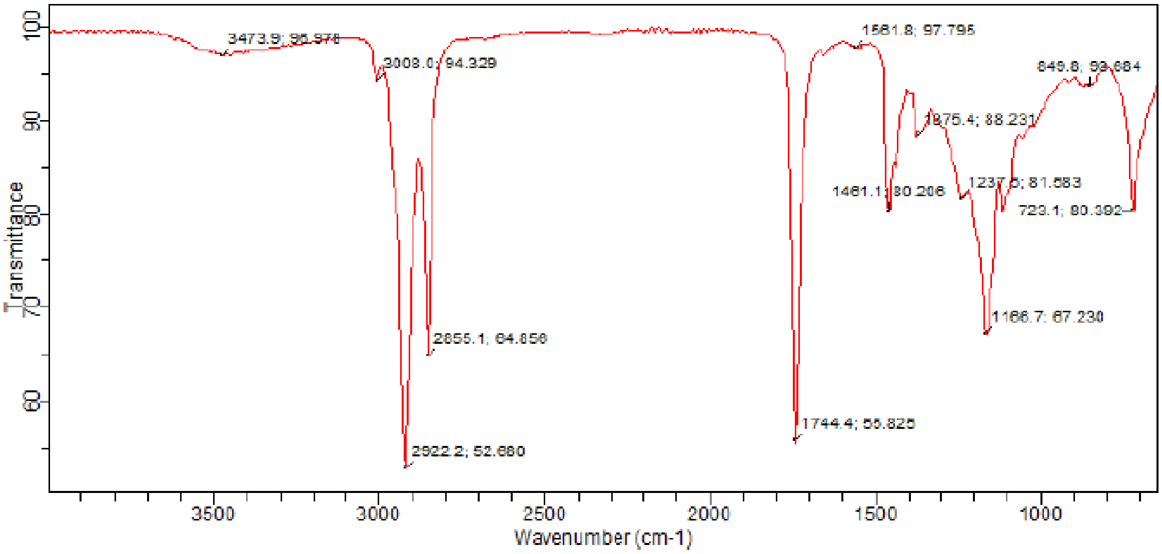


Figure 4.7: FTIR Spectra of NaOH catalyzed Crude *Terminalia Catappa*Methylesther

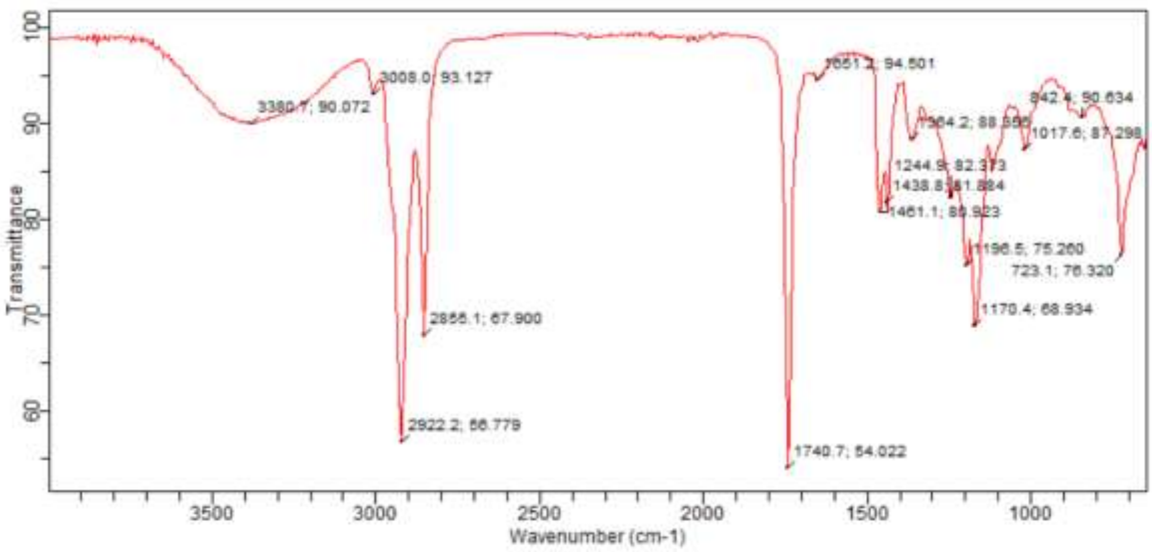


Figure 4.8: FTIR Spectra of NaOH catalyzed Degummed *Terminalia Catappa*Methylesther

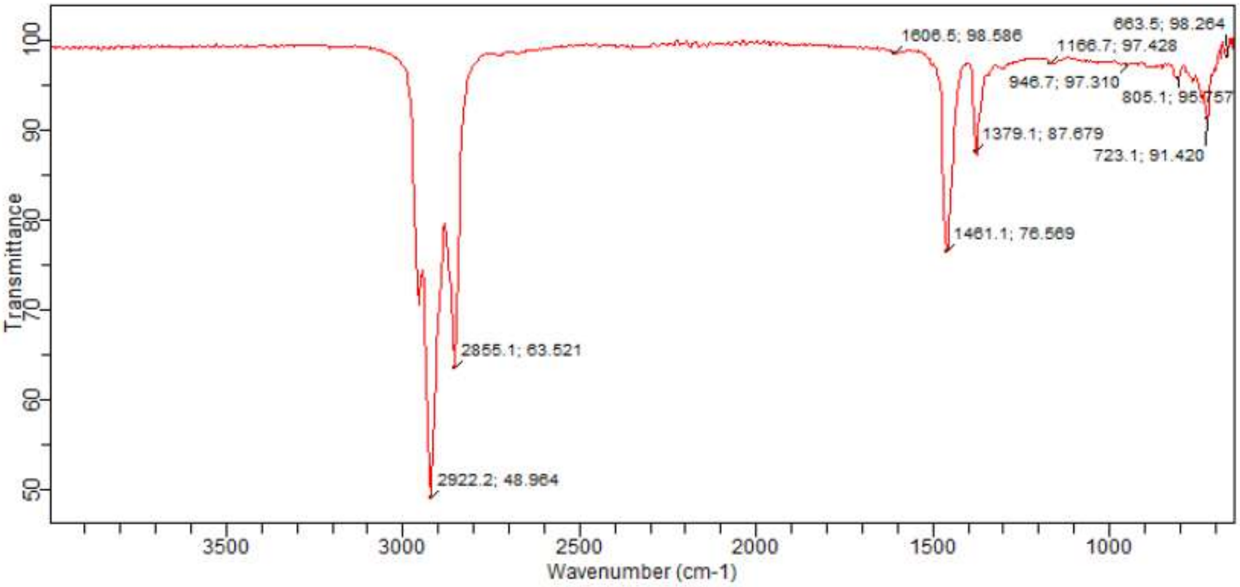


Figure 4.9: FTIR Spectra of fossil diesel

Table 4.4: A summary of the FTIR spectra peaks (cm^{-1}) of *Terminalia Catappa* Seed, *Terminalia Catappa* methylester and fossil diesel

CTC	**DTC**	**TCME**	**DIESEL**	**ASSIGNMENT**
3008	3008	3008	-	-CH stretch
2922.20	2922.20	2922.20	2922.20	-CH2 vibration
2855.10	2855.10	2855.10	2855.10	CH
1744.40	1744.40	1744.40	-	-C=O stretch of Ester
-	-	-	1606	-C=C stretching
1461.00	1461.10	1461.10	1461.10	C-H bend
-	-	1438.80	-	O-CH_3 of methylester group
1375.40	1375.40	1360.50	1379.10	-CH_3 bending
1237.50	1237.50	1244.90	-	=C-O-C stretch
1159.20	1159.20	1170.40	1166.70	-C=O stretch of Ester
-	-	1017.60	-	-C-O stretching of
-	-	-	-	-OCH_2-C
-	-	-	946.70	C-O Stretching
984.41	984.41	-	-	-CH_2 wagging in $RCOCO^-$
723.10	723.10	723.10	723.10	CH_2 Rocking
-	-	-	663.5	C-H bend

CTC = Crude *Terminalia Catappa*

DTC = Degum *Terminalia Catappa*

TCME = *Terminalia Catappa* methylester

Table 4.5: Fatty acid profile of *Terminalia Catappa* methyl ester

Fatty acid		**wt% of Biodiesel**
Myristic acid methyl ester	(14:0)	1.17
Palmitic acid methyl ester	(16:0)	37.73
Palmitoleic acid methyl ester	(16:1)	0.85
Stearic acid methyl ester	(18:0)	8.26
Oleic acid methyl ester	(18:1)	39.89
Linoleic acid methyl ester	(18:2)	9.98
Arachidic acid methyl ester	(20:0)	2.12
Saturated	-	49.28
Mono-unsaturated	-	40.74
Poly unsaturated	-	9.98
Total unsaturated		50.72

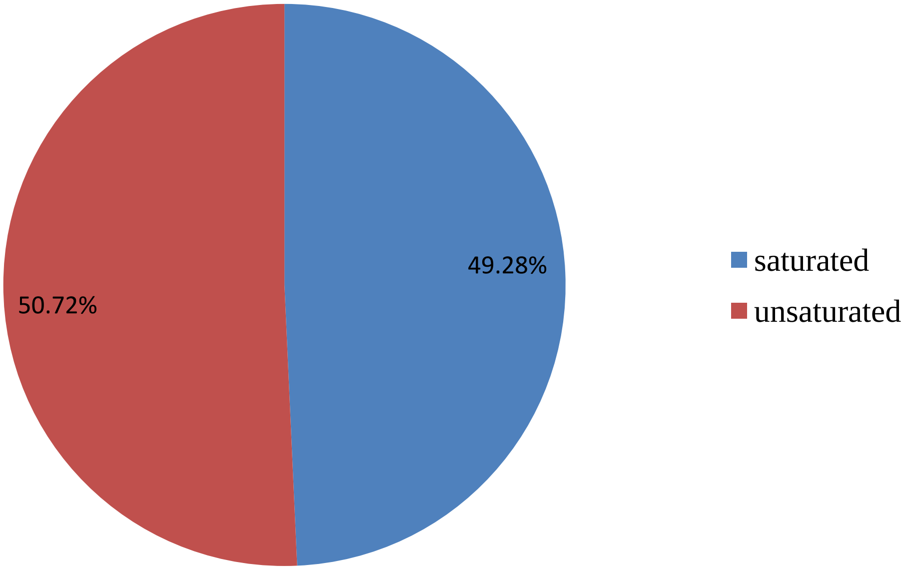


Figure 4.10: Composition of saturated and unsaturated fatty acids of *Terminalia Catappa* methylester

4.7 Physicochemical properties of *Terminalia Catappa* methylester in comparison with fossil diesel

Transesterification was carried out using NaOH, KOH and CaO/Al_2O_3 catalyst. The results of the physicochemical properties are presented in Table 4.6 – 4.7.

The flash point and cloud point of *Terminalia Catappa* methylester were higher than that of fossil diesel. The free fatty acid, acid number and density were less than 1 unit.

4.8 Effect of blending on Biodiesel properties

Fuel properties (Density, Viscosity, Flash point, Cloud point, Cetane number, Water and sediment, Ash content and heating value) of the blended*Terminalia Catappa* methylester with fossil diesel at different volumetric ratio are reported in Table 4.8.

The kinematic viscosity, density and flash point increased as the biodiesel fraction increased in the fuel mixture, while the calorific value decreased as the biodiesel fraction increased in the fuel mixture.

The effect of blending as Ash content shows a constant value of 0.10% by weight for B10-B40 and a gradual increase from B50-B90.

Table 4.6: Physicochemical properties of NaOH catalyzed crude and Degum *Terminalia Catappa* methylester

PROPERTIES	UNIT	CRUDE	DEGUM	ASTM STANDARD	EN STANDARD
Acid value	MgKOH/g	0.44±0.10	0.28±0.21	0.50 max	0.5max
Density	g/cm^3	0.869±0.012	0.863±0.010	-	0.86-0.90
Viscosity (40^{0}C)	Mm^2/s	3.71±0.82	4.60±0.50	1.9-6.0	3.5-5.0
Iodine value	gI$_2$/100g of oil	90.50±1.2	72.42±1.50	-	120 max
Saponification value	MgKOH/g	186.20±1.70	180.10±1.40	-	-
Pour point	^{o}C	3±0.00	2±0.00	-	-
Cloud point	^{o}C	10.0±0.00	8±0.00	-3 to 12	-
Oxidative stability	H	4.20	5.8	3 min	6min
Flash point	^{o}C	158±1.65	153±1.50	93min	120min
Cetane number		49.78±1.82	52.84±1.50	47min	51min
Ash content	% mass	0.018±0.002	0.014±0.001	0.02max	0.02max
Water and sediment	% Vol	0.06	0.04	0.05max	0.05max
Heat of combustion	Mj/kg	40.26±0.70	42.76±0.52	-	-
FFA	%	0.22	0.14	<1%	<1%
Yield of Biodiesel	%	86.64	92.68		

Table 4.7: Physicochemical properties of NaOH, KOH and CaO/Al_2O_3 catalyzed Degum *Terminalia Catappa* seed oil

PROPERTIES	UNIT	NaOH	KOH	CaO/Al_2O_3	ASTM Standard	EN Standard
Acid value	mgKOH/g	0.28±0.21	0.33±0.19	0.18±0.14	0.50max	0.50max
Density	g/cm^3	0.863±0.01	0.865±0.011	0.863±0.01	-	0.86-0.90
Viscosity (40^0C)	Mm^2/s	4.60±0.50	4.10±0.28	4.70±0.62	1.9-60	3.5-5.0
Iodine value	gI_2/100g of oil	72.42±1.50	72.56±0.90	70.42±1.20	-	120 max
Saponification value	mgKOH/g	185.10±1.40	187.26±1.80	178.66±0.60	-	-
Pour point	^oC	2±0.00	2±0.00	2±0.00	-	-
Cloud point	^oC	8±0.00	7±0.00	7±0.00	-3 to 12	-
Oxidative stability	H	5.8	6.2	6.4	3min	6min
Flash point	^oC	153±2.0	148±2.0	151±1.8	93min	120min
Cetane number		52.84±1.50	52.57±1.70	52.63±1.70	47min	51min
Ash content	% mass	0.014±0.001	0.014±0.002	0.015±0.002	0.02max	0.02max
Water and sediment	% Vol	0.04	0.05	0.04	0.05max	0.05max
Heat of combustion	Mj/kg	42.76±0.52	42.90±0.60	43.65±0.62	-	-
FFA	%	0.14	0.17	0.09	<1%	<1%
Yield of Biodiesel	%	92.68	95.50	97.20		

Table 4.8: Physicochemicalproperties of NaOH catalyzed Degum *Terminalia Catappa* Biodiesel – Diesel Blend

PROPERTIES	FOSSIL DIESEL	B10	B20	B30	B40	B50	B60	B70	B80	B90	100% BIODIESEL
Ash content % by max	0.01	0.01	0.01	0.01	0.01	0.011	0.011	0.012	0.012	0.013	0.014
Density g/cm^{-3}	0.846	0.848	0.848	0.850	0.851	0.851	0.853	0.853	0.855	0.858	0.863
Viscosity (40^{0}C) mm^2/s	3.65	3.66	3.72	3.74	3.77	3.80	3.87	3.90	4.20	4.40	4.60
Flash point ^{0}C	82	89	98	103	109	112	119	132	139	146	153
Cloud point ^{0}C	3	3	3	3	4	4	5	5	6	7	8
Cetane number	48.50	48.50	49.20	49.80	50.10	50.60	51.00	51.00	51.30	51.90	52.84
Heating value Mj/kg	43.90	43.72	43.20	42.93	42.67	42.36	42.05	41.92	41.80	41.59	41.76
Water and sediment % by vol.	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.03	0.04
Acid value mg KOH/g	-	0.1	0.1	0.14	0.15	0.2	0.2	0.22	0.24	0.26	0.28

Table 4.9: Physicochemical properties of NaOH catalyzed Degummed*Terminalia Catappa* Biodiesel – Diesel Blend of B10 and B20 in comparison with ASTM standard for B6 –B20 biodiesel-diesel blend

PROPERTIES	**B10**	**B20**	**ASTM STANDARD**	**METHOD**
Ash content % by max	0.010	0.010	0.01 max	D482
Acid value mgKOH/g	0.10	0.10	0.3 max	D664
Water and sediment % by vol.	0.02	0.02	0.05 max	D2709
Density g/cm^{-3}	0.848	0.848	-	D1298
Viscosity (40^{0}C) mm^{2}/s	3.65	3.66	1.9-4.1	D445
Flash point ^{0}C	89	98	52 min	D93
Cloud point ^{0}C	3	3	-	D2500
Cetane number	48.50	49.20	40min	D613
Calorific value	43.72	43.20	-	D5865
Oxidation stability (h)	8.2	8.2	6min	EN14112

CHAPTER FIVE

5.0 DISCUSSION

5.1 Oil Yield of *Terminalia Catappa* Seed

The oil content of *Terminalia Catappa* seed 56.30% obtained in this work is similar to the oil yield of T. catappa 55.05% reported by (Oderinde, 1998) and 53.20% reported by (Adewuyi *et al.,* 2011). The oil content of *T. catappa* obtained in this work is higher than that reported by (Giwa *et al.,* 2014) 51.45%, (Matos *et al.,*2009) 51.80%, (Dos Santos *et al.,*, 2008) 49% and lower than the value obtain by (Adekunle *et al.,*, 2016) 62.88%. However the oil yield is higher than other oil bearing plant such as *Azadirachia indica* (44.50%), *Pangamia pinnata* (33%) and *Ziziphus mauritiana* (33%) (Azam *et al.,*, 2005), *Tithoma diversifolia* (30.33%) and *Glycine max* seed (20.33%) (Adekunle *et al.,*, 2016) and lower than some oil bearing plant; *Dacryodes edalis* flesh (69.60%) and *Irvingia gabonesis* seed (81.94%) (Adekunle, *et al.,* 2016), Jatropha kernel (63.16%) as reported by Emil *et al.,* (2009). The high oil yield of *Terminalia Catappa* seed suggest an economical viability of the seed for biodiesel production.

5.2 Physicochemical Properties of *Terminalia Catappa* Seed Oil

5.2.1 Acid value

The acid value of crude *Terminalia Catappa* seed oil and degummed terminal catappa seed oil are 7.57 mgKOH/g and 3.82 mgKOH/g respectively (Table 4.1). Acid value is an important property used to indicate the quality, age and suitability of oils for used in the biodiesel industry (Akubugwo *et al.,*, 2008). The acid value of crude *Terminalia Catappa* 7.57 mgKOH/g is lower than that reported by Adewuyi *et al.,* (2011) 14.0 mgKOH/g and higher than 6.04 mg KOH/g reported by Matos *et al.,* (2009) for Terminalia *Catappa* seed oil. However these value were observed to be lower than those reported by Minzangi *et* *al.,*(2011), Zaku *et al.,* (2012) and Ibeto *et al.,* (2012) for some non-edible oils of *Azadirachia indica* (17.40 mgKOH/g), *Ricinus Communis* (12.48 mgKOH/g), *Jatropha curcus* (8.43 mgKOH/g), *Brachystegia eurycoma* (27.08 mg KOH/g) and *Cucurbita pepo* (36.47 mgKOH/g). The acid value of *Terminalia Catappa* seed oil is far greater than the recommended value of 2 mgKOH/g for alkaline direct transestrification and therefore will require esterification before it can be transestrified into biodiesel (Conakci and Van Gerpen, 2001).

5.2.2 Moisture content

The moisture content of crude *Terminalia Catappa* seed oil is 2.48% w/w. The moisture content is lower than 4.13% w/w of T catappa seed oil reported by Matos *et al.,* (2009) and lower than those reported by Ibeto *et al.,* (2012) for some non-edible oils of *Brachystegia eurycoma* (8.27%.w/w), *Cucurbita pepo* (4.92% w/w), *Luffa cylidrica* (3.50% w/w) and *Cucurbita pepo* (5.63% w/w). High moisture content creates problems in tranesterificaiton, reduce shelf life and decrease ester conversion (Dermibas 2006; Ibeto *et al.,* 2012). Degumming the oil reduces the moisture content and sediment of *Terminalia Catappa* seed oil from 2.48% w/w to 1.92% w/w.

5.2.3 Ash content

Ash content is the inorganic residue that remain after combustion of the oil in air at specific high temperature. The Ash content of crude *Terminalia Catappa* seed oil is 0.86%. However degumming the oil reduces the ash content to 0.65% by mass (Table 4.1). The Ash content of *Terminalia Catappa* is similar to that of *Luffa cylidrica* seed oil (0.50% by mass) and lower than that of *Brachystegia eurycoma* (2.10% by mass) *Cucurbita pepo* (1.86%) and *Cucurbita pepo* (2.77%). Ibeto *et al.,* (2012). The lower ash content of *Terminalia Catappa* seed oil makes the oil suitable for biodiesel production.

5.2.4 Iodine value

The iodine value of crude *Terminalia Catappa* seed oil and degummed *Terminalia Catappa* seed oil are 82.42gI_2/100g of oil and 78.80gI_2/100g of oil respectively. The high iodine value is supported by the percentage of unsaturated fatty acid of the oil (54.65%). Since iodine value directly affectsstability with regards to oxidation of oils, it suggests that the auto oxidation of unsaturated fatty compounds at different rates depend on the number and position of double bonds. The specie formed during the oxidation process causes the oil to eventually deteriorate. Small amount of more highly unsaturated fatty compounds have a disproportionately strong effect (Knothe and Dunn, 2003). In this regard *Terminalia Catappa* seed oil is relatively stable to oxidation and is likely to be stored for a long time without becoming rancid (Dallatu, 2015). It is therefore likely to be good feedstock in biodiesel industry.

5.2.5 Saponification value

Saponification value gives a measure of the average length of fatty acid chain which makes up the oil. The saponification value of crude *Terminalia Catappa* (195.37mgKOH/g) and Degummed *Terminalia Catappa* (192.57mgKOH/g) are relatively high and this can be attributed to the presence of high free fatty acid content (Hui, 1996). These values fall within the range of 182.5 – 260mgKOH/g reported by Minzangi *et al.,* (2011) for oils obtained from some plant species.

5.2.6 Density

Generally, plant oils with density of 0.820 to±0.71 at 30^0C are considered good for use as biofuels (Minzangi *et al.*, 2011; Bhattacharya *et al.,* 2013). The density of crude and degummed *Terminalia Catappa* seed oil is 0.881gcm^{-3} (Table 4.1). There was no change in density of the oil after degumming. The density of *Terminalia Catappa* seed oil was relatively close to those of Brachystegia eurycoma (0.850gcm^{-3}), cucurbita pepo (0.840gcm^{-3}), peanut seed (0.888gcm^{-3})Kaya *et al.*, (2009), Ibeto *et al.*, (2011).

5.2.7 Kinematic viscosity

The viscosity of crude and degummed *Terminalia Catappa* seed oil is 46mm^2/s at 40^{0}C. The high viscosity of this oil will reduce fuel atomization and cause the oil not to burn completely. This problem can be reduced by transestrificaiton reaction (Atadashi *et al.*, 2011) which lowers the viscosity and enhances other physicochemical properties of the oil (Ferella *et al.*, 2010).

5.3 FTIR Spectra of Crude *Terminalia Catappa* Seed Oil, Degummed *Terminalia Catappa* Seed Oil and *Terminalia Catappa* Methyl Ester

The IR spectra of crude and degummed*Terminalia Catappa* seed oil (Figs 4.1 and 4.2) show strongabsorbance around 2992cm^{-1} due to the symmetric stretching vibration of the aliphatic CH_2 group. This may be due to the high proportion of linoleic acid group (13.83%), (Table 4.2). This is similar to the observation made in yellow oleander seed oil (Dallatu, 2015). They also show absorbance at 1744cm^{-1}, 1461cm^{-1}, 1375cm^{-1} 1159cm^{-1}, 964cm^{-1} and 723cm^{-1}. However difference exists in the spectra of the oils. The crude *Terminalia Catappa* seed oil show absorbance at 913cm^{-1} which is absent in the degummed oil, this may be due to the absence of phospholipids in the degummed oil. The wave frequently of phospholipids (P-O-C stretch) is 850-995/990-1050 (Coates, 2000).

A comparative analysis of the FTIR peaks of the functional groups of the oils and their respective biodiesel show significant differences which are due to the formation of biodiesels. Fatty acid methyl ester of *Terminalia Catappa* (biodiesel) have unique FTIR absorption of carbonyl (C=0) stretching vibration near 1740-1744cm^{-1} and C-O bending vibration in 1170cm^{-1} region. The ester molecule in the oils (Degummed and Crude) on the other hand shows a distinct C-O absorption near 1159cm^{-1}. There are no such absorption due to C=O and C-O functional group in fossil diesel. This spectraseparation among the functional groups of vegetable oils, biodiesel and fossil diesel forms the basis of characterizationand quantization of FAMEs in biodiesel and in blended biodiesel-diesel fuel through IR spectroscopy (Dallatu, 2015).

The influence of transesterification was indicated by the formation of a signal at 1438cm^{-1}(fig 4.6) which corresponds to the deformation vibration of methyl ester group (CO)-O-CH_3 present in biodiesel spectrum and absent in the oil spectrum. Similar result was reported by (Siatis *et al.,* 2006; Yun *et al.,* 2011; Dallatu, 2015). Another visible transformation revealed by the FTIR spectra of FAMEs is a signal around 1170cm^{-1} of C-O group in the ester controlled area and appearance of signal at 964cm^{-1} corresponding to CH_2 in $RCOCO^-$ group present in the oil and absent in the FAMES.

5.4 Fatty acid profile of *Terminalia Catappa* seed oil seed oil and *Terminalia Catappa* methyl ester

The fatty acid composition in *Terminalia Catappa* seed oil analysed by GC-MS (Appendix I-III) are identified as Myristic acid (C14:0), Palmitic acid (C16:0), Palmitoleic acid (C16:1), Stearic acid (C18:0), Oleic acid (C18:1), Linoleic acid (C18:2) and Arachidic acid (C20:0), (Table 4.2). The percentage composition of fatty acid obtained in this study was closely similar to those of other species of *Terminalia Catappa* previously reported by (Dos Santos *et al.,* 2008; Adewuyi *et al.,* 2011, Ng*et al.,* 2015) with the exception of sweat almond (Giwa *et al.,* 2014) of the seven fatty acids, Oleic acid was the most prevalent, accounting for 40.16%, and Palmitic acid (33.68%) was the predominant saturated fatty acid. The total saturated and unsaturated fatty acid contents of the oil are 45.35% and 54.65% respectively. The high percentage of saturated (45.35%) and monounsaturated

(40.82%) fatty acid of *Terminalia Catappa* 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, iodine value to make it a good potential for biodiesel production (Garpen *et al.,* 2004).

The relatively low percentage (13.83%) of polyunsaturated fatty acid in *Terminalia Catappa* seed oil reduces the risk of undergoing auto-oxidation and rancidity thereby making it suitable for storage and for further processing into biodiesel (Dallatu, 2015).

Knothe (2009) reported on oleic acid as the desirable fatty acid among other 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 39.35mj/kg has a significant contribution tothe energy value of *Terminalia Catappa* methylester. The fatty acid profile of *Terminalia Catappa* methyl ester contains(39.89%) oleic acid (Table 4.5).

5.5 Biodiesel Yield

The percentage conversion yield of raw *Terminalia Catappa* seed oil to biodiesel using 1% w/w NaOH catalyst is 86.64±0.19%.Base catalyzed transesterification is preferred over acid catalyzed transesterification reaction for the production of biodiesel at industrial level because it provides better conversion rates and efficiencies (Fukuda *et al.,* 2001). It was observed that the conversion of degummed oil to biodiesel gave higher percentage yield of 92.68±0.31% under the same reaction condition. High percentage increase in the biodiesel of the degummed oil indicate that degumming process led to the removal of high gummy materials and phospholipids in the oil thus enhancing its biodiesel conversion. Phospholipids and gummy materials present in raw oil might affect the transesterification reaction and may be the reason for the low yield of biodiesel observed. The result obtained agreed with the high biodiesel yield reported by (Okullo *et al.*, 2012; Adekunle*et al.*, 2016) for neutralized jatropha and some non-conventional oils than the raw oils.

The degummed oil was also catalyzed with 1% w/w KOH and CaO/Al_2O_3 catalyst to determine the effect of catalyst type on biodiesel yield of the degummed oil. The percentage yields were 95.50±0.26% for KOH, 97.20±0.57% for CaO/Al_2O_3 and 92.68±0.31% for NaOH. A lower yield was observed for the alkali catalyzed biodiesel, this may be as a result of water and soap formed during transesterification process.

5.6 Physicochemical Properties of Biodiesel

The physicochemical properties of the biodiesel (Table 4.6 and 4.7), are used to access the quality of the fuels, they include.

5.6.1 Acid value

The acid value of NaOH catalyzed raw biodiesel was 0.44±0.10mgKOH/g. The acid value of degummed biodiesel was reduced to 0.28±0.21 mgKOH/g (Table 4.6). The percentage decrease in acid value of the degummed biodiesel suggests high resistance to corrosion due to decrease in free fatty acid content of the biodiesel. This might be due to reduction of free fatty acid present in the oil during degumming process and the result obtained is in agreement with the report of (Dermibas, 2008; Adekunle *et al.*, 2016) where degumming process increases the susceptibility of vegetable oil for transesterification during their conversion to biodiesel. Acid value is a measure of the number of acidic functional groups in a sample and is measured in terms of the quantity of KOH required to neutralize the sample (Cvengros, 1998). Usually for a base catalyzed process, the acid value after biodiesel production will be low since the base catalyst will strip the available free fatty acids (Gerpen, *et al.*, 2004). Considering the presence of free fatty acids influences fuel aging due to hydrolytic cleavage of ester bond. In 2006 the ASTM D6751 biodiesel acid number limit was harmonized with the European Union standard for biodiesel to a value of max 0.50mgKOH/g (Mahajan, *et al.*, 2006).

The acid value for KOH and CaO/Al_2O_3catalyzed degummed biodiesel are 0.33±0.19mgKOH/g and 0.18±0.14mgKOH/g respectively (Table 4.7). The acid value of CaO/Al_2O_3 catalysed biodiesel was less than that of KOH and NaOH catalyzed biodiesel, this could be due to incomplete transesterification as a result of water and soap formation. The acid value of all biodiesel samples in this study falls within the acceptable standard of both ASTM and European biodiesel standard.

5.6.2 Density

Density limits of European standards range from 0.860 – 0.900gcm^{-3} (Meher *et al.,* 2006). The density of NaOH catalyzed Raw and degummed biodiesel are 0.860±0.012gcm^{-3} and 0.863±0.010gcm^{-3} respectively (Table 4.6). The density of the KOH and CaO/Al_2O_3catalyzed degummed biodiesel are 0.865±0.010 and 0.863±0.010gcm^{-3} respectively (Table 4.7). Density is a key fuel properly, which directly affects the engine performance. Fuel density directly affects fuel performance, and some of the engine properties such cetane number, heating value and viscosity are strongly connected to density. The density of the fuel also affects the quality of atomization and combustion (Banabas and Todorut, 2011). Fuel density affects the mass of fuel injected into the combustion chamber and thus the air-fuel ratio. This is because fuel injection pumps fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus the changes in the fuel density will influence engine output power due to a different mass of fuel injected (Alptekin and Canakci, 2008). The densities of all biodiesel samples are within the acceptable EN standard and the values were very close this may be due to the density of methanol used in their production and some fatty acid composition.

5.6.3 Kinematic viscosity

The viscosities of biodiesel at 40^0C obtained in this study ranged from 3.71±0.82 mm^2/s for NaOH catalysed raw biodiesel, 4.60±0.50mm^2/s for NaOH catalyzed degummed biodiesel, 4.10±0.28 mm^2/s for KOH and 4.70±0.62 mm^2/s for CaO/Al_2O_3 catalyzed biodiesel (Tables 4.6 and 4.7). According to ASTM and EN standard for biodiesel, kinematic viscosity must be between 1.9 – 6.0mm^2/s and 3.5-5.0mm^2/s respectively. Viscosity is defined as the resistance of liquid to flow. It refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified sized (Raj and Sahayaraj, 2010). High viscosity is the major fuel property which explains why neat vegetable oils have been largely abandoned as alternative diesel fuel (Dunn and Knothe, 2007). Viscosity increases with increase in chain length (number of carbon atoms). This holds also for the alcohol moiety because the viscosity of ethyl ester is slightly higher than that of methyl ester (Knothe and Steidley, 2005) and decreaseswith increase in unsaturation (Nourredini *et al.,* 1992). Moreover high viscosity may lead to the formation of soot and engine deposits due to insufficient fuel atomization. The viscosities of all biodiesel are within the range specified by ASTM and EN standard. The increase in viscosities of degummed biodiesel might be as a result of decrease in degree of unsaturation of degummed oil. Thus biodiesel from raw oil have more potential for fuel application than those of degummed oil.

5.6.4. Iodine value

The iodine value obtained in this study were 90.50±1.20gI_2/100g for NaOH catalyzed raw biodiesel and 72.42±1.50gI_2/100g, 72.56±0.09gI_2/100g and 70.40±1.50gI_2/100g for NaOH, KOH and CaO/Al_2O_3 catalyzed degummed biodiesel. The iodine value provides information about the unsaturation degree of the oil which directly affects it stability to oxidation. The reason for auto-oxidation occurrence is the presence of double-bond in the chain of the fatty compounds. Higher unsaturation of fatty acids leads to the formation of deposits or deterioration of the lubricating property (De La *et al.,* 2010). The EN standard for iodine value in biodiesel is 120gI_2/100g maximum (EN 14214 2003).

The iodine values of all biodiesel are within the EN standard. The lower iodine value of degummed biodiesel means they are more stable to oxidation. The decrease in the iodine value of degummed biodiesel due to degumming process suggestsdecrease in the degree of unsaturation.

5.6.5 Saponification value

Saponification value indicates the ability of the oil to make soap. The saponification values obtain in this study for NaOH catalyzed Raw and degummed biodiesel are 186.20±1.70 and 180.10±1.40mgKOH/g respectively, and 187.26±1.80 for KOH and 178.66±0.60mgKOH/g for CaO/Al_2O_3 catalyzed biodiesel. There was decrease in saponification value of NaOH catalyzed degummed biodiesel due to degumming process. However KOH catalyzed degummed biodiesel has the highest saponification value and this could be due to the formation of water and reaction of catalyst with residual fatty acids. Kulkarni *et al.,*(2006), reported saponification value ranging from 184-194 mgKOH/g for biodiesel samples.

5.6.6 Pour and Cloud point

Pour and cloud points of biodiesel are presented in Tables 4.6 and 4.7. The pour point and cloud point of crude biodiesel are 3^oC and 8^oC respectively, while that of degummed biodiesel are 2^oC and 8^oC for NaOH and 2^0C and 7^oC for both KOH and CaO/Al_2O_3 catalyzed biodiesel. The biodiesel obtained from degummed oil was observed to have lower cloud and pour point than crude biodiesel. This might be due to the reduction in degree of unsaturation of the oil after degumming process. According to ASTM no limit is specified for pour and cloud point. The reason is that the climate conditions in the world vary considerably, thus affecting the needs of biodiesel users in a specific region. (Rashed and Anwar, 2008).

5.6.7 Flash point

The flash point of crude biodiesel (158^oC) is the higher than that of degummed biodiesel which were 153^oC, 148^oC and 151^oC for NaOH, KOH and CaO/Al_2O_3 biodiesel. All the biodiesel samples have higher flash points than the minimum value specified by ASTM (130^oC) and European standard (120^oC). The high flash point of the biodiesel samples mean they are safe to handle, easy to transport and safe for storage, they also have lower risk and reduced chance of uncontrolled deterioration (Sanjay, 2013). The degummed biodiesel have lower flash point than the crude biodiesel. This may be attributed to the removal of phospholipids in the oil during degumming process which may contribute to high flash point observed in the raw biodiesel.

5.6.8 Oxidation stability

The oxidative stability (OS) of crude and degummed NaOH catalyzed biodiesel are 4.2hrs and 5.8hrs respectively while the oxidative stability of KOH and CaO/Al_2O_3 catalyzed degummed biodiesel are 6.2 H and 6.4 H respectively. The OS of the crude biodiesel 4.2 H is highly than the recommended ASTM D6751(3 H) and lower than that specified by EN14214 (6 H), while the OS of the degummed biodiesels were higher than the recommended ASTM and EN minimum standard except that of NaOH catalyzed degummed biodiesel (5.8 H) which is slightly lower than the EN standard (6H). The percentage increase in the OS of degummed biodiesel might be due to removal of phospholipids during degumming process. Nzai *et al.,* (1999) reported that removal of oil phospholipids result in subsequent removal of iron and copper and improves oil oxidative and flavor stability. Oxidation stability is an important technical issue affecting biodiesel quality (Knothe, 2008). A minimum rancimat induction period of 3 and 6hrs is defined for biodiesel using ASTM – D6751 and EN14214 standards respectively.

5.6.9 Cetane number

The Cetane number of NaOH catalysed crude biodiesel is 49.78±1.82 while that of degummed biodiesels are 52.84±1.50 for NaOH, 52.57±1.70 for KOH and 52.63±1.70 for CaO/Al_2O_3. From the result all biodiesel sample have cetane number that is higher than the minimum standard 47 set by ASTM D6751 and 51 set by EN 14214 except, the crude biodiesel that have cetane number less than the EN standard but higher than ASTM standard. Cetane number increases with increase in degree of saturation (Adekunle *et al.,* 2016). The cetane number is a measure of ignition quality of diesel fuel during combustion ignition (Raj and Sahayaraj, 2010). It provides information about the ignition delay time of a diesel fuel upon injection into the combustion chamber. High cetane number signify only short delay; between fuel injection and ignition, and this ensure a good cold start behaviour and a smooth run of engine (Boz *et al.,* 2009).The decrease in degree of unsaturation of degummed oil might be the reason for the increase in cetane number of degummed biodiesels.

5.6.10 Ash content

Ash content describes the amount of inorganic contaminants such as abrasivesolid and catalyst residue and the concentration of a soluble metal soap contained in a fuel sample (Fernando *et al.,* 2007). The Ash content of NaOH catalyzed Raw and degummed biodiesel are 0.018±0.002 %by mass and 0.014±0.001% by mass respectively. KOH and CaO/Al_2O_3 catalyzed biodiesel have Ash content of 0.014±0.002 and 0.015±0.002 respective. Both ASTM and EN limit the amount of ash content to be maximum 0.02 (%mass). All the biodiesel from this study have ash content below the maximum limit set by both ASTM and EN14214. The decrease in the Ash content of value of degummed biodiesel might be due to removal of phospholipids during degumming process.

5.6.11 Water and sediment

Tables 4.6 and 4.7 highlights the water and sediments content of crude and degummed biodiesel. The crude biodiesel have water and sediment value (0.06%v) higher than the recommended ASTM and EN standard limit, it may cause corrosion and affect engine performance. The degummed biodiesels have water and sediment value below the maximum limit set by ASTM and EN. The presence of water and sediment has two forms, which are either dissolve water or suspended water droplets, while biodiesel is generally considered to be insoluble in water; it actually takes up considerably more amount of water than diesel fuel. On the other hand water content of biodiesel reduces the heat of combustion and will cause corrosion of vital. fuel system components; fuel pumps, injector pumps, fuel tubes etc more over more sediment may consist of suspended rust and dust particles or it may originate from the fuel as insoluble compound during oxidation (Van Gerpen, 2005; Dermibas, 2009; Fernando *et al.*, 2010). ASTM and EN standards limit the amount of water and sediment to be max 0.05 (v%).

5.6.12 Heat of combustion

The heat of combustion or heating value is not specified in the biodiesel standards by ASTM and EN. However European standard for using biodiesel as heating oil specifics a minimum heating value of 35mj/kg (Sokoto*et al.*, 2011). The biodiesel obtained from this study have a heating value of 40.26±0.70 mj/kg for raw biodiesel and 42.76±0.52, 42.90±0.60 mj/Kg and 42.65±0.62mj/kg for NaOH, KOH and CaO/Al_2O_3catalyzed degummed biodiesel respectively. Biodiesels obtained from degummed oil have higher heat of combustion than the one obtained from the crude oil. Heating value increases with decrease in unsaturation (Sokoto *et al.*, 2011). The increase in heating value of degummed biodiesel might be as a result of decrease in degree of unsaturation after degumming process. Both biodieselsamples can be potential alternatives to petroleum diesel based on their heat of combustion.

5.7 Effect of Blending on Biodiesel Properties

The viscosity of the biodiesel blends range from 3.66-4.40mm^2/s for B10-B90 blends. The allowable ASTM D7467 for B6-B20 biodiesel-diesel blend is 1.9-4.1mm^2/s. The B10 and B20 blends have a viscosity of 3.66mm^2/s and 3.72mm^2/s respectively and therefore satisfy the acceptable standard for B6-B20 Biodiesel-diesel blend set by ASTM D7467.

The effect of blending on density of the biodiesel diesel blend was minimal and within a close range of 0.848 – 0.858gcm^{-3}, this is because the density of biodiesel and fossil diesel were very close. Dallatu (2015) reported that a pig lard methyl ester blend does not show any effect on density because the density of piglard methylester and fossil diesel are similar.

The flash point of biodiesel increases with increase of biodiesel fraction in the blend. The flash point of the biodiesel-diesel blend increase from 89^{o}C – 146^{o}C for B10-B90 biodiesel-diesel blend. Generally all blends are safer for storage and easier for transportation compared to fossil diesel that have lower flash point (82^{o}C).

The cloud points of the biodiesel-diesel blend increases from, 3^{o}C in fossil diesel to 7^{o}C in B90 blends. The B60-B90 blends were higher than the standard limit of 4^{0}C and these will limit the beneficial use of the blends in cold climates (Haiying *et al.,* 2008). The cloud point of biodiesel is very important for its use in coldclimate country. This is because when a blended fossil diesel is used at low temperature,the biodiesel portion of the blend crystallites and separate out from fossil diesel (Lang *et al.,* 2001), creating problem for the engine flow system which will eventually cause the engine to stop running. The B10-B30 biodiesel-diesel blends have the same cloud points (3^{o}C) as fossil diesel and can therefore be used in diesel engine.

The cetane number of fossil diesel and Biodiesel are 48.50 and 52.84 respectively. There was a steady rise in cetane number with increasing biodiesel fraction in the biodiesel-diesel blend. The cetane numberrange from 48.50-51.90 for B10-B90 blends. The cetane number of all blends were above the minimum limit of 47 and 40 for B100 and B6-B20 biodiesel-diesel blend.

The heating value of fossil diesel (43.90Mj/kg) is higher than that of biodiesel (41.76Mj/kg) obtain from this study. The increase in ratio of biodiesel in the blend sample lowered the heating value continuously toward the pure biodiesel, suggesting an inverse relationship between the heating value and the blending proportion. The difference in heating value between biodiesel and fossil diesel may be due to presence of unsaturated bonds in biodiesel which is absent in fossil diesel. The lower heating value of the biodiesel and their blends would lead to higher fuel consumption.

The water and sediment value of fossil diesel and biodiesel were 0.01% and 0.04% respectively. The increase of biodiesel fraction in the blends increases the water and sediment value. There was constant water and sediment value of 0.01 for B10-B40. The value increases from 0.02-0.03 for B50 – B90 blend. ASTM limits the amount of water and sediment in 100% biodiesel and B6 – B20 blends to 0.05 maximum. Therefore both the biodiesel and the blend satisfy the standard limit set by ASTM.

ASTM specification, limit the amount of Ash content to a maximum of 0.02%mass and 0.01% mass for pure biodiesel and biodiesel– diesel blend respectively. The Ash contentof fossil diesel and biodiesel are 0.01 and 0.014 respectively. There was no change in ash content of B10-B40 blend from that of fossil diesel, however there was an increase in the value from 0.11 to 0.012% mass for B50 – B90 blends. The B10 and B20 blends satisfy ASTM requirement for B6-B20 biodiesel-diesel blend.

The acid value of the biodiesel-diesel blends for B10 and B20 was 0.2MgKOH/g and 0.14MgKOH/g respectively and 0.14-026MgKOH/g for B30 – B90 blends. All biodiesel – diesel blends are below the maximum value of 0.5 and 0.3 MgKOH/g specify by ASTM for pure biodiesel and B6-B20 biodiesel-diesel blend. The B10 and B20 blend can be used in diesel engine with no engine defect.

CHAPTER SIX

6.0 Summary, Conclusion and Recommendation

6.1 Summary

i. The oil yield of *Terminalia Catappa* seed oil was 56.30%.

ii. The FTIR Analysis of *Terminalia Catappa* seed oil showed the presence of carbonyl functional group of the triglycerides at 1744.40cm^{-1} as the most intense and prominent band in the IR spectra, indicating the presence of triglycerides ester. The absence of the signal at 913cm^{-1} in the degummed oil which is present in the raw oil showed that phospholipids and other gummy materials were removed during degumming process. The signal at 1438cm^{-1} in *Terminalia Catappa* methylester showed the presence of O-CH_3 group of FAME and confirmed that transesterification had taken place.

iii. The GC-MS result showed about 90% saturated /monounsaturated fatty acid composition of *Terminalia Catappa* methylester, hence it is a good substitute to fossil diesel.

iv. Degumming process improves the physicochemical and biodiesel properties of *Terminalia Catappa* seed oil compared to the raw oil.

v. Degumming process improves the biodiesel yield, ignition properties and reduce susceptibility of biodiesel obtain after degumming to peroxidation as compared to the raw oil.

vi. Degumming process also reduces the level of saturation in the feedstock and this effect is seen in this various fuel properties for cloud and pour point, cetane number and oxidative stability for NaOH, KOH and CaO/Al_2O_3 catalyzed biodiesel.

vii. Biodiesel produced from degummed oil showed good quality fuel with variation among the catalyst type.

viii. The biodiesel – diesel blend of *Terminalia Catappa* methylester agree with ASTM specification for biodiesel.

6.2 Conclusion

- The oil content of *Terminalia Catappa* seed oil (56.30%) was high enough to be classified as commercially viable source of oil for biodiesel production.
- Degummed oils were better substitute than undegummed oils as raw material for biodiesel production.
- Biodiesel quality parameters, such as density kinematic viscosity, cloud point, cetane number, pour point, iodine value, flash point, acid value, water and sediment, ash content and oxidationstability were all within ASTM D6751 and EN14124 standards except that of the raw biodiesel, that has high water and sediment content and can cause engine deposit and operational problems in diesel engine.
- Fuel properties such as ash content, acid value, water and sediment, density, viscosity, flash point, cetane number and heating value of B10-B20 blends agreed with ASTM D7467 specification for B6-B20 biodiesel-diesel blend and can therefore be used as blended fuel in diesel engine.

6.3 Recommendation

It is recommended that

i. Catalytic activity of CaO/Al_2O_3 catalyst in biodiesel production be tried on other oil sources.

ii. The quality and yield of biodiesel prepared using CaO/Al_2O_3 catalyst should be optimized.

iii. The influence of B10-B20 blends on emission and some performance parameters on diesel engine should be investigated.

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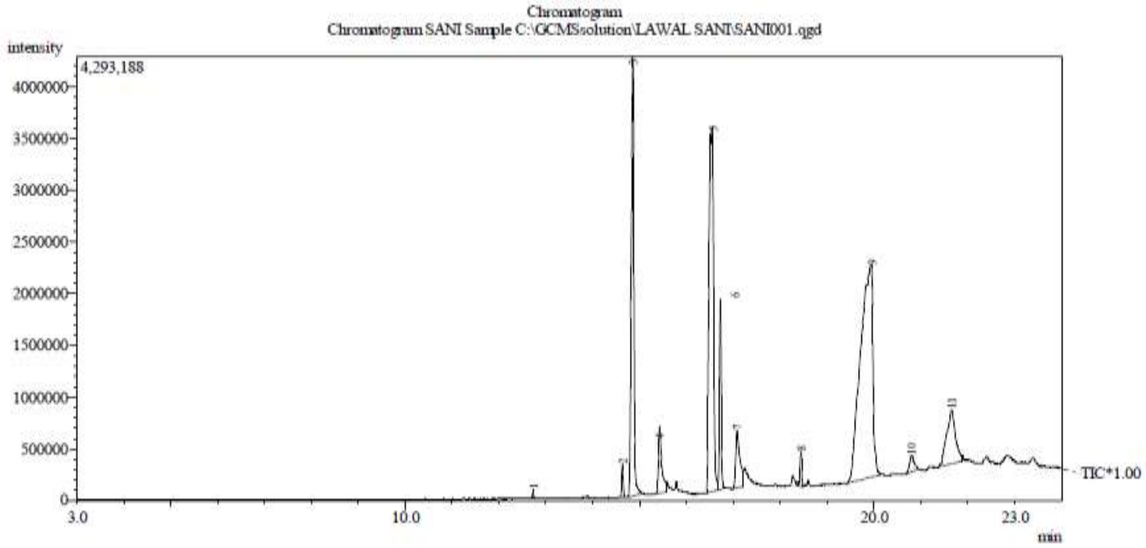
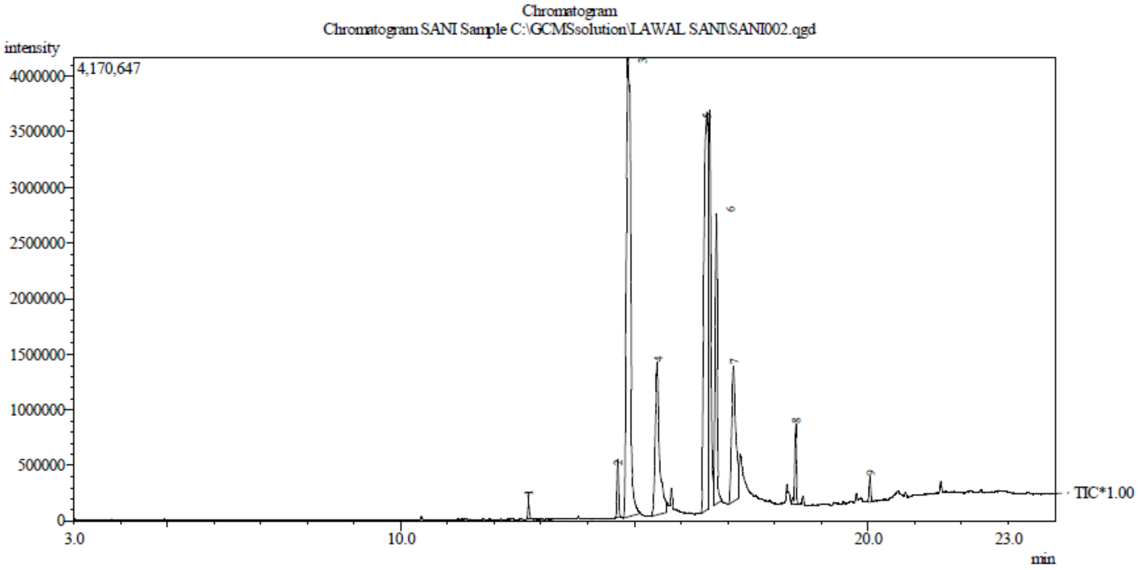
APPENDICES

Appendix 1: GC-MS Spectra of Crude *Terminilia Catappa* Seed Oil



Appendix 2: GC-MS Spectra of Degummed*Terminilia Catappa* Seed Oil



Appendix 3: GC-MS Spectra of *Terminilia Catappa* Methylester