PRODUCTION OF BIOLUBRICANT FROM ALLAMANDA SEED OIL USING BASE METAKAOLIN

BY

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MEng/SEET/2017/6742

DEPARTMENT OF CHEMICAL ENGINEERING
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ABSTRACT

The use homogeneous catalysts, conventional grown edible oils makes the overall cost of biolubricant production high, and so cheap, readily locally materials are required. The aim of this study was to determine the effect of base activated metakolin in the production of biolubricant from Allamanda. The Allamanda oil was extracted and analyzed for their chemical and physical properties such as density, acid value, % FFA, saponification value as well as viscosities at 40 and 100 ℃ and viscosity index. The catalyst (metakaolin) was prepared by beneficiation, calcination at 650 °C for 90 minutes, which was further activated with potassium hydroxide hydrothermally at 90 ^{o}C for 3 hours. The obtained catalytic material was characterized using X-ray diffraction (XRD), Scanning electron microscope (SEM), X-ray fluorescence (XRF) and Brunauer Emmet Teller (BET) techniques. The catalyst shows a high surface area and pore size of 706.906 m^2/g and 2.118 nm. The method employed for the production of biolubricant involved two stages transesterification process, the first stage produced methyl ester of the oil which was optimized using Box-Behnken design module of response surface methodology (RSM) available in " Design Expert$^{®}$ Software" in which methanol to oil ratio was 1:5 and was kept constant. Other variables such as temperature, time and catalyst concentration were varied. The optimum conditions that gave the highest yield of 90.67 % were: 52.5 ℃ , 180 minutes and 0.5 wt%. The produced biodiesel was characterized. In the second stage; the methyl ester was transesterified with trimethyolpropane to produce the biolubricant. Major lubricating properties of the product such as pour point, viscosities at 40 ℃ and at 100 ℃, and the viscosity index were analyzed and found to have value of -12.5 ℃ , 64.0 cSt, 28.0 cSt and 371.59 respectively. The properties of the biolubricant produced was found to be comparable to the ISO VG-68 commercial standards for light and industrial gear applications and other plant based biolubricant.

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ABBREVIATIONS

AV:	Acid Value
FFA:	Free Fatty Acid
PV:	Peroxide Value
IV:	Iodine Value
SG:	Specific Gravity
SP:	Saponification Value
VI:	Viscosity Index
AME:	Allamanda methyl esther
ANOVA:	Analysis Of Variance
RSM:	Response Surface Methodology
BBD:	Box-Behnken Design
ASTM:	American Standard for Testing Materials
AOCS:	American Oil Chemists' Society
ISO-VG:	International Standard Organization for Viscosity Grade
PP:	Pour Point
FP:	Flash Point
MW:	Molar Weight
NPG:	Neopentyl Glycol
TMP:	Trimethylolpropane
TAG:	Triacylglycerol
TE:	Triester
KOH:	Potassium hydroxide
ME:	Mono-ester
DE:	Diester
XRD:	X-ray Diffraction
XRF:	X-ray Fluorescence

BET:	Brunauer Emmet- Teller
SEM	Scanning Electron microscope

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the study

Energy is the fundamental requirements for various form of socio-economic activities globally (Chalvatzis and Loanidis, 2017; Orzturk *et al.*, 2017; Wirba *et al.*, 2015). Fossil fuels are increasingly associated with the emissions of greenhouse gases, majorly CO_2, leading to climate change, emergence of drought, spread of diseases and variation in population sizes of both plant and animal species. The depletion and or unknown world's crude oil reserves, increasing crude oil prices, and issues related to conservation have brought about the renewed interest in the use of bio based materials. Fossil fuels such as petroleum, coal and natural gas which have been used to meet the energy needs of the people and they are associated with negative environmental impacts such as global warming. Supply of these non-renewable energy sources is threatening to run out in a foreseeable future (Mohammed, 2015).

It has been widely reported that the petroleum based oils can lead to serious ground water pollution, soil pollution, surface water contamination, air pollution and agricultural material and food contamination. Moreover, gases CO, CO_2, NO_x and SOx are liberated together with nanoparticle treated metals (Hg, Ca, P, Zn, Mg and Fe) during the combustion of mineral oil, which results in a negative impact on the environment. It was also reported that mineral oil is carcinogenic as continuous inhalation of this lubricant emission may cause inflammatory and analgesic effects on the human respiratory system. In addition, by-products derived from the degradation of the lubricants are toxic and can lead to soil infertility (Hossain *et al*., 2018).

Renewable energy derived from biomass is presently one of the most important sources of energy. Energy obtained from these sources is characterized with the capacity to lessen greenhouse gas emissions, contribute to sustainable development environmentally, socially and economically (Shahabuddin *et al.*, 2013, Khurshid, 2014). Strong environmental concerns and growing regulations on contamination and pollution of the environment by the petroleum based lubricants have increased the need for renewable and biodegradable lubricants (Menkiti *et al.*, 2015).

Biodiesel is a renewable clean fuel that can serve as a possible alternative to petroleum diesel. It is derived from vegetable oil and animal fat through transesterification (Hassani *et al.*, 2014; Wang *et al.*, 2014; Karthikeyan *et al.*, 2014). Almost in all commercial production of biodiesel, edible oils are used as feedstock and the high prices of these oils increased the overall cost of the biodiesel production (Enweremadu and Alamu, 2010). Commercial production of biodiesel from edible oil in the developing economy like Nigeria is not very feasible since the nation cannot satisfy the food requirements of these oils. The alternative way of reducing the biodiesel production cost is to use less expensive feedstock which includes: non-edible oils, animal fats and waste cooking oil. Biodiesel serve as raw material for biolubricant synthesis (Musa and Aberuagba, 2012).

Research has shown that chemical modification techniques such as transesterification of biodiesel with secondary alcohol can be used for the production of lubricant with better temperature performance and appreciable fluidity. Bio-lubricants are known to have good lubricity; they are biodegradable, renewable and are non-toxic to environments (Opeyemi, 2010).

The general principle of producing bio-lubricant from vegetable oil involves a two-step transesterification reaction of triglyceride and alcohol to produce fatty acid acyl esters

(FAAE) and further reaction of FAME and TMP to yield TMP ester (Nkem and Nwakaudu, 2019; Samson, 2015). Common polyhydric alcohols used in the transesterification of fatty acids methyl ester are: neopentyl glycol (NPG), pentaerythritol (PT), trimethylolpropane (TMP) and ethylene glycol (Mohammed *et al*., 2012; Phani, 2013; Bilal *et al*., 2013; Yeti *et al*., 2014; Wang *et al*., 2014; Musa *et al*., 2015; Menkiti *et al*., 2015; Mohammed *et al.*, 2015; Said *et al*., 2014).

Homogeneous alkaline transesterification has been known to be the most viable way for commercial production of biodiesel. This method is associated with several drawbacks (Zanette *et al.,* 2014). Solid heterogeneous catalytic transesterification is an alternative process that offers simplification and economy of catalyst removal and more eco-friendly (Vyas *et al.,* 2010).

Clays are interesting catalytic materials due to their low cost and environmental friendly. Clays are modified either by acid or base, which causes the disaggregation of clay particles, elimination of impurities and dissolution of external layers, altering the chemical composition and structure of clays (Teku, 2017).

Kaolin clay is a cheap and versatile raw material that can be found in many geographical locations and has been used successfully in the synthesis of mesoporous aluminosilicates and various microporous zeolite frame works. Raw kaolin clay has almost no acidity and to improve the acidity of the kaolin clay, it is essential to add elements into its frame work. Kaolinite is a group clay that can be used as catalyst (Nascimento *et al*., 2011). Liu *et al*. (2018) reported that many researchers have reported that modified kaolin (metakaolin) clay catalyst can catalyze vegetable oils with methanol to produce fatty acid methyl esters (FAME). The catalytic activity of metakaolinite in the transesterification reaction of waste cooking oil with methanol was reported to give high biodiesel yields. Metakaolinite catalyst can be reused because it exhibited only a slight loss of activity even after eight consecutive reaction cycles (Ramirez - Ortiz *et al.,* 2012).

The known environmental advantages of using clay as catalyst is that even after the utilization of catalytic activity, it can be used as a raw materials for cement, ceramics or other industries that used kaolin as its raw material (Zatta *et al.,* 2011). However, the catalytic activity of kaolinite in the transesterification reaction still remains poorly studied (Nascimento *et al.,* 2011).

Allamanda (golden trumpet) flowers bears seed that contains appreciable quantity of oil. The flower belongs to the apocynaceae. It is native to Brazil. It is commonly called golden trumpet, common trumpet and yellow Allamanda. It cures jaundice, malaria, vomiting and diarrhea. It also acts as an antibacterial, anticancer, effective diuretic, laxative and purgative. It is also nutritional such as carbohydrate, alkaloids, fatty acid, flavonoids and high dose may cause diarrhea. According to Egwim *et al*., (2013) the oil content of Allamanda seed is 57% using mechanical extraction.

There are no much research literatures on the synthesis and characterization of metakaolin from a typical Nigerian kaolin as heterogeneous catalyst for production of biodiesel and to the best of the author’s knowledge, scanty studies have been reported on bio-based lubricant from a typical Nigerian non-edible seed oil using metakaolin as catalyst.

1.2 Statement of the Research Problem

The use homogeneous catalysts in the production of biodiesel and biolubricant makes the cost of production high due to extra cost of product purification, they are not friendly economically and are also corrosive.

Also the use of conventionally grown edible oils as the major feedstock for biodiesel and biolubricant production causes imbalance between their utilization as energy sources and food consumption and which contributes to the higher cost of biodiesel and biolubricant production.

1.3 Aim and Objectives

The aim of this research work is to determine the effect of base activated metakaolin in the production of biodiesel and biolubricant from Allamanda seed oil and this aim will be achieved through the following objectives:

i. Extraction and characterization of oil from Allamanda seed
ii. Synthesis of metakaolin heterogeneous catalyst and characterization of the catalyst using XRD, XRF, SEM, and BET techniques
iii. Synthesis and characterization of biodiesel from the extracted Allamanda seed oil
iv. Synthesis and characterization of Allamanda based biolubricant using the biodiesel produced

1.4 Justification of the Study

The cost of catalyst production and the oil influences the overall biolubricant production, therefore there is need to use cheap, readily available, locally sourced materials for the production. Solid catalysts are environmental friendly and are easy to produce compared to homogenous catalysts.

Allamanda oil seed yields reasonable amount of oil which can be enough for biolubricant production and will further establish the potential of the plants in different parts of the world.

1.5 Scope of the Study

The scope of this study is limited to extraction and characterization of oil from Allamanda seed, preparation and characterization of metakaolin, production of biodiesel and biolubricant using transesterification and characterization.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Lubricant and Lubrication

A lubricant is a substance that reduces friction and wear by providing a protective film between two moving substances in close range. They are substances used to improve the working efficiency and decrease loss in energy and materials as a result of movement of surface in contact. The idea of friction, wear and lubrication are expressively important in the preparation of lubricant and the selection of base materials. Lubrication is the use of a substance which is the lubricant in reducing friction in other to improve the movement (John, 2015).

A good lubricant has the following properties:

i. Good boiling point
ii. Low freezing point
iii. High viscosity index
iv. Thermal stability
v. Corrosion prevention
vi. High resistance to oxidation

The single largest application for lubricants, in the form of motor oil is protecting the internal combustion engines in motor vehicles and powered equipment (Mohammed, 2015).

2.2 Biolubricants

Biolubricants are esters of heavy alcohols with alkyl chain usually higher than a C_5 unit, it is usually derived from vegetable oil-based feedstock and it has lubricating properties similar to mineral oil based lubricants (Musa *et al*., 2016). Biolubricants are lubricants that biodegrade rapidly and which are non-toxic to human beings and aquatic habitats. Biolubricants are greener, renewable, and non-toxic and emit zero greenhouse gas (Hossain *et al*., 2018). A Lubricant may be plant oil-based or derived from synthetic esters produced from modified renewable oils or from mineral oil-based products (Mohammed, 2015). Biolubricants give significant benefits as a substitute for mineral based lubricant in industrial and maintenance applications because of their unequal characteristics (Amit and Amit, 2012). Biolubricants have higher viscosity index, less vapour emissions, higher flash points and lower volatility which enhances better safety to environment (Bilal *et al.*, 2013). Biolubricants are vegetable oil based lubricants that are biodegradable, renewable and are non-toxic to land and aquatic environments (Samson, 2015).

2.3 Feedstock for Biolubricant Production

2.3.1 Vegetable Oil

Vegetable oils comprised of edible and non-edible. The edible oils such as palm kernel oil, sun flower, soya bean, coconut oil, palm oil, groundnut oil, are used for human usage which is also used for biodiesel and biolubricant production. In order to reduce the cost of production and to avoid food for fuel conflict, non-edible oils are used as the major source for biodiesel and biolubricant production. Compared to edible oils, non-edible oils are affordable and readily available (Hossain, 2018). They are obtained from rape seed, rosin seed, Jatropha curcas, castor seed, and rubber seed. Waste cooking oils are also used in the production of biolubricant (Olajide, 2014).

Vegetable oils are mostly made up of two structure blocks which are glycerol and fatty acids. Glycerol has only one type but the structures of the fatty acids can widely varies and the fatty acids can be expressively involved to the glycerol which consists of three alcohol groups in which the end product may restrain on fatty acid (monoglycerides), two fatty acids (diglycerides) or three fatty acids (triglycerides) (Olajide, 2014). For the transesterification process, different types of vegetable oils and animal fats such as soya bean oil, palm oil, andiroba oil, pique oil, cumaru oil are involved in the alcoholysis in the presence of catalyst (Samson, 2015).

Table 2.1 provides the list of some edible and non-edible oils their respective oil contents and yields

Table 2.1: List of edible and non-edible oil, their respective oil content and yield

(Samson, 2015)

S/No	Feedstocks	Oil content (%)
1	Jatropha curcas	50 – 60
2	Calophyllum inophyllum	65
3	Moringa oleifera	40
4	Soybean	15 – 20
5	Palm oil	30 – 60
6	Coconut	63 – 65
7	Rapeseed	38 – 46
8	Sunflower	25 – 35
9	Peanut oil	45 – 55

Table 2.2 shows the production rate of vegetable oil in some countries

Table 2.2: Vegetable Oil Productions in some Nations (Abubakar, 2015)

Country	Million tonnes per annum
United state	11.0
Malaysia	9.6
China	8.9
Indonesia	7.1
India	6.5
Argentina	4.9
Brasil	4.6
Nigeria	1.9
Others	31.7

2.3.1.1 Allamanda Plant and Oil

Allamanda commonly called Allamanda, common trumpet vine, golden trumpet vine, golden trumpet, yellow Allamanda, yellow bell, yellow trumpet vine, it is nature to tropical South America, that is, Brazil, French Guiana, Gujana and Surinam. It is widely cultivated in gardens in Australia, particularly in sub-tropical and tropical regions. Yellow Allamanda prefers moist, well-drained soils in tropical regions. It is a vine or shrubby plant with some climbing stems (that is, scandant shrub). It often forms into a clump about 2 m tall and 2-3 m wide, but can grow much higher when climbing up over other vegetation (that is, up to 6 m in height) (Petricevich and Abarca-Vargas, 2019).

It fruit capsules are round (pod or pod like) (4 cm across) densely covered with soft spines (1 cm long). The seeds are somewhat flattened (that is, compressed) tan in colour and are slightly winged or have a thin (that is membranous) margin. It reproduces by seed and also be propagated via stems segments. It is probably mainly spread in garden waste that is dumped along roadside and in bush land. It seeds are then dispersed from these initial infestations by wind and water. Stem segments may also be spread down waterways during floods (Petricevich and Abarca-Vargas, 2019). The oil content of the Allamanda seed is 57% (Egwim *et al*., 2013).

With the abundance of forest and plant based non-edible oil in the country, Allamanda, no much attempt has been made to use esters of this non-edible oils as substitute for diesel except jatropha (Egwim *et al.*, 2015)

Plate I: Allamanda plant

2.3.2 Polyols

The use of transesterification with secondary alcohol (polyols) such as (TMP), neopentylglycol (NPG) and pentaerythritol (PE) has been widely acknowledged as a viable chemical modification techniques for the synthesis of polyol ester which is characterized with excellent viscosity index and low temperature properties such as pour points (Kamalakar *et al.,* 2015). Polyol reacts with the resulting biodiesel. The reaction with polyol is meant to eliminate the occurrence of hydrogen atom in β-position of the vegetable oil or animal fat which led to substantial improvement in the thermo-oxidative properties of bio-based lubricant.

The property of these esters is purely dependent on the fatty acid profile, the length of fatty acid chain, the available quantity or number of unsaturated bonds and the location of these bonds (Kamalakar *et al.,* 2015). Common polyhydric alcohols used in the transesterification of fatty acid methyl ester are trimethylolpropane (TMP), neopentyl glycol (NPG), pentacrythnol, glycerol (Hossain *et al*., 2018; Musa *et al*., 2016). Trimethylolpropane is however the most known alcohol for biolubricant production because the biolubricants produced is characterized with superior lubricating properties. Trimethylolpropane is also known for its high melting point and branched structures which are important features for biolubricant production (Musa *et al.*, 2016).

2.3.3 Catalyst

In general, there are three categories of catalysts used for biodiesel production, they are known as alkalis, acids and enzymes (Khurshid, 2014; Talha and Sulaiman, 2016; Romano and Sorichetti, 2011). As compared to enzyme catalysts, alkali and acids catalyst are more commonly used in biodiesel production and were then categorized into homogeneous and heterogeneous catalyst. Homogenous catalysts (acid) such as sulphuric acid, sulphonic acid, hydrochloric acid, organic sulphonic acid and ferric sulphate are commonly used in transesterification (Talha and Sulaiman, 2016). While the commonly used homogeneous alkaline catalysts are sodium or pottasium hydroxide dissolved in methanol (Romero *et al.*, 2011) and pottasium methoxide, sodium methoxide, sodium ethoxide (Talha and Sulaiman, 2016).

Heterogeneous catalyst that have been considered for biodiesel production include enzymes, titanium silicates, and compound from alkaline earth metal, anion exchange resins and guanidines in organic polymers (Romano and Sorichetti, 2011).

Homogeneous (Traditional) catalysts (basic or acid poses advantages including high activity (complete conversion within 1 hr) and mild reaction conditions (from 40 to 65^oC and atmospheric pressure). However, the use of homogeneous catalyst leads to soap production. Beside, in the homogenous process, the catalyst is consumed thus reducing the catalytic efficiency which causes increase in viscosity and the formation of gels. Homogeneous catalysts are corrosive (Lee *et al*., 2014)

In addition, the method for the removal of the catalysts after reaction is technically difficult and a large amount of waste water is produced in order to separate and clean the products, which increase the overall cost of the process. Thus the total cost of the biodiesel production based on homogeneous catalysis is not yet sufficiently competitive as compared to the cost of biodiesel production from petroleum. And alternative is the development of heterogeneous catalysts that could eliminate their additional running costs associated with the aforementioned stages of separation and purification. In addition, the use of heterogeneous catalysts does not produce soap through free fatty acid neutralization and triglyceride saponification (Romero *et al.,* 2011). Heterogeneous catalysts also reduce the generation of pollutants, promote easy recovery, reusability and a cost effective green process, efficient and inexpensive heterogeneous catalysts help to minimize the overall cost of biodiesel production. Heterogeneous catalysts are considered vital in certain harsh conditions such as high temperature and pressure (Thangaraj *et al.,* 2018). Heterogeneous catalysts are non-corrosive (Khurshid, 2014).

2.3.3.1 *Clay*

Clay is a finely – grained natural rock or soil material that combines one or more clay minerals with possible traces of quarts (SiO_2), metal oxides (Al_2O_3 and MgO) and organic matter.. Geologic clay deposits are mostly composed of phyllosilicate minerals containing variable amount of water trapped in the mineral structure. Clays are plastic due to particle size and geometry as well as water content, and become hard, brittle and non-plastic upon drying or firing. Depending on the soil's content in which it is found, clay can appear in various colour from white to dull grey or brown to deep orange-red (Peterson, 2019; Jordan, 2014).

Clay minerals are hydrous aluminino silicates and are abundant in soils and sedimentary rocks. They are very important minerals as a result of their surface properties and the fact that they are reactive, hence making them very important in industrial application and environmental control. The properties of clay minerals such as acidity high surface area and cation exchange capacity make them play important roles such as catalyst supports and adsorbent for toxic substances. They are mainly composed of layers and are therefore referred to as phyllosilicate minerals (Teku, 2017). Depending on the academic source, they are three or four main groups of clays: kaolinite, montmorillonite-smectic, illite and chlorite. Clay mineral layers are held together mainly by Van der Waals bonding and some contribution from electrostatic interaction or hydrogen bonding (Teku, 2017).

2.3.3.2 *Kaolinite clay*

Rocks that are rich in kaolinite are known as kaolin or China clay. The name is derived from gaoling, a village near Jingdezhen, Jiangxi province, China. Kaolin is a soft, earthy, usually white mineral, produced by chemical weathering of alluminumsilicate minerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, given it a distinct rust hue. Lighter concentration yield white, yellow or light orange colours (Teku, 2017).

The chemical formula for kaolinite is:

$Al_2\,O_5\,SiO_2\,(OH)_4$

Plate II: Kaolinite image (Teku, 2017)

Kaolin is resistant to acid leaching due to its high octahedral aluminum content, and the transformation of kaolin into metakaolin will increase the susceptibility of the former to the aluminum and iron cations leaching from the octahedral layer. The phase transformations that occur when kaolin is calcined at high temperatures are demonstrated by the chemical reactions illustrated as follows (Teku, 2017).

$2SiO_2Al_22H_2O \longrightarrow 2SiO_2Al_2O_3 + 2H_2O_{(g)}$ (2.1)

Kaolinite ~537℃ metakaolinite

$2SiO_2Al_2O_3 \longrightarrow Al_2O_3Si_2 + SiO_2$

Metakaolinite ~983℃ primary 1:1 mullite (amorphous) (2.2)

(Al- Si spinel)

2.3.3.3 *Sources of Kaolinite clay in Nigeria*

The bulk of the Kaolinite clay deposits in the country are either sedimentary or residual in origin and are usually associated with granitic rocks. Occurrences of kaolin have been recorded in different parts of the country and specific abundant deposits have been identified in parts of Enugu, Anambra, Kaduna, Katsina, Plateau, Ondo, Ogun, Oyo, Bauchi, Sokoto, Niger and Borno States, Nigeria. Of these reserves, about 800 million tons of probable/proven deposits have been quantified (Teku, 2017). For this work the kaolinite clay used was obtained from Kutigi, Lavun Local Government in Niger State, Nigeria.

2.3.3.4 *Application of kaolinite clay*

Kaolin is one of the most valuable of the industrial clays which is used in most manufactured products. Prominent uses include paper filling and coating; paint, plastic, adhesive and ink pigment; rubber reinforcing agent; ceramic raw materials for porcelain, dinnerware, tiles and 35 enamels; catalyst for petroleum cracking and auto exhaust emission catalytic control devices; cosmetics base; and digestive coating remedy. Kaolin is used in ceramics, medicine, coated paper, as a food additive in toothpaste, as a light diffusing material in white incandescent light bulbs, and in cosmetics (Jorge *et al*., 2011).

It is also used in paint to extend titanium dioxide (TiO_2) and modify gloss levels; and in adhesives to modify rheology. Kaolin was long used in the production of common smoking pipes in Europe and Asia. The largest use is in paper production, including ensuring the gloss on some grades of paper (Bawa, 2012). Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle or as liquid slurry.

2.3.3.5 *Metakaolin as heterogeneous catalyst*

Metakaolin is one of the heterogeneous catalysts used to produce biodiesel through transesterification of vegetable oils. Heterogeneous catalysts exhibit many advantages such as environmentally friendly, easy separation and simple post treatments (Liu *et al*., 2018). Functionalized heterogeneous catalyst such as clays, carbons, zeolites, mesoporous silica and metal oxide has become an active research area over several decades due to their interesting catalytic performance (Narkhede *et al*., 2015).

The study on clay based eco-friendly catalysts becomes the need of the day. Clay catalysts are less expensive, reusable and non-corrosive and have no disposal problems (Prabbakaran and pushpaletha, 2017).

Modified kaolinite (metakaolin) has proved to be efficient solid catalyst and catalysts support in various reaction. This is because of their robust enhancement in surface area, thermal stability and acidity. This has led to improve conversion, yield and selectivity in several reactions (Alaba, 2015).

Studies have been conducted on the use of modified Kaolin from kaolinite as heterogeneous catalysts for biodiesel production. Calcination at the temperature range of 550 to 590^{o}C modifies Kaolinite to metakaolin (Alaba, 2015).

Acid activation enhances kaolinite acidity, surface area, pore size and volume as well as it catalytic properties. This makes it a suitable precursor for a solid acid catalyst for petrochemical processes (Lenarda *et al*., 2007) Organic and inorganic acid activate Kaolin chemically (Hussain *et al.*, 2016).

The solubility of kaolinite varies from acid to acid, ration of Kaolin to acid, operating temperature, leaching period, Kaolinite varies from acid to acid, ration of kaolinite to acid operating temperature, leaching period, Kaolinite particle size as well as the concentration of the acid. Kaolinite solubility increases with acid concentration and leaching period but excess ive leaching leads to decrease in surface area (Panda *et al.*, 2010). It was reported that under the same activation condition, conversion increase with increasing specific surface area (De Oliveira *et al.,* 2013).

$$Al_2Si_2O_5\,(OH)_4\ Al_2O_3 2SiO_2 + 2H_2O \tag{2.3}$$

2.3.4 Biodiesel

Biodiesel is a renewable clean fuel that can serve as a possible alternative to petroleum diesel. It is derived from vegetable oil and animal fat through transesterification (Olutoye *et al*., 2015; Karthikeyan *et al.,* 2014). The production of this clean fuel from different feedstock and its usage has improved greatly in many progressive nations globally and the technology for synthesis of biodiesel from vegetable oils and animal fats has been well-established. Nigeria as a country is blessed with the capacity and ability to explore this technology for domestic energy supply and export when it comes to manpower and material resources (Bugaje, 2013).

Biodiesel is defined as a non-petroleum based diesel fuel which consist of mono alkyl esters of long chain fatty acid derived for transesterification of renewable lipid sources (Vegetable oils and animals fats) and alcohol in the presence of an Acid (H_2SO_4 or HCl) or alkali catalyst (NaOH or KOH), (Rouse, 2008; Mohammed, 2018; Gerpen, 2005; Dunford, 2013).

Biodiesel has been considered as one of the interesting alternative and environmentally benign fuels (Yusuff *et al.,* 2017). Alcohol that can be used in biodiesel production are those with short chains, including methanol ethanol, butanol and amylic alcohol (Romano and sorichetti 2011).

The most widely used alcohol is methanol (CH_3OH) and ethanol (C_2 H_3OH) because of their low cost and properties. Methanol is often preferred to ethanol in spite of its high toxicity, because its use in biodiesel production requires simple technology; excess alcohol may be recovered at a low cost and higher reaction speeds are reached. Methanol is light, volatile and colorless. It is considered a safe fuel. However, it is in fact flammable and burns with an invisible flame and it biodegrade quickly when compared with petroleum fuels. Methanol is a polar liquid at ambient temperature (25^0C) in spite of attracting water molecules in stored case; it still has bad solubility in water and petrol or organic compound (khurshid, 2014). The choice of which alcohol to use is determined by its cost, water content, easy of recovery for recycles and quantity required (Teku, 2017)

Biodiesel bears similar properties to Petroleum diesel (Gerpen, 2005; Khurshid, 2014). Biodiesel can either be used with pure form (B100) in diesel vehicle or blended with traditional petroleum diesel (Mohammed, 2018; Dunford, 2013) for example (B20), Blends include B2 (2% Biodiesel). (Romano and Sorichetti, 2011; Teku, 2017).

Biodiesel is usually used as a petrol diesel additive to reduce level of particulates, carbon monoxide and hydrocarbons from diesel powered vehicles (Teku, 2017). Biodiesel contains electronegative elemental oxygen; therefore, it is slightly more polar than diesel fuel and as a result of the viscosity of biodiesel is higher than that of diesel fuel (Mohammed, 2018). Biodiesel has environmental advantages such as low toxicity biodegradability, low levels of Carbon dioxide and monoxide emission (Mohammed, 2018; Khurshid, 2014; Teku, 2017). It does not contribute to net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect (Mohammed, 2018).

Biodiesel can be used in existing diesel engines without modification (Dunford 2013). The biodiesel yield of 80 to 100% can be obtained depending on the feedstock, amount of alcohol, catalyst, reaction temperature and time (Mahammed, 2018; Mathiyazhagan and Ganapathi 2011; Daramola *et al.,* 2016). Biodiesel can be obtained by four methods which are pyrolysis or thermal cracking, micro emulsification, direct use and blending and transesterification (Sharma, 2015; Sani *et al.*, 2012).

2.3.4.1 *Metakaolin for Biodiesel production*

Ramirez-ortiz *et al.,* (2012) used metakaolin as a catalyst for transesterification of waste cooking oil and obtained 95% biodiesel yield at catalyst (Metakaolinite) of 5 wt %, molar ratio of oil to methanol 1:23, Reaction time of 4 h and reaction temperature of 160^o C. The authors reported that the results showed that Metakaolinite is a prominent, in expensive, reusable and thermally stable catalyst for the transesterification of waste cooking oil.

Teku, (2017), also reported the use of Metakaolin derived from kaolin for the transesterification of waste cooking oil and the optimum yield of biodiesel was 92.7% in 2 hours reaction time, reaction temperature of 60^oC, amount of catalyst 4 wt%, methanol to oil ratio of 15:1.

Dang *et al.,* (2013) reported the application of kaolin based catalysts in biodiesel production via transesterification of vegetable oils in excess. Methanol and the conversion efficiencies of the vegetable oils which are soybean and palm oils are $97.0\pm 3.0\%$ and $95.4\pm3.7\%$ respectively. The Authors reported that the Metakaolin produced recommended for use as catalyst support, due to its improved specific surface area and pore volume, and due to its thermal stability which can be of additional advantage in elevated temperature catalytic applications.

Alaba, (2015) also reported the synthesis of solid acid catalyst from Kaolin for efficient production of biodiesel from Shea butter and sulphated nanoporous HY zeolite (SHY) gave biodiesel yield of 90.76% at 200^{o}C for 6 h. The Author reported the result indicates the pore structure and acid strength decide the acidity of solid acids catalysts in biodiesel production.

Subsequently, Liu *et al.*, (2018) used an efficient solid acid catalyst (Ce/Kaolin clay) for transesterification of cotton seed oil to fatty acid methyl esters (FAME) and the yield of FAME was up to 91% at methanol flow rate of 4.0 ml/min, reaction time of 3 h, reaction temperature of 60^{o}C and catalyst amount of 15g and the author also reported that the result indicated that the Ce/kaolin clay catalyst has a good potential for use the large scale production of FAME.

2.4 Methods of Biolubricant Production

Different methods are used to produce biolubricants such as esterification, transesterification, hydrogenation, and hydrogenation-esterification (Hossain *et al*., 2018).

2.4.1 Esterification

Generally, ester based biolubricants can be prepared through esterification reactions between polyhydric alcohols with fatty acids in the presence of acid catalyst. The employed polyols such as neopentyl glycol (NPG), trimethyolpropane (TMP), pentaerythritol (PE) and glycerol (Gly) are able to render different characteristics to the biolubricant product. Meanwhile, a different carbon chain member of carboxylic acids, such as acetic acid, propronic acid, oleic acid, valeric acid, caprylic acid and levullinic acid, can be used for the esterification (Hossain *et al*., 2018). Different fatty acids and polyol feedstock render different characteristics to biolubricant products for automatic and industrial usage (Hossain *et al*., 2018).

2.4.2 Hydrogenation

Hydrogenation of esters is an important upgrading process for the synthesis of biolubricants, surfactants, plasticisers and fatty alcohols which have many applications in agrochemicals, pharmaceuticals and fine chemicals. The reduction of esters and ketones is by employing hydrogen molecule at higher temperature and pressure for producing ester-based biolubricant that have a significant importance in our daily life. The normal ester-based lubricant have a high oxygen content and unsaturation level, which are not suitable for engine oils or fine chemicals and are not biodegradable. On the other hand, biolubricants produced through hydrogenation process, increase the hydrogen content and saturated carbon chain can be used as engine oils which might satisfy all types of lubrication (Hossain *et al*., 2018).

2.4.3 Hydrogenation – esterification

One step hydrogenation-esterification is another upgrading process in which bio-oils are converted into biofuel (biolubricants). The final products are suitable for combustion and become static oxygenous hydrocarbons, as they are hydrogenated esters in which esterification and hydrogenation are the fundamental reactions. The main constraints of bio-oil are fatty acid, aldehydes and ketones and phenols, which have a negative effect on the properties of bio-oils. Acetic acid, levulinic acid, surfural, hydroxyacetone, phenol and ethane diol are considered as model compounds for producing biolubricants. To convert these mixtures into combustible and stable compounds (esters), a one-step hydrogenation-esterification (OHE) process is performed over different bi-functional, Lewis acid catalysts in methanol/ethanol (Hossain *et al*., 2018).

2.4.4 Transesterification

Transesterification reaction is another conventional process for producing biolubricants using triglyceride-based feedstock and alcohols in the presence of catalyst. Transesterification is reportedly superior to other techniques due to its lower capital and energy consumption (Wang *et al.*, 2014).

2.5 Transesterification of Vegetable Oil to Produce Biolubricant

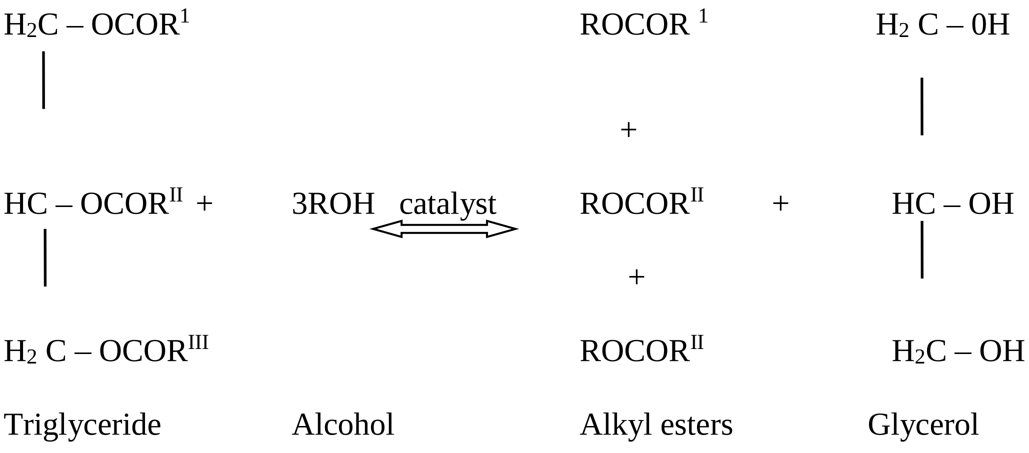
In biolubricant production, two stages of transesterification is involved in which biodiesel is first produced then biolubricant is produces in the second transesterification with biodiesel and polyol in the presence of a catalyst. Transesterification modification in the carboxyl group is the process of using an alcohol such as methanol or ethanol in the presence of a catalyst like sodium hydroxide or potassium hydroxide to chemically break the molecule of the raw vegetable oil into their alkyl esters (biodiesel) with glycerol as a byproduct. Few trans-esterification reactions are reported with higher alcohols C_8 to C_{14} for use as lubricant. The process of transesterification is affected by the mode of reaction, molar ratio of alcohol to oil, type of alcohol, type and concentration of Catalyst, reaction time and temperature (Binyamin *et al.*, 2015). Production of biolubricants from triglycerides (animal fats or vegetable oils) involves two stages, which are production of fatty acid methyl esters and followed by production of biolubricant.

2.5.1 Production of Biodiesel

Biolubricants are vegetable oil based lubricants that are biodegradable, renewable and are non-toxic to environments (both terrestrial and aquatic). It is a formulation produced from vegetable based oils together with additives. A biolubricant can be produced from vegetable oil (rapeseed oil), from synthetic esters obtained from modified renewal oils or from petroleum based products (Salimon *et al.*, 2014).

Fatty acid methyl esters (biodiesel) are produced by transesterification of vegetable oil with methanol in the presence of a catalyst (Mukhtar, 2017). This is one of the processes used in biodiesel production. It is the commercial and conventional methodology use for the biodiesel production, it is also known as alcoholysis (Sales, 2011; Teku, 2017). Transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol (Refaat, 2010).

These reactions are often catalyzed by the addition of an acid or base. The transesterification consists of three consecutive and reversible reactions. The stoichiometric ratio for the transesterification reaction is 3 moles of alcohol and 1 mole of triglyceride. An extra amount of alcohol is added in order to move the reaction to the methyl esters formation (Sales, 2011).



$$\begin{array}{lcccl} H_2C-OCOR^{1} & & & ROCOR^{1} & H_2C-0H \\ \vert & & & + & \vert \\ HC-OCOR^{II} \;+ & 3ROH & \xleftrightarrow{\text{catalyst}} & ROCOR^{II} \;+ & HC-OH \\ \vert & & & + & \vert \\ H_2C-OCOR^{III} & & & ROCOR^{II} & H_2C-OH \\ \text{Triglyceride} & \text{Alcohol} & & \text{Alkyl esters} & \text{Glycerol} \end{array}$$

Figure 2.1: Transesterification reaction (Omotoso and Akinsanoye, 2015).

Transesterifcation of triglyceride is a stepwise and reversible process in which diglyceride and monoglyceride are produced as intermediates in the reaction of alcohol with triglyceride. When methanol is used as the alcohol in the production of biodiesel, triglycerides molecules react with methanol to produce diglycerides and methyl ester in a subsequent reaction; diglyceride reacts with a second molecule of methanol to form monoglyceride and a second molecule of methyl ester. While in the final reaction, monoglycerides reacts with a third molecule of methanol to yield one mole of methyl ester and glycerol. Figure below show this consecutive and reversible process (Mukhtar, 2017).

$$\text{Triglyceride} + \text{R'OH} \rightleftharpoons \text{Diglyceride} + \text{ROOR'}$$

$$\text{Driglyceride} + \text{R'OH} \rightleftharpoons \text{Monoglyceride} + \text{ROOR'}$$

$$\text{Monoglycerid} + \text{R'OH} \rightleftharpoons \text{Glyceride} + \text{ROOR'}$$

Figure 2.2: Reaction of Triglyceride, Diglyceride and Monoglyceride with methanol (Mukhtar, 2017)

2.5.2 Biolubricant Production

In transesterification of vegetable oil for polyol ester (biolubricant) synthesis, biodiesel (alkyl ester) is an immediate product. Biolubricants are produced via transesterification of fatty acid methyl esters and polyols such as Trimethylolpropane (TMP), neopentyl glycol (NPG), pentaerythriol (PT) and glycerol in the presence of catalyst (Musa et al., 2016). This reaction occurs via three steps. Trimethylopropane monoester (TMPME) and trimethylopropane dieters (TMPDE) are the immediate produce while the triester (trimethylopropane) is the end desired bio based lubricant. Methanol is a resultant co-product from the reaction. The methanol (CH_3OH) is eliminated through processing to ensure completion of reaction (Said *et al.,* 2014).

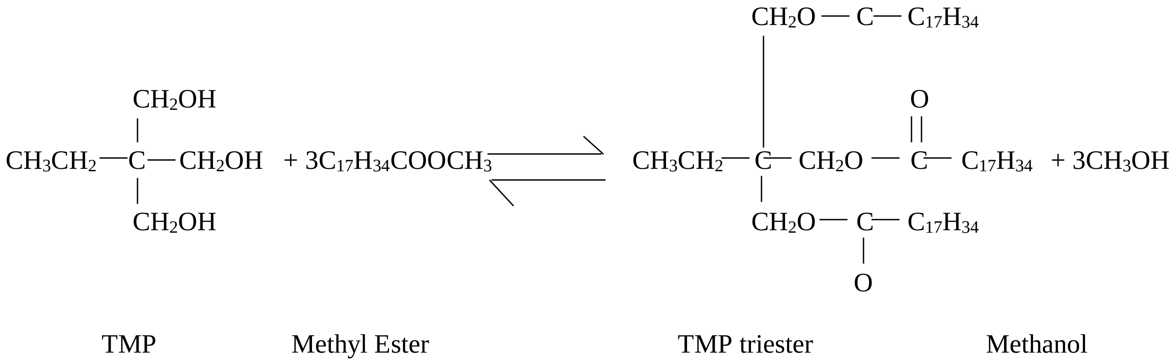


Figure 2.3: Transesterification reaction of neem methyl ester with TMP to produce biolubricant (Samson, 2015)

2.6 Properties of Biolubricant

2.6.1 Viscosity

Viscosity which is regarded as the most essential property of any lubricating oil is the measure of fluid resistance to flow at different range of temperatures. It is a determining factor of the operating characteristics of a lubricant. If the oil viscosity is too high it can slow down the movement of the sliding surfaces and if the oils viscosity is too low, a liquid oil film cannot be maintained between two moving or sliding surfaces. The viscosity of lubricants is measured at 40^oC and 100^oC through a device called viscometer. Generally, increase in temperature leads to decrease in viscosity of oil and vice versa (Mukhtar, 2017).

2.6.2 Viscosity Index

Viscosity Index (VI) measures the behaviour of different lubricants at different range of temperature. A high viscosity index is an alluring characteristic since lubricants are desired to perform over an extensive temperature range from high operating temperature to an ambient temperature when engine components are at rest. In addition, for a lubricant to be used continuously under temperature change, its viscosity should not change much with change in temperature (Mukhtar, 2017).

2.6.3 Flash Point

Flash point is the minimum temperature at which a substance gives off vapour large enough to form an ignitable mixture with air (Musa *et al.*, 2015). Lubricants with lower flash point are inclined towards fire hazard. The flash point of a substance should be high for minimum volatilization at maximum temperature and to allow safe operation of equipment (Mukhtar, 2017).

2.6.4 Fire Point

Fire point is the minimum temperature that a lubricant will maintain burning for five seconds, when a little fire is brought close to it. It determines the combustibility of biolubricant and it is an imperative component to be considered when storing or handling biolubricant with combustible materials (Mukhtar, 2017).

2.6.5 Cloud point

Cloud point is the temperature at which clouds of crystals are seen in a liquid. It is often used to determine if a lubricant will be used in low temperature regions. The operating temperature should be kept beyond the cloud point to avoid clogging of filters in a device (Mukhtar, 2017). Under cold climate conditions, higher cloud point can affect the performance of an engine in a negative way (Musa *et al.*, 2015).

2.6.6 Pour Point

The lower temperature at which a liquid is still able to pour is referred to as pour point. This property is one of the main problems for plant based oils to be used as a lubricant. Normally, oil extracted from plants without any chemical modification will show a poor pour point value of roughly just above 0^oC. Pour point determines the suitability of lubricant oil in relatively low temperature regions. Generally, lubricating oils used for devices operating at low temperatures should have low pour point to avoid solidification which can cause jamming. Researchers established that the pour point value of lubricating oil can increase by the presence of waxes (Mukhtar, 2017).

2.6.7 Volatility

Volatility of lubricant determines the evaporative loss characteristics. Increase in volatility of a lubricant enhances rapid rate of evaporation of smaller hydrocarbon molecules present in the lubricant due to increase in temperature, and in that case, the volatility of lubricant should be low. Volatility is essential in devices that require high operating temperature and where low viscosity oils are used. The flammability of a lubricant increases as its volatility increases (Mukhtar, 2017).

2.6.8 Total Acid Number

The total acid number of lubricant is the weight in milligrams of sodium hydroxide required to neutralize one gram of oil. This parameter indicates that all the materials present in the oil are capable of reacting with sodium hydroxide under stated test condition. It is also a measure of acidity of a lubricant and it is capable of determining the degradability of a lubricant while in use (Mukhtar, 2017).

2.6.9 Density

This is a fundamental physical property of oils, which is a ratio of mass to volume of a liquid or solid. Density is an important property of oil which gives an indication of the delay between injection and combustion of fuel in a diesel engine and the energy per unit mass. These can affect the efficiency of the fuel atomization for combustion systems without air (Mukhtar, 2017).

2.7 Factors Affecting Biolubricant Production

The factors that affect biolubricant production are as follow:

2.7.1 Reaction Temperature

Temperature is the one of the major parameter that affects the rate of reaction. In transesterification the higher the temperature, more energy is delivered to overcome the minimum activation energy required in the reaction, which resulted in more yield. Temperature of the reaction is an important parameter which influences biolubricant yield. As the temperature increases, the rate of reaction also increases and the reaction time is shortened due to the reduction in the viscosity of the oils (Alemayehu and Abile, 2014).

Abubakar (2015), reported the effects of temperature on conversion of palm methyl ester (PME) to palm biolubricant was carried out in the oscillatory flow reactor (OFR) via transesterification of PME and trimethylolpropane (TME) with sodium methoxide used as catalyst. The reaction temperatures investigated were between110 ℃ to 150 ℃ and optimum yield of trimethylolpropane ester (TE) achieved at 140℃.

Yeti (2014), studied the effect of temperature on transesterification of calophyllum methyl esters (CMEs) and trimethylolpropane (TMP) between110 ℃ to 150 ℃ with calcium oxide as catalyst, the optimal yield (79%) of biolubricant product was achieved at 130 ℃.

In another related studies Said *et al*., (2014) reported the property of temperature on the production of biolubricant from jatropha methyl-ester (JME) and TMP with paphiaundulata shell waste between 90 ℃ to 130 ℃ and reported the highest percentage of tri-ester (78.67%) was found at temperature of 110 ℃. The low temperature tends to reversible reaction. The transesterifcation of jatropha methyl ester with trimethylolpropanol and sodium methoxide ($NaOCH_3$) as catalyst was also reported by (Abubakar, 2015), that the highest amount of triester formed was 47% at 200 ℃. Besides, the most favorable response temperature was recommended at 150 ℃ with 45% of tri-ester produced. This is as a result of irrelevant enhancement on triester translation at 200 ℃ than 150 ℃. Response at higher temperature can cause the most unstable JME component to vaporize which reduce the total residence time.

However, Bilal *et al.,* (2013) studied the synthesis of biolubricant from Jatropha curcas seed oil and reported temperature of 120 °C for 2.5 hours. Ainaatul and Salimon, (2013), studied the synthesis of rubber seed oil (RSO) biolubricant using the esterification process. The effect of reaction temperature (110 –160℃), and. Full conversion of TMP ester with 78% of TE was achieved at the temperature of 150 ^{o}C. Ainaatul and Salimon (2012), reported a study on the optimization of esterification reaction of rubber seed oil (RSO) with trimethylolpropane (TMP) using H_2SO_3. The studied showed that RSO was successfully converted to biolubricant with 78% yield at reaction temperature (150 ^{o}C)

2.7.2 Molar Ratio

Yeti *et al*., (2014), reported the effect of molar ratio on transesterification of calophyllum methyl esters (CMEs) and trimethylolpropane (TMP) between 3.5 and 4.3:1 with calcium oxide as catalyst, the optimal yield of 79% of the biolubricant product was achieved at 3.9:1 of CMEs and TMP respectively. However Bilal *et al.,* (2013) used 3.5:1 of jatropha methyl ester with ethylene glycol in production of biolubricant. Another study by Musa *et al.,* (2015) showed a 96.56% yield of biolubricant resulting from transesterification of castor oil biodiesel with trimethylolpropane (TMP). The reaction was achieved at a molar ratio of 4:1.

Said *et al.,* (2014) also investigated the production of polyol ester from Jatropha biodiesel transesterification using *Paphiaundulata* shell waste as heterogeneous catalyst. The reaction was conducted at a ratio of Jatropha Methyl ester to Trimethylolpropane of 4:1, the author reported the optimum 78.67% composition of triester (TE). Menkiti *et al.,* (2015) synthesized

Fluted pumpkin biolubricant (FPBL) by transesterification techniques. The effect of mole ratio (4-6) was studied on the biolubricant yield. The highest triester yield of 81.42% was obtained at the FPME: TMP mole ratio (6:1).

2.7.3 Catalyst Type and Concentration

The amount and type of catalyst used for transesterification reaction process normally depends on the purities of the feedstocks and technique used for the transesterification process. For the purified feed stock; any kind of catalyst might be used. However feed stock with much moisture and free fatty acids content homogeneous catalysts are not suitable because this could results in soap formation. The fatty acid alkyl ester produced increases with increase in amount of catalyst because more active sites are available by addition of more catalyst to the transesterification process (Alemayehu and Abile, 2014).

In transesterification of vegetable oil, catalyst used could be classified as alkali, acid, enzyme or heterogeneous catalysts, sodium hydroxide and potassium methoxide (Khurshid, 2014; Talha and Sulaiman, 2010; Romano and Sorichetti, 2011). Abubakar, (2015), studied the effect of catalyst on biolubricant production using rapeseed methyl ester with TMP and 0.5 % sodium methoxide as catalyst at 110-120^{o}C for 10 hours and obtained 99 % tri-ester.

In another related study, determination of the effect of catalyst amount, was also reported by the author (Abubakar, 2015), experiments were carried out with 0.7, 0.8, 0.9 and 1% w/w (sodium methoxide) catalyst based on total weight of POME and TMP. The other reaction conditions are 120 °C for 2 hours with molar ratio: 3.8:1 (POME/TMP) and agitator speed and 0.9% were found to be the optimum.

Bilal *et al.,* (2013) used 0.8% w/w of sodium methoxide of the total reactant. Muhammed *et al.,* (2012) reported 1% of sodium methoxide catalyst of the weight Jatropha methyl ester.

The effects of catalyst concentration on transesterification process as it promote the yield of biolubricant.

The development of tri-ester (TE) is small (62.34%) at 1% (w/w) of sulphuric acid but increases as catalyst concentration increases up to 79% at 2% (w/w). The development of tri-ester decreased as the concentration of sulphuric acid increases up to 4%. Higher concentration of sulphuric acid lead to the increased in the quantity of water in the reaction, although water have been removed in the first stage of the process as sulphuric acid is an aqueous and it also distress the finish product and this becomes more viscous with much darker colour (Ainaatul and Salimon, 2012).

2.7.4 Stirring speed

Proper mixing of the feed stock (Alcohol and oil) enhances contact between the feedstock and promote esterification reaction. Motorized mixing is mostly used in transesterification process, generally mixing power should be improved to make sure quality and homogenous mixing of the feed stock and the speed of agitation plays a vital role in the improvement of the desired product, the mixing of oil and catalyst promote the reaction, (Alemayehu and Abile, 2014). Low stirring speed shows low product development and higher stirring speed favours soap formation and this is as a result of the reverse reaction of transesterification reaction (Bilal *et al.*, 2013).

2.7.5 Time of Reaction

Time is one of the parameters considered in biolubricants productions. Ainaatul and Salimon, (2013) studied the synthesis of rubber seed oil (RSO) biolubricant using the esterification process. The effect of reaction time (2-11 hours) was investigated on the biolubricant yield. Full conversion of TMP ester with 78% of TE was achieved at 5 hours reaction time. Ainaatul and Salimon (2012), also reported a study on the optimization of esterification reaction of rubber seed oil (RSO) with trimethylolpropane (TMP) using H_2SO_3. The studied showed that RSO was successfully converted to biolubricant with 78% at reaction time 5 hours.

Yeti *et al.*, (2014) reported a study on the production of biolubricant from Calophyllum methyl esters studying the effect reaction time on the yield of biolubricant. In the study, biolubricant was produced by transesterification reaction of trimethylolpropane (TMP) and *calophyllum* methyl esters in the presence of a catalyst (calcium oxide). The author reported 79.0 % yield of trimethylolpropane ester at optimum reaction time of 5 h.

Aziz *et al.*, (2014) reported the optimization of transesterification of palm oil methyl ester and pentaerythritol by using response surface methodology (RSM). The affecting parameter was selected at reaction time (1–5 h), in order to produce pentaerythritol ester (tetraester). The optimum 1 h reaction time was obtained with the result of the pentaerythritol ester's yield of 40.13%.

2.8 Applications of Biolubricants

Biolubricants have been used as alternative lubricants in industries and automotive as they reduce friction and wear and operating noise and also improve heat transfer. They have a longer adherence period on metal surface as they have polar-based chemicals structures, whereas petroleum-based lubricants are non-polar hydrocarbons and do not exhibit adhering properties on metal surfaces. The application of biolubricant products in automotive industry includes; hydraulic fluids, metal working oils, two stroke and three stroke engine oils and chainsaw fluids. In addition, biolubricants are used as engine oils, transmission fluids, gear box oils, and brake and hydraulic fluids and are able to provide a slippery surface, reduce metallic corrosion and enhance performance of the machinery (Hossain *et al*., 2018)

2.9 Advantages and Disadvantages of Biolubricants

2.9.1 Advantages of Biolubricants

i. They produce a cleaner, safer, less toxic environment
ii. They cause fewer skin problems for those working with engines and hydraulic systems.
iii. The physical and chemical properties of biolubricants are safer owing to their higher flash point, low pour point, constant viscosity and less vapour and oil mist.
iv. They can reduce pollution in storm water from leaks in engines, hydraulic systems and brake lines.
v. They are highly biodegradable and their cost is less over the product's lifecycle, as less maintenance and storage and disposal systems are needed (Hossain *et al*., 2018).

2.9.2 Disadvantages of Biolubricants

i. They produce low emission due to the high range of boiling temperature of esters.
ii. They are 3 -5 times more expensive than petroleum oils (Hossain *et al*., 2018)
iii. High cost and limited availability of biolubricant feedstock (Mukhtar, 2017)

2.10 Summary of Some Previous Research Study Relating To This Study

Table 2.3 gives the summary of some related studies previously researched.

Table 2.3: Previous research related to this study on Biolubricant production

S/N	Title	Feedstock and Conditions	Yield	Author
1	Statistical optimization of Biolubricant production from Jatropha curcas oil using TMP as a polyol	Jatropha curcas oil JME: TMP=3.9:1 Temp=120 ^{0}C Time=3hrs Catalyst= KOH(0.85w/w)	96.95%	Musa *et al.,* (2016)
2	Synthesis and characterization Of Calcium methoxide as heterogeneous Catalyst for TMP esters conversion Reaction	Palm oil PME: TMP=1:6 Temp=180 ^{0}C Time=8 hrs Catalyst loading=0.3 %w/w	92.389%	Masood *et al.*, (2012)
3	Process optimization and modelling of biolubricant base stock synthesis From crude palm oil	Palm oil TMP:POME=1:4.99 Temp=159.9 ^{0}C Time=3 hrs31min 63 sec	84.681%	Nkem and Nwakaudu (2019)

4	Synthesis and characterizatation of TMP based biolubricants from castor oil	Castor oil TMP:COME=1:4 Temp=120 ^{0}C Time=60 min Catalyst= 0.8 wt%	96.56 %	Musa *et al.*, (2015)

CHAPTER THREE

3.0 MATERIALS AND RESEARCH METHODOLOGY

3.1 Materials

The Tables 3.1 and 3.2 show the list of equipment/ apparatus and materials used in this research work respectively.

Table 3.1: List of Equipment and Apparatus used for Biolubricant production

Equipment	Manufacturer	Source
Oven	Gallenkamp	CHE LAB, FUT, Minna, Nigeria
Digital Weighing balance	Citizen	CHE LAB, FUT, Minna, Nigeria
Furnace	SXL-5-12	MAT & MET LAB, FUT, Minna, Nigeria
Heating mantle	Dibby	CHE LAB, FUT, Minna, Nigeria
Water Deionizer		CHE LAB, FUT, Minna, Nigeria
Magnetic stirrer		ABE LAB, FUT, Minna, Nigeria
Separating funnel	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Sieve	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Thermometer	Rex	CHE LAB, FUT, Minna, Nigeria
Beaker	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Conical flask	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Measuring cylinder	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Density bottle	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Burrete	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Pipette	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Soxhlet extractor	Pyrex, England	CHE LAB, FUT, Minna, Nigeria
Retort stand and clamp	-	CHE LAB, FUT, Minna, Nigeria

CHE LAB – Chemical Engineering

ABE LAB - Agricultural and Bio resources

MAT & MET- Materials and Metallurgical

FUT- Federal University of Technology

Table 3.2: List of materials for Biolubricant production

Chemicals	**Purity (%)**	**Manufacturer**
Potassium Hydroxide Pellet	95	Burgoyne & Co. Mumbai India
Hexane	95	Analar BDH
Potassium Iodide Solution	92	M&B England
Phenolphthalein Indicator		
Sodium Thiosulphate	95	M&B England
Carbon tetra chloride (CCl_4)	96	Analar BDH
Wij solution		Hopkins & Williams London
Deionised Water	100	CHE Department, FUT Minna
Trimethylolpropane	98	
Filter paper		
Methanol	97	
Piston and Mortar		
Kaolin clay		
Allamanda oil seed		

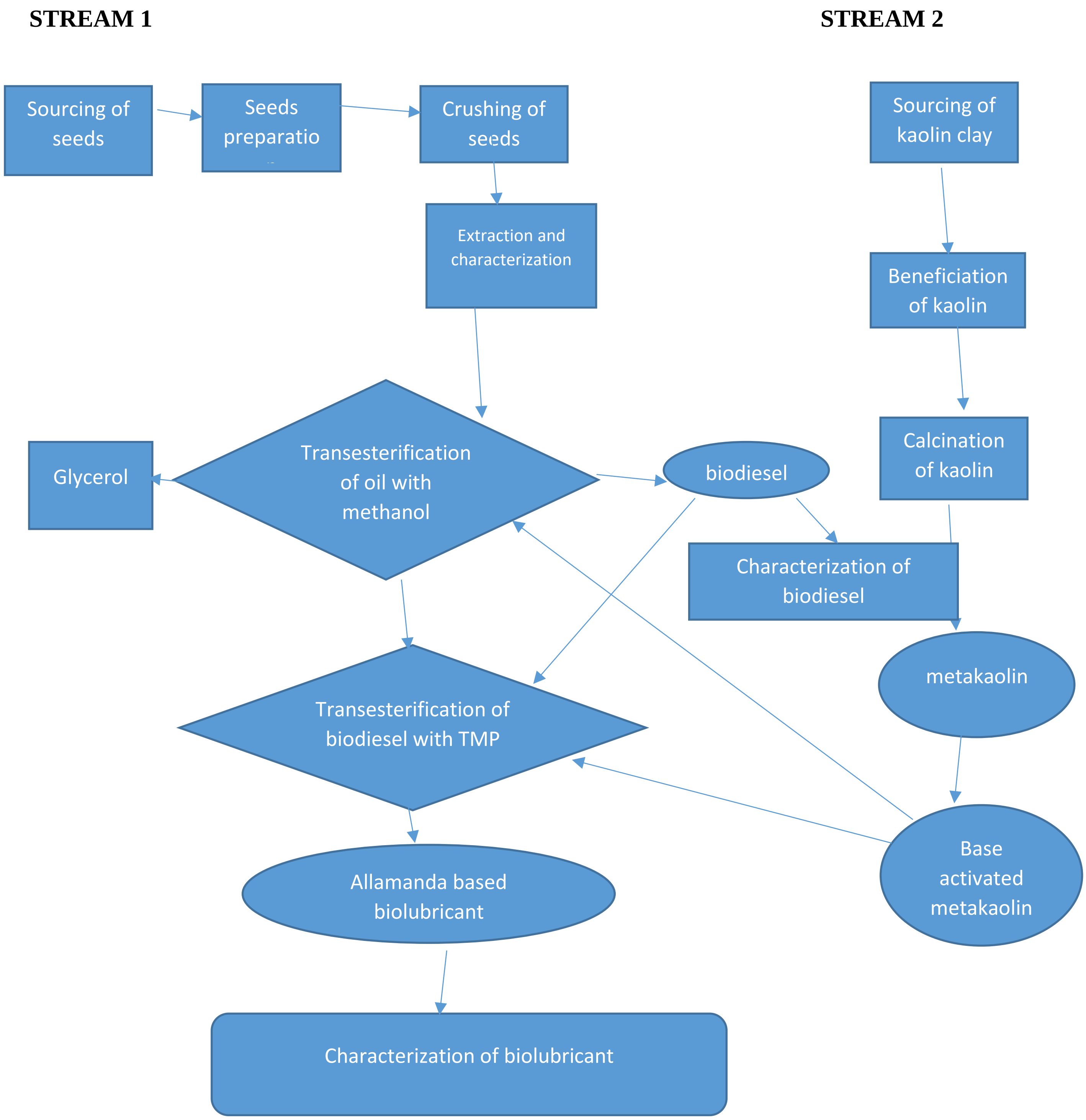


Figure 3.1: Flow diagram of steps for producing Allamanda based Biolubricant

3.2 Research Methodology

3.2.1 Allamanda Seed sourcing and Preparation for oil Extraction

The Allamanda seeds were source from Chiromawa Estate, Bosso Road and Type B Quarters, Minna, Niger State of Nigeria. The seeds were broken using stone to obtain the nut. The nuts were milled using grinder.

Plate III: Allamanda seed

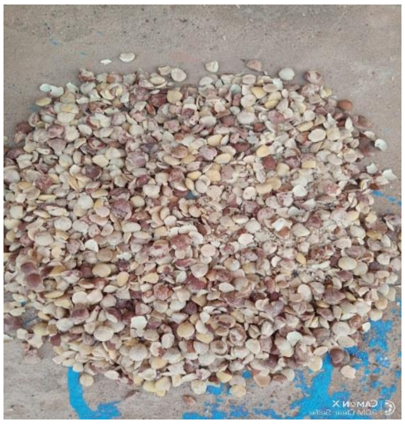


Plate IV: Allamanda kernel

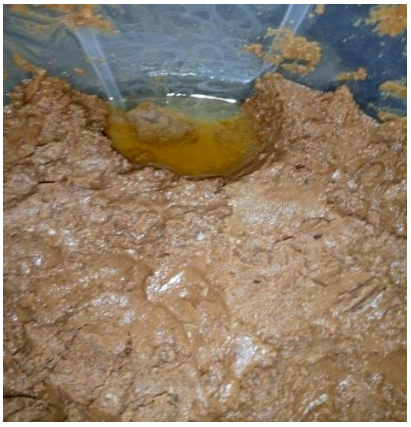


Plate V: Milled Allamanda seed

3.2.2 Extraction of Allamanda Seed Oil

Fifteen grams (15 g) of the sample was placed in the thimble and was inserted into the chamber of the Soxhlet extractor. 250 cm^3 of hexane was poured into the round bottom flask and the Soxhlet was heated to 60–65℃ and was left to run for 6 hours. The extracted oil was poured from the round bottom flask and was placed in an oven to at 105℃ to remove any moisture or residual solvent that may be present. The percentage yield was calculated as:

$$\text{Percentage oil yield (\%)} = \frac{weight\ of\ oil}{weight\ of\ sample\ on\ dry\ matter\ basis} * 100 \qquad (3.1)$$

(a) **(b)**

Plate VI: (a) Allamanda seed oil Extraction process (b) Extracted Allamanda seed oil

3.2.3. Characterization of extracted Allamanda seed oil.

The Allamanda seed oil was characterized for its physiochemical properties to determine it suitability for biodiesel production.

3.2.3.1 *Determination of moisture content*

Five grams (5 g) of the sample was weighed into the a weighed crucible the crucible and sample taken were then transferred into the oven and was set at 100 ^{o}C index and allowed to dry overnight. At the end of 24 hours, the crucible plus sample were removed from the oven and transferred to the desiccator and cooled for 10 mins and weighed (Mohammed 2018).

$$\%\text{moisture content} = \frac{W_3 - W_O}{W_1 - W_O} \times 100 \qquad (3.2)$$

Weight of empty crucible = W_0

Weight of crucible + sample = W_1

Weight of crucible +Oven dried sample = W_3

3.2.3.2 *Determination of specific gravity / density*

An improvised specific gravity bottle was washed and rinsed with acetone and dried. The bottle was filled with the water and its weight together with the content was taken. The water was then poured out and the bottle was rinsed with acetone and dried. The oil was then poured into it and the weight of the content in addition to the bottle was taken.

The specific gravity of the oil was thus calculated using specific gravity (Mohammed, 2018).

$$\text{Specific gravity} = \frac{Weight\ of\ oil}{Weight\ of\ equal\ volume\ of\ water} \times 100 \quad (3.3)$$

$$\text{Density} = \frac{Weight\ of\ oil}{Volume\ of\ oil} \quad (3.4)$$

3.2.3.3 *Determination of acid value and free fatty acids*

A 25 cm^3 of petroleum ether and 25 cm^3 of ethanol were mixed in 250 cm^3 beaker. The resulting mixture was added to10 g of oil in a 100 cm^3 conical flask and a few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M KOH to the end point with consistent shaking for which a dark pink colour was observed and the volume of 0.1M KOH Noted (Evwierhoma and Ekop, 2016)

The mathematical expression for this is given as:-

$$\text{Acid Value} = \frac{(V \times N \times 56.1)}{Weight\ of\ sample} \quad (3.5)$$

Where V = volume of potassium hydroxide used

N =Normality of potassium hydroxide

$$\%\ \text{FFA} \times 1.99 = \text{Acid value} \quad (3.6)$$

$$\text{And}\ \%\ \text{FFA} = \frac{Acid\ value}{2} \quad (3.7)$$

3.2.3.4 *Determination of saponification value*

Two grams (2 g) of the sample was weighed into a conical flask; 25 cm^3 of ethanoic potassrum hydroxide was then added. The content which was constantly stirred was allowed to boil gently for 60 min. a reflux condenser was placed on the flask containing the mixture and a few drops of phenolphthalein indicator was added to the warm solution and then titrated with 0.5 M Hydrochloric acid to the end point until the pink colour of the indicator disappeared (Mohammed, 2018).

$$SV = 56.IN\,\frac{(V_o - V_i)}{m} \tag{3.8}$$

Where:

Vo- volume of the solution used for the blank test

Vi – volume of the solution used for determination.

N – normality of HCl used, m = mass of sample.

3.2.3.5 *Determination of iodine value*

Specific weight (0.25 g) of the sample was weighed into a flask and it was dissolved into 10 cm^3 of chloroform 25 cm^3 of wiji's Iodine solution was mixed vigorously and was allowed to stand in a dark corner for exactly 30 mins. The excess 1odine was determine by addition of 10 cm^3 of 15% of potassium iodide solution; 100 cm^3 of water was added and titrated with 0.1M normal sodium thiosulphate using starch as indicator. The titration was continued until the blue black colour disappeared after vigorous shaking. A blank solution was also carried out without the oil with the same condition.

The 1odine value (IV) is given by the expression

$$IV = 12.69\,C(V_i - V_o)\text{ m} \tag{3.9}$$

Where: C – concentration of sodium thiosulphate used,

V_1- volume of sodium thiosulphate used for the blanks

V_2- volume of sodium thiosulphate used for determination,

m- mass of the sample.

3.2.4 Preparation of metakaolin

The raw kaolin was first beneficiated. The kaolin solution was then placed in an oven for 48 hours at a temperature of 150℃–200℃. The dried clay was ground and sieved to obtain finely powdered kaolin. The finely powdered kaolin was then calcined in an electric furnace at about 650℃ for 90 min to obtain a metakaolin. The metakaolin was activated by pouring 50 g of metakaolin in 150 ml of the prepared KOH solution and heated to and maintained at 90 ℃ for 3 h in a magnetic stirred water bath (Liu *et al.*, 2018). The resultant slurry was cooled to room temperature before washing with deionized water until the pH of the washed water was almost neutral. The final mixture was then dried in an oven at 100 ℃.

Plate VII: beneficiation and calcination processes

3.2.5 Characterization of the Catalyst

3.2.5.1 *X-ray diffraction (XRD) analysis*

X-ray diffraction patterns were obtained with a Bragg–Brentano powder diffractometer using CuKα radiation (λ = 1.54184 Å) and a graphite monochromator at an accelerating voltage of 45 kV with 40 mA flux in the diffracted beam. The samples were disk-shaped pressed powders. This is used for phase identification of crystalline material; XRD patterns of the raw and synthesized catalysts were recorded.

3.2.5.2 *X-ray fluorescence (XRF) analysis*

The elemental oxide compositions of the catalyst were analysed by XRF spectroscopy (XRF—Oxford, ED-2000, England) under energy-dispersive mode for precise measurement of both light and heavy elements.

3.2.5.3 *Scanning electron microscope (SEM) analysis*

Scanning electron micrographs were taken on a JEOL-JSM 5600 LV microscope, equipped with a 6587 EDS (energy dispersive X-ray spectrometry) detector, using an accelerating voltage of 20 kV. The samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. The SEM for the morphologies of the raw and synthesized samples was determined.

3.2.5.4 *Brunauer–Emmet–Teller (BET) analysis*

Brunauer-Emmett-Teller analysis was used to determine the surface area, mean pore diameter, and pore volume. BET analysis was used to determine the surface area, pore size and pore volume of the raw, calcined and alkaline activated samples.

3.2.6 Response Surface Optimization of Process Variables for Biodiesel Production

The response surface optimization of the effect of process variables on biodiesel production from Allamanda seed oil was carried out using Box-Behnken (BBD) design module of response surface methodology (RSM) available in Design Expert® Software as shown in Table 3.4. Three independent variables (temperature, reaction time and catalyst concentration) and one dependent variable (percentage yield of biodiesel) were considered. A total of 17 runs were performed. Statistical analysis of variance (ANOVA) was carried out using design expert 11.1.2.0 software. The range and levels of the variables investigated were chosen based on literature, for the temperature, reaction time and catalyst concentration (Mohammed, 2018; Teku, 2017; Qin *et al*., 2017; Egwim *et al.*, 2015*;Liu et al.*, 2018; Abdulkarim *et al.,*2013 and Khurshid, 2014) as shown in Table 3.3

Table 3.3: Experimental design for biodiesel production

Variables		**-1**	**0**	**+1**
Time (min)	A	60	120	180
Temperature (°C)	B	40	52.5	65
Catalyst concentration (%wt.)	C	0.5	2.75	5.0

The relationship between the biodiesel yield and the independent variables was established by fitting experimental data into a second order model. The general form of regression response model is in the form given in equation (3.3)

$$Y = b_0 + \sum_{i=1}^{k} b_{i\,X_i} + \sum_{i=1}^{k} b_{iiX_i^2} + \sum_{i<1}^{k} b_{ijX_{iX_j}} + e \qquad (3.10)$$

where Y is the response (dependent); X_i and X_j are the variables (Independent) variable; b_o is the intercept; b_i is the first order coefficient of the model; b_{ii} is the quadratic coefficient of i factor; b_{ij} is the linear coefficients of the model for the interaction between i and j factors; k is the number of variables optimized in the experiment while e is the error associated with response.

Table 3.4 shows the design matrix for biodiesel production.

Table 3.4: Box Behnken Design Matrix for Biodiesel Production

	Factor 1	**Factor 2**	**Factor 3**
Run	A:Time (min)	B:Temperature (^oC)	C:Catalyst (wt%)
1	60	65.0	2.75
2	120	65.0	5.00
3	120	52.5	2.75
4	180	40.0	2.75
5	120	65.0	0.50
6	60	52.5	5.00
7	180	52.5	0.50
8	120	40.0	5.00
9	120	40.0	0.50
10	120	52.5	2.75
11	120	52.5	2.75
12	180	52.5	5.00
13	180	65.0	2.75
14	120	52.5	2.75
15	120	52.5	2.75
16	60	52.5	0.50
17	60	40.0	2.75

3.2.7 Synthesis of Biodiesel from Allamanda seed oil

The reactions were carried out in a 500 cm^3 glass reactor equipped with a thermometer and magnetic stirrer at atmospheric pressure, placed on a heating mantle. The fixed 50 ml of Allamanda oil and the desired amount of the metakaolin activated with KOH catalysts (0.5-5.0 wt%) were added to the reactor, and then the methanol was introduced to the oil at constant methanol to oil ratios of 5:1. The reaction was operated at 40-65 ℃ with varied reaction time of 60-180 minutes. After the reaction was completed the sample was allowed to stand for 5 minutes before the reaction mixture was poured into a separating funnel to separate the biodiesel phase from the glycerol phase. The biodiesel was repeatedly washed with warm water until the wash water becomes colourless. The biodiesel was dried on a hot plate at 105 ℃ to evaporate away residual water and the yield was calculated as:

$$\text{Yield} = \frac{mass\ of\ biodiesel}{mass\ of\ oil} \times 100 \qquad (3.11)$$

Plate VIII: Biodiesel production processes

3.2.8 Characterization of Biodiesel

The physiochemical properties of fatty acid methyl ester (FAME) such as kinematic viscosity, density, flash point, cloud point, pour point, fire point, smoke point, acid value, and were determined according to ASTM methods.

3.2.8.1 *Determination of specific gravity*

A 50 ml neatly dried empty bottle was measured, its weight taken as $x_{1.}$ Distilled water was used to fill the bottle, weighed and reported as $x_{2.}$ Same density bottle was used but the water was substituted with biodiesel sample after drying, the weight of the bottle with biodiesel was recorded as $x_{3,}$ then the specific gravity was evaluated using the following equation (Mohammed, 2018).

$$\text{Specific gravity} = \frac{x_3 - x_1}{x_2 - x_1} \tag{3.12}$$

3.2.8.2 *Determination of density*

About 250 ml graduated cylinder and inserting into the cylinder a known mass of a hydrometer to note if it floats in the oil or it can be calculated from a known specific gravity of the oil with weight of water (1000 g) and then the density was calculated (Mohammed, 2018).

$$\text{Density} = \frac{Weight\ of\ oil}{Volume\ of\ oil} \tag{3.13}$$

3.2.8.3 *Determination of Cloud Point*

Biodiesel was poured into a fixed level jar for a test; it was then put into a cold water bath. The measured temperature where the biodiesel starts to form cloud around the base of the jar now becomes the FAME cloud point (Abdulkarim *et al*., 2012). After noting the cloud point temperature, the jar was removed from the water bath and cooled.

3.2.8.4 *Determination of kinematic viscosity*

A viscometer with a third spindle was placed inside a beaker filled with hot biodiesel of 40℃ and 100℃ allowed to stay for a period of about 30 minutes with the speed of the spindle set on automatic. The biodiesel was allowed to flow freely until the meniscus moved from the initial marked time to the final mark and the readings displayed on the screen of the viscometer. A stop watch was used for the timing, this step was repeated three more time, the mean value was recorded and that gave the viscosity of the biodiesel (Mohammed, 2018).

3.2.8.5 *Determination of flash point*

The ASTMD93 method has been used to determine the flash point of the biodiesel. The sample to be analyzed was placed in a brass cup in such a quantity that just touches the mark inside the cup and closed. The sample was heated with Bunsen burner and the temperature was adjusted in such a way that it increases 7°F per minute, and sample continuously stirred. As the sample approach the temperature of the flash, the injector burner was lighted on and then injected into the sample at 12 seconds interval until a distinct flash was observed within the container and the injector burner put off. At this point the close flash point was noted with the aid of a thermometer then recorded. The calorific value computed from saponification and iodine values using correlations reported by (Mohammed, 2018).

$$\text{Calorific value (CV)} = 49.43 - 0.015IV - 0.041SV \tag{3.14}$$

3.2.9 Synthesis of Biolubricant

This was achieved by transesterification of the methyl ester with TMP to produce Allamanda based TMP ester, a biolubricant. The Allamanda methyl ester was heated to 60℃. TMP was measured into the 500ml three-neck round bottom flask fitted with a thermometer and a magnetic stirrer. The substance was heated to 110℃ with constant stirring until it melted.

The heating continued at that temperature for another 15 minutes to allow moisture form due to the hygroscopic nature of TMP to dry (Masood *et al*., 2012). Then, a known quantity of Allamanda methyl ester (AME) was introduced into the reactor with respect to the molar ratio of AME: TMP (4:1). The catalyst (0.8% w/w) was then added and the reaction was conducted at a temperature of 120 ℃ for two hours thirty minutes (2.5 h) (Bilal *et al.,* 2013). After the reaction the mixture was allowed to cool and poured into the separating funnel after the time elapsed and was allowed to separate and the biolubricant was decanted and the catalyst was filtered out, the product was washed with distilled water in separating funnel continuously until the pH of the solution was 7 and was dried at a temperature of 105℃. The lubricating properties of Allamanda based TMP esters were evaluated according to ASTM standards.

The percentage yield of biolubricant was determined according to (Musa *et al*., 2016) as:

$$\%\text{yield of biolubricant} = \frac{mass\ of\ \ dried\ biolubricant}{mass\ of\ methyl\ ester\ used}\ x\ 100 \qquad (3.15)$$

3.2.9.1 *Analysis and characterization of the synthesized biolubricant*

The properties of the biolubricant were determined using the procedures in section 3.2.8 except for Viscosity index which is determined by using the values of viscosity at 40 and 100 ^{o}C to calculate the viscosity index, when the value of viscosity at 100 ^{0}C is less than 70 cSt. ASTM D 2270 method and equation (3.16) were used to calculate the viscosity index (VI).

$$VI = \frac{L-U}{L-H}\ x\ 100 \qquad (3.16)$$

Where: VI =is viscosity index, U= viscosity at 40 ^{o} C the of biolubricant

L and H where are the kinematic viscosity of the reference oils (May *et al.*, 2013).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Characterization of Allamanda seed oil

Table 4.1 gives the summary of the results for the physicochemical properties of the Allamanda seed oil used in this study.

Table 4.1: Physicochemical properties of allamanda seed Oil

Properties	**Unit**	**Experimental value**	**ASTM D6751**
Oil yield (%)	(%)	64	
Moisture Content	(%)	2.85	-
Free fatty acid	(%)	2.96	2.5 max
Density	g/cm^3	0.924	0.818-0.926
Acid Value	mg KOH/g	5.891	10
Viscosity	mm^2/s	20.5	
Specific Gravity		0.928	0.816
Iodine Value	$gI_2/100$ g	40.659	
Peroxide Value	Meq/kg	8.629	
Saponification Value	Mg KOH/g	158.483	189-198
pH value		5.96	

The oil yield from Allamanda seed oil was 64%. This value is higher than 57, 52.79, 40, 18.35, 49.69 and 44.6% reported for the extraction of oil from Allamanda seed oil, jatropha, soybean, desert date and palm kernel oil respectively by (Egwim *et al.,* 2015; Mohammed, 2018; Audu, 2017). This appreciably high oil content obtained in this study established the potential of the seed as an energy crop and encouraged dependence on non-edible oil as feedstock for biodiesel production. It also promotes food security and availability. Besides it reduced the cost of biodiesel production. Moisture is an unwanted property that tends to reduce the quality of vegetable oil .The low moisture content (2.86%) confirms that the oil is of good quality and was not prone to rancidity easily. Higher moisture content causes emulsification during transesterification of the oil. The free fatty acid (FFA) value for Allamanda seeds oil was 2.75 mg KOH/g with a corresponding acid value of 5.89 mg KOH/g. This FFA value is lower compared to the report by (Audu, 2017), but a bit higher than the value expected by the standard. This value of free fatty acid is not suitable for homogeneous base catalyst transesterification as reported by (Mohammed, 2018).

The acid value for oil required for homogeneous base transesterification should not be greater than 1% (2 mg KOH/g). It is important to state that base activated metakaolin has tolerance for FFA. Hence the oil can be used directly without neutralization. This is an obvious advantage of this catalyst in transesterification of vegetable oil. The specific gravity of Allamanda seeds oil at 25 ℃ was 0.928 which is a bit higher than the standard value of 0.816. Viscosity is a measure of resistance to flow. The viscosity of Allamanda oil was found to be 20.5 mm^2/s. This value is lower compared to the standard value of 3.5 mm^2/s, the high viscosity associated with the crude vegetable oil is the main reason why it cannot be used directly in diesel engine as this causes several operational problems such as deposition of carbon, reduced engine durability and contamination of lubricant.

Therefore, there is the need to reduce viscosity through transesterification. Iodine value is used to measure the level of unsaturation in fatty acids in oil. The limitation of unsaturation of fatty acid is important since heating highly unsaturated fatty acids results in polymerization of glycerides which can lead to formation of deposits (Musa and Aberuagba,

2012) and it is an indicator of double bonds in the molecular structure in terms of classification of fats and oils. Iodine values below 100 confirmed that the oil is non-drying (Oti and Eze-Ilochi, 2017). Hence, Allamanda seed oil is non-drying because its iodine value was lower than 100 that is, the oil has good oxidation stability. From Table 4.1 above, the iodine value of Allamanda seed oil was found to be 40.65 gI_2/100 g. This value differs from 43.30 gI_2/100 g reported by (Audu, 2017). This variation could possibly be due to difference in plant growth condition, genetic makeup and oil extraction method employed.

The saponification value is a measure of the tendency of the oil to form soap during transesterification reaction (Mohammed, 2018). The saponification value (158.483 mg KOH/g) obtained in this study was lower when compared with the value reported for the Allamanda seed oil and it is also lower than the standard range which may be a good quality for the oil to be used in further processing without foaming soap (Audu, 2017). The specific gravity of 0.928 was obtained from the oil which implies that oil is less dense than water.

4.2 Characterization of Catalyst

4.2.1 X-Ray Diffraction (XRD) Analysis

The XRD patterns of raw and calcined kaolin (metakaolin) were shown in Figures 4.1 and 4.2. The XRD of the raw kaolin depicts sharp peaks and intense showing an ordered structured (Tironi *et al.*, 2012) which are typical of crystalline materials. The peaks of 2ϴ values at 12.46, 24.99, 38.5, 55.16, and 62^o, represent the crystalline structure of kaolinite with quartz as major impurities having their main peaks at 20.94, 26.69, 36.59, and 50.20^o. This observation is consistent with the one reported by (Teku, 2017). The XRD characteristics peaks of raw kaolin almost disappeared after thermal treatment leading to the formation of metakaolin. Explicitly, disordered metakaolin was formed in this work after dehydroxylation of kaolin at 650 ℃ for 90 min which could be observed on the XRD pattern of calcined kaolin as the crystalline peaks disappeared and transformed the crystalline kaolin to amorphous metakaolin. This is evident in the drastic drop in the peak of intensity in Figure 4.2. The remaining peaks in this range could be ascribed to traces of mica and quartz in calcined kaolin (Dang *et al*., 2013).

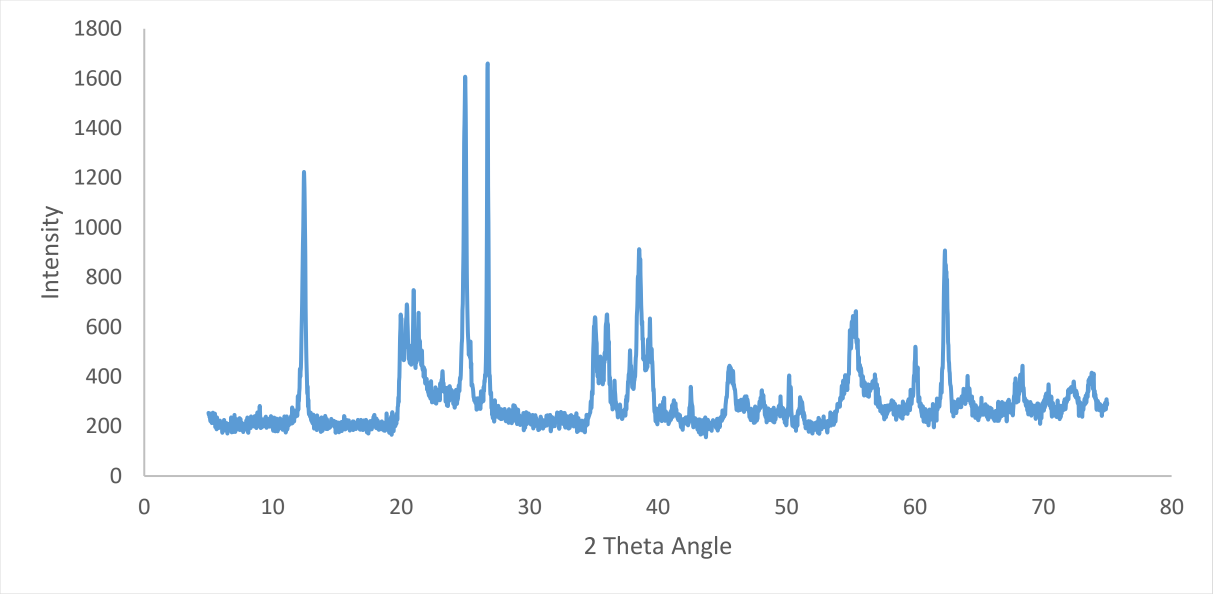


Figure 4.1: XRD for Raw kaolin

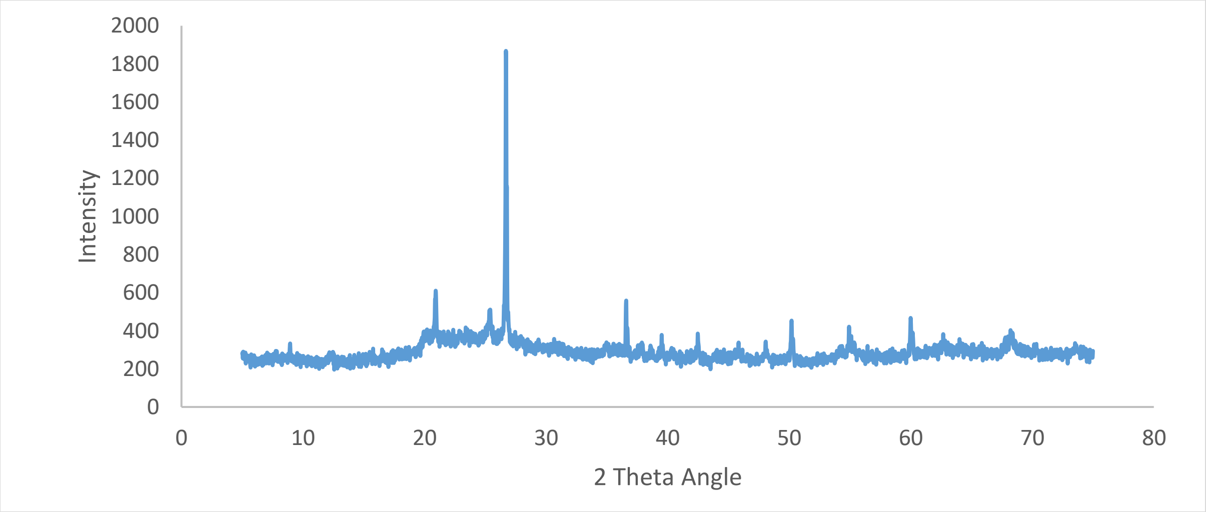


Figure 4.2: XRD for calcined kaolin

4.2.2 X-Ray Fluorescence (XRF) Analysis

The oxides composition of the raw and calcined kaolin was determined using XRF instrument and results obtained is shown in Table 4.2

Table 4.2: XRF of raw and calcined kaolin

Components	**Raw (%)**	**Calcined (%)**
SiO_2	58.41	59.96
Al_2O_3	32.25	33.79
SO_3	0.01	0.12
Na_2O	0.47	0.40
K_2O	0.49	0.49
CaO	0.05	0.06
MgO	0.73	0.70
TiO_2	1.68	1.67
Fe_2O_3	1.42	1.45
MnO	0.01	0.01
LOI	4.53	1.35

From Table 4.2, the most abundant oxides are SiO_2, Al_2O_3, TiO_2, and Fe_2O_3 and minor amount of SO_3, K_2O, Na_2O, CaO, MgO, and MnO. The SiO_2, and Al_2O_3 compositions increased with about 2% from 58.41 to 59.96% and 32.25% to 33.79% respectively after thermal treatment.The predominance of SiO_2, and Al_2O_3 associated mainly with quarts and kaolinite minerals. TiO_2, and Fe_2O_3 are the main discolouring components and their presence can be associated with hematite, goethite and anatase materials (Oyebanjo *et al.*, 2020).

4.2.3 Scanning Electron Microscopy (SEM) Analysis

Plate IX shows the surface morphologies of the raw and calcined kaolin

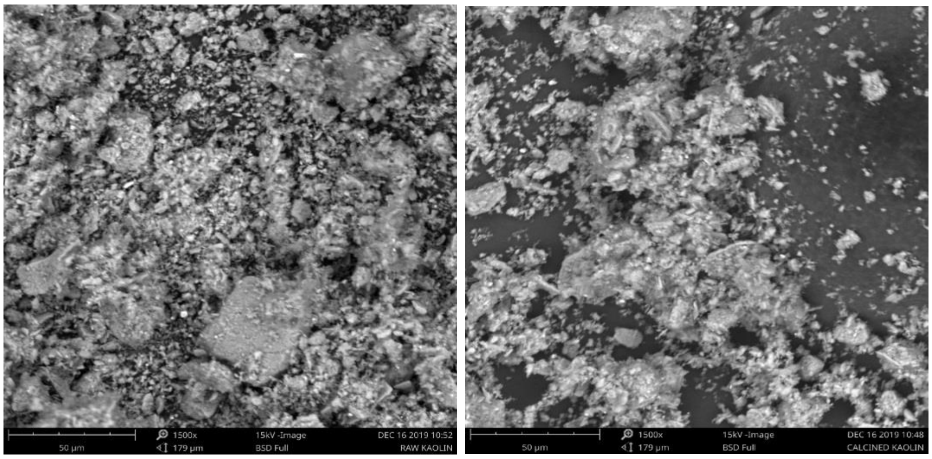


Plate IX: SEM images of (a) raw and (b) calcined kaolin

The SEM images shows the morphologies and textures of the raw and calcined kaolin. The raw kaolin sample in plate IX (a) shows different layers of different sizes which indicates the order of silica and alumina layers in kaolinite (Teku, 2017). The calcined kaolin sample in plate IX (b) shows a uniform morphology, though with slight disorder in the plates.it also showed increase in number

4.2.4 Brunauer -Emmett- Teller (BET) Analysis

Table 4.3 shows the textural properties of calcined and activated kaolin

Table 4.3: Textural properties of calcined and alkaline activated kaolin

Sample	Surface area (m^2/g)	Pore volume(cc/g)	Pore size (nm)
Raw kaolin	173.516	0.086	2.126
Calcined kaolin	636.531	0.3244	2.113
Alkaline activated metakaolin	706.906	0.4255	2.118

The BET analysis presents the surface area, pore volume and size of the raw kaolin, metakaolin and activated metakaolin and as revealed in Table 4.3 it showed that raw kaolin has a surface area of 173.516 which upon calcination increased to 636.531 m^2/g, alkaline activated metakaolin clay was majorly a mesoporous material of high surface area of 706.906 m^2/g. The high surface area observed may be attributed to high amount of silicates present. Liu *et al.*, (2018) reported that catalyst with higher surface area is more likely to exhibit higher catalytic activity. And according to Mudi *et al.* (2018), porous materials having a surface area value above 100 m^2/g is considered a potential material for catalyst and catalyst support. The pore volume and size were determined to be 0.4255 cc/g and 2.118 nm. The results also indicated that the materials also contain the Dubinin-Radushkevich (DR) Method micropore and mesopore with volume and size of 0.4255cc/g and 2.118nm*P* respectively. This pore size falls within the range 2 – 50 nm and therefore indicates that the metakaolin produced is mesoporous in nature.

4.3 Biodiesel production yield

Table 4.4 shows the yield of the biodiesel with its corresponding operating conditions using Box-Behnken design matrix

Table 4.4: Box Behnken Design matrix for biodiesel yield

	Factor 1	**Factor 2**	**Factor 3**	**Response 1**
Run	A:Time Min	B:Temperature (℃)	C:Catalyst w%	% Yield
1	60	65.0	2.75	78.67
2	120	65.0	5.00	82.67
3	120	52.5	2.75	76.67
4	180	40.0	2.75	75.33
5	120	65.0	0.50	78.67

Table 4.4: Box Behnken Design matrix for biodiesel yield continued

	Factor 1	Factor 2	Factor 3	Response 1
Run	Time (min)	Temperature (°C)	Catalyst (w%)	Yield (%)
6	60	52.5	5.00	82.00
7	180	52.5	0.50	90.67
8	120	40.0	5.00	76.00
9	120	40.0	0.50	62.67
10	120	52.5	2.75	75.67
11	120	52.5	2.75	71.67
12	180	52.5	5.00	85.67
13	180	65.0	2.75	78.00
14	120	52.5	2.75	67.00
15	120	52.5	2.75	71.33
16	60	52.5	0.50	65.33
17	60	40	2.75	66.00

Table 4.5 shows the regression model fitting and stastistical analysis of biodiesel production from Allamanda seed oil

Table 4.5: Regression Model Fitting and Statistical Analysis

Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**p-value Prob>F**	
Model	795.46	9	88.38	5.07	0.0219	significant
A-Time	177.35	1	177.35	10.17	0.0153	
B-Temperature	180.50	1	180.50	10.35	0.0147	
C-Catalyst Concentration	105.12	1	105.12	6.03	0.0438	
AB	25.00	1	25.00	1.43	0.2702	
AC	117.36	1	117.36	6.73	0.0357	
BC	21.78	1	21.78	1.25	0.3007	
A^2	66.53	1	66.53	3.81	0.0918	
B^2	15.87	1	15.87	0.9100	0.3719	
C^2	84.32	1	84.32	4.83	0.0639	
Residual	122.11	7	17.44			Not significant
Lack of fit	62.42	3	20.81	1.39	0.3666	
Pure Error	59.69	4	14.92			
Cor Total	917.571	16				

4.4 Regression Model Fitting and Statistical Analysis

Statistical analysis of data in Table 4.4 was used to fit a second order polynomial model that shows the relationship between the response (biodiesel yield) and variables (time, temperature and catalyst loading) investigated as shown in equation (4.1).

$$\%\text{Yield} = -19.21520 + 0.098812\text{A} + 2.31295\text{B} + 5.91975\text{C} - 0.003333\text{AB} - 0.040123\text{AC} - 0.082963\text{BC} + 0.001104A^2 - 0.012427B^2 + 0.883951C^2 \quad (4.1)$$

The positive terms associated with the coefficient of time (A), temperature (B), catalyst loading(C) indicates that there is a direct proportional increase in biodiesel yield as these main variables increases. On the other hand, negative coefficient indicates that an inversely proportional decrease in biodiesel yield as variables increases within the limit of experimental range. Statistical analysis of variance was carried out to evaluate the degree of fitness and significance of the regression model and individual variables studied (see Table 4.4). Statistically, the p-value (Probability of error value) is a key parameter for measuring the level of significance of a regression model, variables and their respective cross products. The lower the p – value, the higher the level of significance of variables involved (Chen *et al.*, 2008; Lee *et al.*, 2011). Generally, if the p value is less than 0.050, it means that the model is significant.

The p-value and Model F – value of 0.0219 and 5.07 respectively shown in Table 4.3 reveals that the model is significant. The adequacy of regression model was further established by the co-efficient of determination (R^2). The coefficient of determination (R^2) measures the degree of fitness of the regression model.

According to Akintunde *et al*. (2015), higher R^2 value greater or equal to one depicts a good model fit. The R^2 value of 0.8669 implies that 86.69% of the variability in the response is explained by the model. The value suggests that the regression model equation satisfactorily describes the relationship between the biodiesel yield and variables investigated in this study. The model will therefore provide a good estimation of the biodiesel yield. The coefficient of correlation (R^2) shows the relationship between the experimental and predicted biodiesel. Higher value of R^2 closer to unity (1) signifies a good proximity between the experimental and predicted values (Akintunde *et al.*, 2015).

The calculated R value of 0.6958 depicts a good correlation between the experimental and predicted values. The coefficient of variation (CV) measures the level of precision and reliability of experimental data. The low value (5.53%) obtained indicates high precision and reliability of experimental data. The result of lack of fit evaluation revealed a p - value of 0.3666 which is insignificant. This implies that regression model developed correlated well with experimental data. Mohammed, (2018) reported that an insignificant lack of fit is highly desirable since it is a clear indication that nearly all contributions to the response are considered by the regression model. The standard deviation of 4.18 shows that the degree of deviation from response average value is also low.

4.5 Optimization of effect of process variables on biodiesel yield from Allamanda seed oil

The effect of temperature, time and catalyst loading on biodiesel yield from Allamanda oil is shown in Table 4.4.

4.5.1 Effect of reaction Temperature

Biodiesel production through transesterification reaction is greatly influenced by temperature. Higher reaction temperature reduces reaction time and increases yield. The effect of reaction temperature was studied from 40℃ to 65℃ as shown in the Table 4.4, the conversion begins rapidly and increased with temperature up to 52.5℃ and reaction time of 180 min. the biodiesel yield increased from 76% to approximately 91% as the temperature increased from 40 to 52.5℃, subsequently decreased to 78% when the temperature was increase to 65℃. This observation is consistence with the report of Liu *et al*., (2018), the author reported highest yield at temperature of 60℃ and yield of 91%. It was equally reported that temperature close to the boiling point of methanol vaporized the methanol and the oil begin to burn which will result to less yield. Decrease in biodiesel yield at higher temperature is attributed to excessive loss of methanol due to evaporation. The optimum temperature for this study is 52.5℃.

4.5.2 Effect of reaction time

The rate of conversion of the oil to biodiesel increases with increase in reaction time (Marinkovic *et al*., 2016). Effect of reaction time was investigated between 60 and 180 min as shown in Table 4.4. Biodiesel increases steeply at the beginning of the reaction. A conversion of 82% was obtained within the first 60 min of the reaction. This increase in yield is due to increasing mixing and dispersion of methanol in the oil phase homogeneity that favours the high yield within this short time. The biodiesel conversion continued to increase marginally as the time increases until equilibrium was attained at 180 min. the optimum reaction time in this study is lower than the time of 4 h reported by (Qin *et al*., 2017). The difference observed can be attributed to difference in feedstock properties, catalytic activity and operating conditions.

4.5.3 Effect of catalyst loading

The effect of alkaline activated metakaolin loading on biodiesel yield from transesterification of Allamanda seed oil was investigated between 0.5 to 5 w% as shown in Table 4.4. The yield from 65 to 91% at 0.5w%, increasing the concentration above 0.5w% resulted in decrease in the yield. This decrease can be due to the formation of soap in the presence of high amount of catalyst which increase viscosity of the reactant and cause the diffusion of the reactant to the catalyst difficult (Buasari *et al*., 2015; Marwan and Indarti, 2016; Qin *et al*., 2017). The optimum catalyst loading in this study was 0.5w% with highest yield of approximately 91%. The catalyst concentration obtained was lower than the concentration reported for biodiesel by (Teku, 2017; Ramirez-Ortiz *et al*., 2011). This variation may be due to difference in fatty acid compositions of the starting material, catalytic activity and or operating conditions. The low catalyst loading is however impressive since a reasonable and equitable biodiesel yield can be obtained in comparison with previous studies where higher catalyst loadings were used.

4.6 Response surface optimization of interactive effect between process variables

The response surface plot provides useful guide about the interactive effect and optimum level for maximum response deduction in a multivariate system variables.

4.6.1 Effect of temperature and time on biodiesel yield

The Figure 4.3 shows the three dimensional surface and contour plot of the effect of temperature and time on biodiesel yield

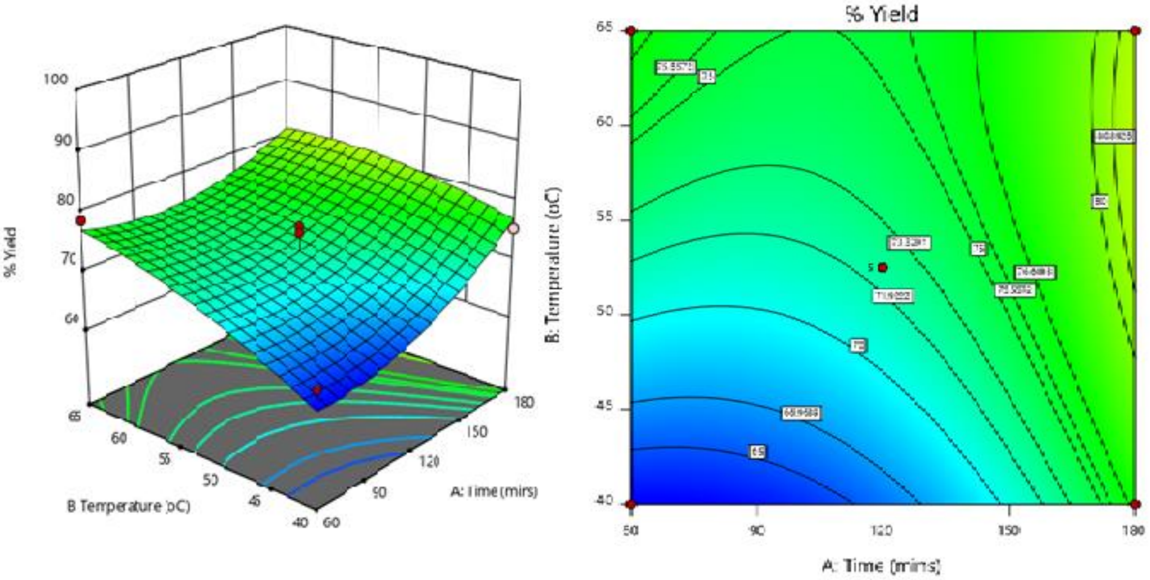


Figure 4.3: Effect of temperature and time on biodiesel (a) three dimensional surface (3D) and (b) contour plot at 2.75 wt% catalyst loading and methanol to oil ratio of 1:5

The response surface plot provides useful information about the interactive effects and optimum conditions for maximum response deduction in a multivariate system. Figure 4.3a and b shows the 3D surface and contour plot for combined effect of temperature and time on biodiesel yield at a constant methanol to oil ratio of 1:5 and catalyst loading of 2.75 wt% respectively.

Figure 4.3b shows that increase in reaction temperature from the lower temperature of 45℃ to the higher temperature of 65℃ resulted into corresponding increase in the yield up to temperature of 62℃ and from 62℃ the increase in the yield was small and which could be as a result of the temperature approaching the methanol boiling point. Increase in time up to 180 min also resulted to increase in the biodiesel yield. The interactive effect of the variables revealed that continuous simultaneous increase in temperature and time improves the biodiesel yield, this results negates the report of Mohammed, (2018), in which increase in temperature and decrease in time favours high yield. From the contour plot which reflected in the 3d surface, it was observed that increase in both time and temperature above the optimum conditions of 180 min and 52.5℃ resulted in decrease in yield.

4.6.2 Effect of catalyst loading and time on biodiesel yield

The effect of catalyst loading and time on biodiesel yield when reaction temperature and methanol to oil ratio was kept constant at 52.5 °C and 1:5 respectively is shown in 3D surface and contour plot were shown in Figure 4.4

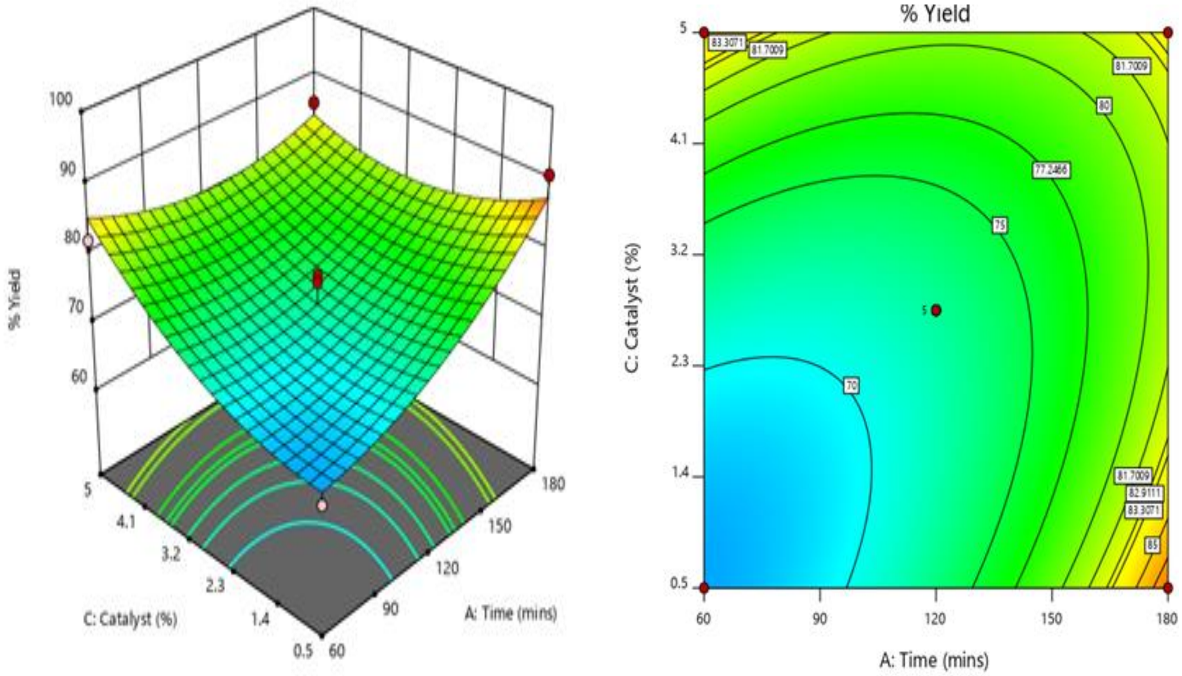


Figure 4.4: The effect of catalyst loading and time on biodiesel yield (a) three dimensional surface (3D) and (b) contour plot at 2.75 wt% catalyst loading and methanol to oil ratio of 1:5

The increase in catalyst loading from 0.5 to 5.0 wt% resulted into reduction in biodiesel yield with increase in reaction time as observed in Figure 4.4b. The interactive effect of the variables revealed that continuous and simultaneous increase in catalyst loading and time decrease the biodiesel yield. The two variables significantly affects biodiesel yield, as the catalyst loading was increased at a short time reaction the yield increased and when the time was increased with lower catalyst loading the yield increased. The optimum catalyst loading and time were 0.5wt% and 180 min

4.6.3 effect of catalyst loading and temperature on biodiesel yield

The interaction between catalyst and temperature on biodiesel yield at a reaction time of 120 minutes and methanol to oil ratio of 1:5 is shown in Figure 4.5.

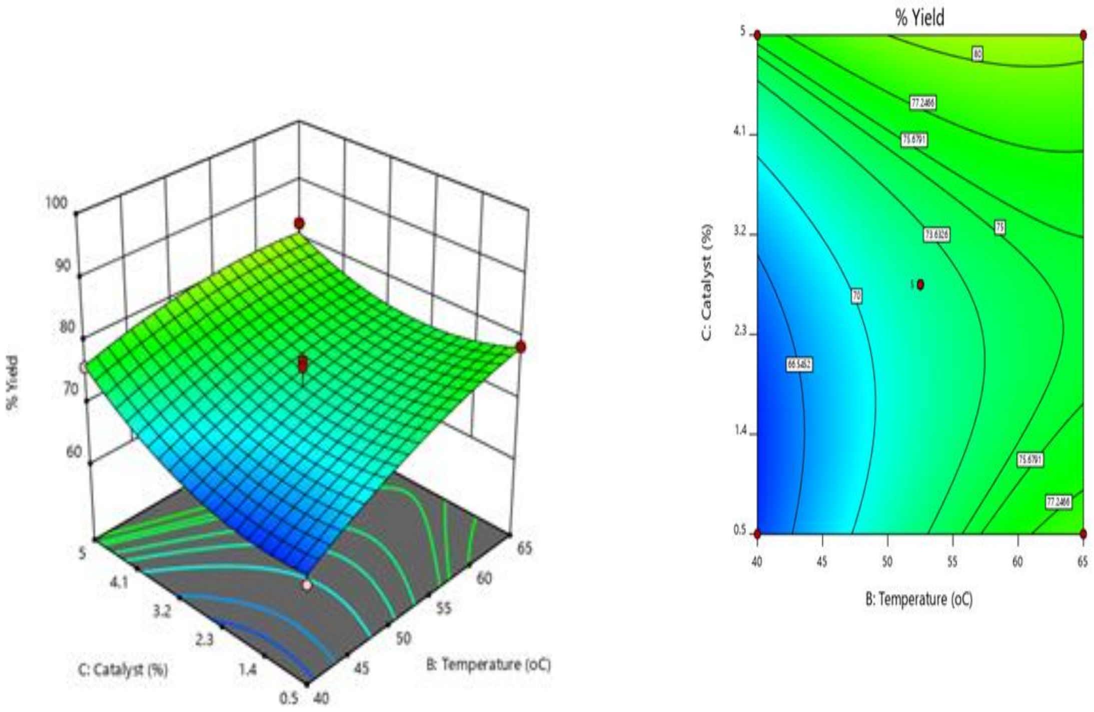


Figure 4.5: The effect of catalyst loading and temperature on biodiesel yield (a) three dimensional surface (3D) and (b) contour plot at 2.75 wt% catalyst loading and methanol to oil ratio of 1:5

From the Figures, it was observed that increase in catalyst loading and temperature resulted in increase in biodiesel yield, but when these variables interact, simultaneous increment gives high yield up to 60 ℃ but higher temperature and high catalyst loading results in reducing the yield which indicate from the contour plot that there is synergy between these variables. The optimum catalyst loading and temperature were 0.5 w% and 52.5 ℃.

4.7 Characterization of Allamanda methyl Ester

The fuel properties of Allamanda biodiesel are summarized in Table 4.6 with comparison to other oil biodiesels and the recommended biodiesel international standards ASTM D6751 and EN14214 and petrol diesel. Biodiesel fuel properties must meet certain specifications such as the United States (ASTM D6751) and European Norm standard (EN14214).

The kinematic viscosity of Allamanda biodiesel was determined to be 1.04 mm^2/s as against $20.5mm^2/s$ for raw Allamanda oil. The obvious reduction in viscosity was due to efficiency of completion of transesterification. The obtained value falls below the ranges specified by ASTM D6741 standard and EN 14214 standards for biodiesel. It is also appreciably lower than 2.5 mm^2/s and 3.7 mm^2/s reported by (Teku, 2017; Onukwuli and Ude, 2018) for waste cooking oil (WCO) and African peer seed oil (APSO) biodiesels. The difference can be attributed to variation in process condition and catalyst type. Acid values provide an indication of age and quality of the biodiesel. The acid value obtained in this work was 0.58 mg KOH/g. This result is in agreement with the specified American and European standard. It is however slightly higher than 0.35 and 0.15 mg KOH/g reported for WCO biodiesel by (Teku, 2017) and APSO biodiesel (Onukwuli and Ude, 2018).

Table 4.6: Fuel properties of biodiesel in comparison with standard and literatures

Properties	**Diesel**	**ASTM D6571**	**EN**	**Test method (ASTM)**	**WCO biodiesel**	**APSO Biodiesel**	**This study**
Specific gravity	0.82-0.86	0.88	0.860	D1298	0.889	0.88	0.87
Flash point (℃)	> 55	93 min	130min	D92	154	180	152
Pour point (℃)	- 33 to -15	12 max	–15-10	D97	4	3	-6.8
Cloud point (℃)	-15 to -5	–3-10	-	D2500	6	14	1.40
Kinematic viscosity(mm^2/s)	2.5 - 3.5	1.9–6.0	3.5–5.0	D445	2.5	3.7	1.04
Acid value (mg /KOH)	-0.35	≤0.5	0.5	D664	0.35	0.15	0.58
Density (g/cm^3)	0.876	0.86	0.86-0.90	D1298	0.86	0.858	0.88
Author					Teku, (2017)	Onukwuli & Ude (2018)	

The flash point is the minimum temperature required for fuel to ignite when an ignition source is brought close to it. A fuel with a low flash point implies that the fuel is not safe for handling. The flash point obtained in this work is 152 ℃. This value is appreciable higher than the lower limit specified by the ASTM D and EN standard. This value is also lower than 154℃ and 163℃ reported for WCO biodiesel by (Teku, 2017) and (Onukwuli and Ude, 2018) for APSO biodiesel but still meet the requirements. Cloud point is the temperature at the smallest crystals become noticeable when cooled (Salaheldeen *et al*., 2015).

The cloud point obtained in this study was 1.40°C.the obtained value is within the ASTM standard (D6751), this result is considerably lower than 6°C and 14℃ reported by (Teku, 2017) and (Onukwuli and Ude, 2018). This variation of the cloud point might be due to difference in the percentage saturation of the oil. The low cloud point reported in this work suggests that the biodiesel has low tendency for gel formation and therefore can perform satisfactory under cold climate. According to Mohammed, (2018), high cloud point of biodiesel affect the engine performance and quality emission under cold climatic conditions.

Pour point is the lowest temperature at which there is formation of gel due to cooling. The pour point obtained in this work is -6.8℃. This property is within the ASTM D6751 EN 14214 standard requirements. The result is very much lower than 4℃ and 3℃ reported for WCO biodiesel (Teku, 2017) and (Onukwuli and Ude, 2018) for APSO biodiesel. The difference in pour points may be due the differences in fatty acid composition catalyst type and. Biodiesel energy content is lower that of petroleum diesel on volumetric basis, but biodiesel is characterized with improved combustion efficiency because of its oxygen content and improved lubricity which partly compensate the impact of the lower energy content.

4.8 Synthesis and characterization of Biolubricant

The lubricant properties of the synthesized Allamanda oil based biolubricant were analyzed to determine its suitability for use as a biolubricant base fluid. The results are shown in Table 4.7 in comparison with the ISO (International Standards Organization) viscosity grade requirements and petroleum based lubricant. The kinematic viscosity, viscosity index pour point and flash point were determined using American society for testing and material (ASTM).

Table 4.7: Properties of Allamanda biolubricant compared with petroleum lubricant and ISO VG

Properties	Allamanda biolubricant	Petroleum based Lubricant	ISO VG 32	ISO VG 46	ISO VG 68
Yield	93.5%				
Viscosity @40℃ (c St)	64.0	10.801	> 28.8	>41.4	>61.40
Viscosity @100℃(c St)	28.0	3.136	>4.1	>4.1	>4.1
Viscosity Index	371.59	165.4	>90	>90	>198
Pour point(℃)	-12.5	-9	< -10	< -10	< -10
Flash point(℃)	249			220	
Cloud point(℃)	-0.7				

The viscosity property is indirectly proportional to temperature and directly proportional to pressure and film formation. Oil with Higher viscosity offer higher resistance to flow and if the viscosity of oil is low, it gives low resistance to flow (Mobarak *et al.*, 2014). The viscosities at 40℃ and 100℃ are important lubricity properties; they are useful in determining the fluidity of the lubricant at low and high temperatures; they also show thermal stability of the lubricant (Bilal *et al.*, 2013). The transesterification has increase the kinematic viscosity of Allamanda methyl ester at 40 ^{0}C from 20.7 to 64.0 cSt, this shows improvement in biolubricant properties. But the viscosity of Allamanda biolubricant at 40 ^{o}C shows it is in close proximity with the ISO VG 68 and could meet the requirement since its viscosities is within the standard of ISO VG 68 range. The viscosity index (VI) shows the feature of the lubricants viscosities once temperature changes are applied. When the viscosity index of lubricant is high, it indicates that the change in viscosities at higher temperature will be minimal. In general, viscosity index is an important lubricity property and the higher its value, the better the lubricant. The VI of Allamanda biolubricant is 371.591, however, the Allamanda biolubricant can be used as light gear oil; crankcase and hydraulic fluids based on the ISO viscosity grade specifications.

Pour point is one of the properties that determines the performance of lubricants. The pour point is the lowest temperature at which a liquid is capable to flow. However, low pour point temperature value is needed for effective performance of lubricant in cold environments (Abubakar, 2015). The pour point obtained for the synthesized Allamanda biolubricant was −12.5℃, which was found to be in line with ISO VG standards.

Flash point is the lowest temperature at which a liquid gives an adequate concentration of vapor, above it to form a combustible mixture with air and it is inversely proportional to the fuel volatility (Atabani *et al.*, 2012). The flash point of Allamanda biolubricant was improved from 152℃ to 249℃ due to chemical modification on the Allamanda biodiesel. The flash point obtained for the synthesized Allamanda biolubricant was 249℃. Flash point at high temperature make the lubricants are safe from fire hazard (Mathew *et al.,* 2015).

The Cloud point is the temperature at the smallest crystals become noticeable when cooled (Salaheldeen *et al*., 2015). The cloud point obtained in this study was -0.70

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The following conclusions were made from the results of the work carried out:

1. The Allamanda oil was extracted and was characterized to determine its physico-chemical properties to determine its suitability for biolubricant production

2. Metakaolin was synthesized through beneficiation using calcination and activation; it was thereafter characterized using XRD, XRF, BET and SEM techniques

3. Biodiesel was produced from the Allamanda seed oil using the activated metakaolin to obtain the highest yield of 90.67% at 180 min reaction time,

52.5 ℃ reaction temperature, 0.5 w%, catalyst concentration and constant 1:5 methanol to oil ratio. The properties of the produced biodiesel were investigated and were compared to the ASTM D6751, EN 14214 and petrol diesel specifications

4. Biolubricant from Allamanda oil methyl ester was successfully synthesized by chemical modification through transesterification using metakaolin as catalyst. The conditions of production of the biolubricant are; 120 ^{0}C temperature for 2 h, 30 minutes at 0.8 % catalyst concentration, 1:4 TMP to AME molar ratio and tri-ester yield was 93.5%. The properties of synthesized biolubricant were found to be comparable to those of other plant based lubricant and that of international standard organization (ISO) conform to those of viscosity grade 68 (VG 68). The synthesized bio-lubricant can serve in place of conventional petroleum oil.

5.2 Recommendations

From investigated results and studies, the following recommendations were suggested:

1. Further research should be carried out for the statistical optimization of Allamanda methyl ester transesterification using Respond surface Methodology (RSM) such as central composite design and Taguchi methods.
2. The effect of metallic oxides loaded on the catalyst should be investigated
3. Other polyols (such as Glycerin, Ethylene glycol) should be used to produce biolubricant from Allamanda methyl ester and the results should be compared with that of TMP
4. Catalyst reusability should be studied.
5. Optimization and kinetic studies of the biolubricant production using the synthesized catalyst should be carried out.

5.3 Contribution to knowledge

Biolubricant was produced from Allamanda base biodiesel using based metakaolin and yield was 93.57% at 120 ^{o}C for 2 hours 30 minutes, 0.8% catalyst concentration and 1:4 TMP to AME molar ratio. The properties of the produced biolubricant comformed to international standard organization viscosity grade 68 (ISO VG 68).

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