# PRODUCTION OF BIOLUBRICANT FROM ALLAMANDA SEED OIL USING ACID ACTIVATED METAKAOLIN

**BY**

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**MEng/SEET/2017/6710**

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**MINNA**

**OCTOBER, 2022**

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**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE MASTER OF ENGINEERING IN CHEMICAL ENGINEERING**

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# ABSTRACT

This research work is aimed at producing biolubricant from Allamanda seed oil using acid activated metakaolin as catalyst to resolve problems such as environmental pollution, food security and high cost of product after production by using an environmentaltyyyyly friendly feedstock, non edible feedstock and developing a heterogeneous catalyst from kaolin. The kaolin was dug from it site of location in kutigi, lavun local government area, Niger State. The kaolin was beneficiated using wet sieving and sedimentation method, the beneficiated kaolin was calcined at 650 $^oC$ for 90 minutes and was activated with 2 Moles of $H_2SO_4$. The produced catalyst was characterized using the following analysis; X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET), the BET shows the surface area, pore volume and pore size of the raw kaolin, calcined and activated metakaolin, there was increase in surface area of the raw kaolin, calcined and activated metakaolin, the surface area of the activated metakaolin was 954.405 $m^2/g$ which corresponds with (Mudi et al., 2018), that any porous material with surface area above 100 $m^2/g$ is considered a good material for catalyst. XRF results indicated that the kaolin is rich in silicon and aluminum oxide. The Allamanda oil was extracted using soxhlet extraction method and the oil was characterized to analyze the physiochemical properties of the oil, hexane was used as the solvent for extraction. The biolubricant was produced by the two stages transesterification reaction, the first stage involves the reaction between the extracted Allamanda oil and methanol at a constant ratio of 5:1 with other parameters such as reaction time, reaction temperature and catalyst concentration was varied using Box-Behnken design module of Response Surface Methodology (RSM) available in "Design Expert® Software" to produce the Allamanda oil based biodiesel. The optimum operating conditions that gave the highest biodiesel yield of 91.3 % were 65 $^oC$, 120 miuntes and 0.5 wt % and the produced Allamanda oil based biodiesel was characterized, the biodiesel had an acid value of 5.20 mgKOH/g. The second stage involves the transesterification of allamanda oil based biodiesel and trimethylolpropane to produce biolubricant at molar ratio of 4:1, reaction temperature of 120 $^oC$, reaction time of 2hours 30 minutes and catalyst weight of 0.5 % wt. Vital lubricating properties of the produced biolubricant such as viscosity at 40 $^oC$ and 100 $^oC$, pour point, flash point and viscosity index were determined and found to be 77.0 cSt, 26.0 cSt, -11.2 $^oC$, 261.0 $^oC$ and 376.15 $^oC$. The produced biolubricant met the following standard; ISO VG 32, ISO VG 46, ISO 68 which shows that the produced biolubricant can be used in automobile engines and hydraulics and can also serve as substitute to the conventional petroleum based lubricant.

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# ABBREVIATIONS

AME: Allamanda Methyl Esters
BET: Brunauer- Emmett- Teller
CP: Cloud point
FA: Fatty acids
FAME: Fatty acid methyl esters
FFA: Free fatty acids
FP: Fire Point
ME: Methyl esters
MW: Molecular Weight
LOI: Loss of Ignition
PP: Pour point
SEM: Scanning Electron Microscopy
TMP: Trimethylolpropane
TE: Triesters
VI: Viscosity index
XRF: X-ray Fluorescence
XRD: X-ray Diffraction

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background to the Study

In recent years there had been alarming increase in adverse effect of products obtained from fossil fuels such as petroleum, coal and natural gas to humans and their environments. This led to substantial measures in transition towards bio-based products to reduce these adverse effects caused by fossil fuel based products (Willing, 2001).

In reducing the use of fossil fuel based products, an alternative is the bio-based products such as biodiesels and bio-lubricants (Chowdhury *et al*., 2013). There are various types of lubricants available around the globe including refined oil, synthetic oil, vegetable oil and mineral oil. Petroleum oil based lubricants had taken over the markets though not environmentally friendly because of its non-biodegradability and toxicity (Encinar *et al*., 2011).

Allamanda seed was chosen as the feed stock for this research work because it is an environmentally friendly raw material, it is available in commercial quantity and is a non edible plant that has great potential as feed stock for the production of biodiesel and biolubricant. Allamanda oil is considered non edible oil due to the presence of toxic esters in it (Rumana, 2004).

Biodiesel is a renewable diesel fuel alternative that can be made by chemically combining any natural oil or fat with an alcohol such as ethanol or methanol, methanol had mostly been used as alcohol for producing biodiesel in commercial quantity (Christopher *et al*., 2002).

Biodiesel is a better alternative for petroleum oil based diesel, the combustion of fossil fuels during previous centuries had drastically added to the level of carbon monoxide (CO) and other "greenhouse gases" that traps heat in our atmosphere (Haas, 2005).

Generally, lubricants are substance introduced to reduce friction between metal surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move. Lubricants are basically classified according to the source of their feed stock; mineral oil lubricants and bio-lubricants (Mandl, 2010).

Lubricants that are synthesized from plant oils and other environmentally friendly sources are referred to as biolubricants. Biolubricants are attractive to global consumers because of its environmental benefits and the fact that it is made from renewable sources (Alamu *et al*., 2007). The production of biolubricant is necessary to serve as a substitute lubricant to replace or supplement conventional lubricant due to its numerous advantages such as biodegradability, renewability and lower gaseous emission profile (Sharma *et al*., 2010). The viscosity of biolubricants does not vary with temperature as much as the petroleum based lubricants, this makes biolubricants suitable for high temperature applications as high as 259 $^{o}$C and above and they produce fewer emissions due to higher boiling temperature ranges of esters (Sharma *et al*., 2010).

Biolubricants are also cost saving on account of less maintenance due to longer intervals between re-lubrication (Monyem and Van-gerpen, 2001). The lubricity of biolubricant is 2 to 4 times better than their petroleum based corresponding lubricants, this is enhanced with the polar nature of lubricants and also enhances the affinity towards the metal surfaces resulting in substantially increased thin film strength (Ghazi *et al*., 2010).

In many production processes in industries, catalyst is a very important factor that affects the rate of reaction. Catalyst are generally substance that increase or decrease the rate of reaction, they are basically classified according to their physical state, their chemical nature or the nature of the reactions that they catalyze. They are categorized into homogenous and heterogeneous catalyst (Nadia, 2018).

Some of the reason for chosen heterogeneous catalyst over homogenous catalyst are because different reaction phases are possible, heterogeneous catalyst has wide range of operating conditions (high pressure/temperature), they require specialized set of analytical methods (for example, X-ray methods), insensitivity of the presence of free fatty acid (FFA), lower toxicity, the possibility of catalyst recovery and reuse (Nadia, 2018). Metakaolin is the anhydrous calcined form of the clay mineral kaolinite, acid activated metakaolin was used as catalyst in the course of this work because its capacity of withstanding temperature as high as 160 $^{o}$C at constant stirring (Kristof *et al*., 2002).

## 1.2 Statement of the Research Problem

Adverse effect of petroleum based lubricant on the environment were due to its non-biodegradability, high carbon emission and toxicity. Edible feed stock for biolubricant production increases the cost of the product and compete with food security. Hitherto, homogeneous catalysts used for the production of biolubricant undergo soap formation during processing and low yield. Thus, adding to the cost of production.

## 1.3 Aim and Objectives of the Study

This research work is aimed at developing an acid activated catalyst from kaolinite clay for the production of biolubricant through optimization of the transesterification process parameters using Box-Behnken design module of Response Surface Methodology (RSM) available in "Design Expert ® Software" and using Allamanda seed oil as feedstock.

The aim of this research work will be achieved through these objectives:

i. Preparation and characterization of an acid activated metakaolin using the following analysis (X-ray Diffrraction, X-ray Fluorescence, Scanning Electron Microscopy and Brunauer- Emmett- Teller).
ii. Extraction and characterization of Allamanda Seed Oil; (determination of physiochemical properties).
iii. Transesterification of Allamanda seed oil, optimization of the produced biodiesel using Box-Behnken module of Response Surface Methodology available in "Design Expert Software" and the characterization of the process parameters for the produced Allamanda oil based biodiesel.
iv. Transesterification of the produced biodiesel with trimethyolpropane (TMP) to produce an Allamanda oil based biolubricant and the characterization of the biolubricant.

## 1.4 Justification of the Study

Biolubricants are biodegradable, renewable and environmentally friendly. The usage of waste and nonedible feedstock that are readily available aided in reducing cost of the produced biolubricant. Also, it does not compete with food supply and food security. The Production of an acid activated catalyst from kaolin clay helped in cost reduction of the produced biolubricant.

## 1.5 Scope of the Study

The scope of this research work is limited to the extraction of oil from Allamanda seeds sourced from Ciromawa estate, along Bosso Road, Niger State; as feed stock for biodiesel production. Development and characterization of an acid activated catalyst from kaolin clay. Production and optimization of Allamanda oil base biodiesel and transesterification of the produced biodiesel to obtained the biolubricant, the biolubricant was produced with molar ratio of 4:1, reaction temperature of 120 $^{o}$C, catalyst weight of 0.5 % wt and reaction time of 2 hours 30 minutes.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1 Allamanda Cathartica

Allamanda cathartica is commonly called golden trumpet, yellow bell, yellow Allamanda, guinea herb or trumpetvine, it is a species of flowering plant of the genus Allamanda in the family Apocynaceae (Petricevich and Abarca-Vergasa, 2019). Yellow Allamanda (Allamanda cathartica) is regarded as an environmental weed in northern Queensland, it is one of the exotic ornamental vines that have become invasive in this region after escaping from garden plantings (Petricevich and Abarca-Vergasa, 2019). This specie was first recorded as naturalized in Queensland in 1945. By 1992, it was recognized as weed of roadsides in the wet tropics region of northern Queensland but it was not then considered to be a highly priority environmental weed (Chaithra and Satish, 2016).

Allamanda cathartica has continued to increase and is widely naturalized in the rain forests of northern and central Queensland, yellow Allamanda was recently ranked among the top 25 species on a prioritized list of weeds of the wet and dry tropics regions in northern Queensland (Chaithra and Satish, 2016).

This specie also grows along creeks and roadsides and in disturbed natural vegetation in northern Western Australia. It was recorded as naturalized in this state in 1993 and is locally naturalized on creeklines on Koolan Island (Petricevich and Abarca-Vergasa, 2019).

Allamanda cathartica can also be found in other parts of the world including Nigeria; it was sourced from Ciromawa Estate along Bosso Road, Minna, Niger State, Nigeria.

### 2.1.1 Description of Allamanda Plant

Allamanda is a vine shrub climbing up to 2m high 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-Vergasa, 2019). Allamanda cathartica has smooth, red stems that bleed milky sap when cut, it leaves are glossy, dark green, leathery and lance shaped, it flowers are bright yellow trumpet shape, consisting of five overlapping petals, 6-10 cm across, appear in clusters at the ends of steams (Petricevich and Abarca-Vergasa, 2019).

Yellow Allamanda fruit is a seed capsule, round with soft spines 4 cm across, seeds are spherical in shape and slightly winged, yellow Allamanda spreads via the dumping of garden refuse and plants climbing from gardens into adjoining areas, it seeds are spread on wind and water (Chaithra and Satish, 2016).

Yellow Allamanda prefers moist, well drained, soils in tropical regions, at present it is mainly a weed of road side and nearby bushlands in the wet tropical of areas, but is also reported to grow along creeks and disturbed natural vegetation in other parts of the world (Chaithra and Satish, 2016).

### 2.1.2 Uses of Allamanda carthatica

One of the studies of Allamanda carthatica has indicated the potential anti-inflammatory, laxative, antioxidant, antibacterial and antifungal properties from Allamanda flower extracts (Petricevich and Abarca-Vergasa, 2019). In traditional medicine an infusion of the bark and leaves is used as purgative, the leaf extracts had displayed inflammatory, antifertility potency in male, antimicrobial activity against multiple drug resistant clinical pathogen and also found to exhibit antioxidant activities, membrane stabilizing property and healing activities

(Petricevich and Abarca-Vergasa, 2019). Other studies had shown that Allamanda carthatica cures colic, jaundice, diarrhea, malaria and vomiting, it also contains nutrients such as alkaloids, fatty acids, carbohydrate, flavonoids and saponins (Chaithra and Satiah, 2016).

Allamanda tree produces it fruits at a very high rate during the raining season, from April to September, the sustainability of this tree can be assured if continuously watered even during the dry season.

### 2.1.3 Oil extraction technique

There are several techniques of oil extraction employed in obtaining oil from seeds.

i. **Enzymatic oil extraction process**

The enzymatic oil extraction process has become a promising process for extraction of oil, in this technique suitable enzymes are used to release oil from crushed kernels. It major merit is that it is environmentally friendly and does not produce volatile organic compounds as atmospheric pollutants (Rumana, 2004). One main demerit associated with this process is the long process time which is necessary for enzymes to liberate oil bodies.

ii. **Hot water extraction**

In this technique of oil extraction, water bath is used for the extraction of the oil. The seeds are crushed, placed in a beaker and mixed with solvent (hexane). It is then placed in water bath at fixed temperature and fixed time with external agitation at same period of time. When the time is completed, the agitation is stopped and the heavier crushed seeds settles at the bottom of the beaker and the clear mixture of oil and hexane is separated by filtration process (Rumana, 2004).

iii. **Mechanical presses**

Extraction of oil using mechanical presses is the most conventional among the oil extraction techniques but oil extracted using this process requires further treatment of factorization and degumming. The major problem of this process is that their design suits some particular seeds (Rumana, 2004).

iii. **Solvent extraction process**

Solvent extraction process is the technique of removing one constituent from a solid by means of a liquid solvent also known as leaching. The process is sometime employed either for the production of a concentrated solution of a valuable solid material or in other to free an insoluble solid, such as pigment from soluble materials with which it is contaminated (Rumana, 2004).

iv. **Soxhlet Extraction**

This technique allows extraction of oil from the seed samples using the distillation extraction method. In the Soxhlet extractor, the sample soaks in hot solvent usually hexane that is periodically siphoned off, distilled and returned to the sample. This process continues until the siphoned-off solvent becomes clear. The advantage of soxhlet apparatus over hot water extraction is that, there is no filtration necessary and oil yield is better than hot water extraction process (Rumana, 2004).

## 2.2. KAOLIN

Kaolin, or china clay, is nearly white in colour. It is distinguished from other industrial clays based on its fine particle size and pure colouring. It ability to disperse in water make it an ideal pigment, kaolin is derived from the mineral kaolinite which comes from the earth's crust (Oribayo *et al*., 2013). It is an aluminum silicate represented as $Al_2O_3$-$2SiO_2$-$2H_2O$.

The primary constituent in kaolin is the mineral kaolinite, a hydrous aluminum silicate formed by the decomposition of minerals such as feldspar (Oribayo *et al*., 2013).

### 2.2.1 Industrial application

Kaolin is used in industries because of its unique physical and chemical properties. Shape, particle size, colour, softness and non-abrasiveness are physical properties that are especially important (Attah and Oden, 2010). Chemical properties, such as comparatively low base exchange capacity, as well as relative insolubility, are governing in many uses (Attah and Oden, 2010).

#### 2.2.1.1 *Paper industry*

The primary use of kaolin is in the paper industry. It serves as a paper coating which improves appearance by contributing to brightness, smoothness and gloss. It also improves printability, it is used by paper industry as a filler reducing cost and the use of tree-based resources (Attah and Oden, 2010).

The largest single user of kaolin is the paper industry because when kaolin is used, paper product prints better and are made whiter and smoother, kaolin used as a filler in the interstices of the sheet adds ink receptivity and opacity to the paper sheet (Manukaji, 2013). Kaolin used to coat the surface of the paper sheet makes possible sharp photographic illustrations and bright printed colors (Manukaji, 2013). Kaolin constitutes nearly one-third the weight of today’s slick sheet magazines.

#### 2.2.1.2 *Ceramic industry*

Kaolin is used in ceramic whiteware products, insulators, and refractories. In whitewares, kaolin helps in accurate control of molding properties, adds dry and fired strength, dimensional stability and a smooth surface finish to the ware (Victor, 2017). The excellent dielectric properties and chemical inertness of kaolin makes it well suited for porcelain electrical insulators. In refractory applications, the dimensional stability, high fusion point and low water content, along with high green strength, make kaolin an important constituent (Victor, 2017).

#### 2.2.1.3 *Paint industry*

Kaolin is used in paint industry because it is chemically inert and insoluble in the paint system; it has a high covering power, gives the paint desirable flow properties and is low in cost (Victor, 2017).

#### 2.2.1.4 *Rubber industry*

Kaolin is used as filler in many rubber goods. It adds strength, abrasion resistance and rigidity to both natural and synthetic rubber products. In general, most rubber products extrude more easily after kaolin filler is added (Manukaji, 2013). The major reason that kaolin is used in rubber compounds is its whiteness and low cost. Although kaolin costs less than most other rubber pigments, it has excellent functional properties (Victor, 2017).

#### 2.2.1.5 *Other uses*

Kaolin has a variety of other uses in products including cable insulation, specialty films and fertilizer, glass fiber, white cement and refractory insulation bricks. New uses are being discovered frequently and ensure that the mineral will remain in demand for a long time.

## 2.3 Lubrication

Lubrication is the science of reducing friction between two solid bodies in relative motion by interposing a lubricant between their rubbing surfaces. Lubrication is the most vital singular factor in plant maintenance (Aldajah and David, 2009). It keeps the plant young; contribute to better profits by improving the wear components, equipment availability and reliability. Much work has been done in this direction by improving lubrication, mechanization, modification of the existing lubricating system, elimination of lubricant wastage and thus bringing down the consumption of lubricants and wear parts (Aldajah and David, 2009).

### 2.3.1 Lubricant

A lubricant is any substance introduced to minimize friction between surfaces in mutual contact, which aid in reducing heat generated when the surfaces moves. It also has the function of transporting foreign particles, transmitting forces and cooling of the surfaces in mutual contact. The property of reducing friction is known as lubricity (Aldajah and David, 2009).

A good lubricant generally possesses these characteristics:

i. High resistance to oxidation

ii. Corrosion prevention
iii. Thermal stability
iv. High viscosity index
v. Low freezing point
vi. High boiling point
vii. Hydraulic stability

One of the paramount applications of lubricants is in the form of motor oil, it helps in protecting the internal combustion engines in powered equipment and in motor vehicles (Aldajah and David, 2009). Typically, lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefin, esters, silicones, fluorocarbons and many others are sometimes used as base oils (Aldajah and David, 2009).

Lubricants such as 2-cycle oils are added to fuels like gasoline which has low lubricity, sulfur impurities in fuels also provide some lubrication properties, which have to be taken in account when switching to a low-sulfur diesel; biodiesel is a popular diesel fuel additive providing additional lubricity (Aldajah and David, 2009).

### 2.3.2 Purpose

A lubricant performs the following functions.

i. Prevent corrosion
ii. Keep moving parts apart
iii. Reduce friction
iv. Carry away contaminants and debris

v. Transfer heat

vi. Protect against wear

#### 2.3.2.1 *Prevent corrosion*

Many lubricants are formulated with additives that forms chemical bonds with surfaces or that excludes moisture to prevent corrosion and rust. It reduces corrosion between two metallic surfaces and avoids contact between these surfaces to avoid immersed corrosion (Suraj, 2015).

#### 2.3.2.2 *Keep moving parts apart*

Lubricants are typically used to separate moving parts in a system. This separation has benefit of reducing friction, wear and surface fatigue, together with reduced heat generation, operation noise and vibrations (Suraj, 2015). Lubricants achieve this in several ways; the common is by forming a physical barrier that is, a thin layer of lubricant separates the moving parts. This is analogous to hydroplaning; the loss of friction observed when a car tire is separated from the road surface by moving through standing water, this is termed hydrodynamic lubrication (Suraj, 2015). In cases of high surface pressures or temperatures, the fluid film is much thinner and some of the forces are transmitted between the surfaces through the lubricant.

#### 2.3.2.3 *Reduce friction*

Typically, the lubricant-to-surface friction is much less than surface-to-surface friction in a system without any lubrication, thus the use of lubricant reduces the overall system friction (Bernard, 2006). Reduced friction has the benefit of reducing heat generation and reduced formation of wear particles as well as improved efficiency, lubricants may contain additives known as friction modifiers that chemically bind to metal surfaces to reduce surface friction even when there is insufficient bulk lubricant present for hydrodynamic lubrication for example, protecting the valve train in a car engine at startup (Bernard, 2006).

#### 2.3.2.4 *Carry away contaminants and debris*

Lubricant circulation systems have the ability of carrying away internally generated debris and external contaminants that get introduced into the system to a filter where they can be removed, lubricants for machines that regularly generate debris or contaminants such as automotive engines typically contain detergent and dispersant additives to assist in debris and contaminant transport to the filter and removal (Bernard, 2006). Over time the filter will get clogged and require cleaning or replacement, hence the recommendation to change a car's oil filter at the same time as changing the oil, in closed systems such as gear boxes the filter may be supplemented by a magnet to attract any iron fines that get created (Bernard, 2006).

In circulatory system the oil will only be as clean as the filter can make it, thus it is unfortunate that there are no industrial standards by which consumers can readily assess the filtering ability of various automotive filters, poor automotive filters significantly reduces the life of the machine (engine) as well as making the system inefficient (Bernard, 2006).

#### 2.3.2.5 *Transfer heat*

Gas and liquid lubricants can transfer heat; liquid lubricants are much effective on account of their high specific heat capacity. Typically, the liquid lubricant is constantly circulated to and from a cooler part of the system, although lubricants may be used to warm as well as to cool when a regulated temperature is required (Lois and Arkoudeas, 2012). This circulating flow also determines the amount of heat that is carried away in any given unit of time. High flow systems can carry away a lot of heat and have the additional benefit of reducing the thermal stress on the lubricant, thus lower cost liquid lubricants may be used (Lois and Arkoudeas, 2012).

The primary drawback is that flows typically require larger sumps and bigger cooling units, a secondary drawback is that a high flow system that relies on the flow rate to protect the lubricant from thermal stress is susceptible to catastrophic failure during sudden system shut downs and an automotive oil cooled turbocharger is a typical example (Lois and Arkoudeas, 2012). Turbochargers gets red hot during operation and the oil that is cooling them only survives as its residence time in the system is very short (that is, high flow rate). If the system is suddenly shut down (pulling into a service area after a high-speed drive and stopping the engine) the oil that is in the turbo charger immediately oxidizes and will clog the oil ways with deposits. Over time these deposits can completely block the oil ways, reducing the cooling with the result that the turbocharger experiences total failure, typically with seized bearings (Lois and Arkoudeas, 2012).

#### 2.3.2.6 *Protect against wear*

Lubricants prevent wear by keeping moving parts apart, lubricants may also contain anti-wear or extreme pressure additives to boost their performance against wear and fatigue (Bernard, 2006).

### 2.3.3 Types of lubricant

Lubricants may be gaseous, liquid, plastic or solid, lubricants are classified according to their physical state includes materials and coatings that are self-lubricating. The additives listed under solids are usually not lubricants themselves but contribute important lubricating properties, when added to oil (Bernard, 2006).

#### 2.3.3.1 *Gaseous lubricant*

The followings are gaseous lubricants

i. Air
ii. Helium
iii. Carbon dioxide

#### 2.3.3.2 *Liquid lubricants*

**Mineral oil (from petroleum crude)**

i. Straight or unadulterated.
ii. Compound with fixed oils or their derivatives.
iii. Compound with special additives.
iv. Compound with fixed oils or their derivatives, plus chemical additives such as polymers and metal soaps.

**Fixed oil**

i. (acid less tallow oil and lard oils)
ii. Vegetable (Allamanda oil, castor oil, rapeseed oil, palm kernel oil and jatropha oil).

**Synthetic fluids**

i. Silicones
ii. Silicate esters

iii. Phosphate esters
iv. Polyglycols
v. Diabasic acid esters
vi. Chlorofluro carbon polymers

**Soluble oils or compound**

i. Mineral oil compound with emulsifying agents.
ii. Synthetic fluids compounded with emulsifying.

#### 2.3.3.3 *Solid lubricants*

Solid lubricants are rarely used directly but commonly it is added with other lubricants to increase some of its properties. Examples of solid lubricants are graphite, molybdenum disulfide, mica, talc or soap, lead carbonate and wax (Bernard, 2006).

#### 2.3.3.4 *Additives*

Additives are the substances which are added with the lubricants to fortify some of their properties, some of the additives are metallic phosphates, few additives, metallic oleates, metallic chloride, metallic sulfides, metallic stearates, metallic oxides and metallic oxalates (Bernard, 2006).

#### 2.3.3.5 *Selection of lubricants*

Factors to be considered to select a good lubricant are:

i. The operating factors of equipment, such as speed, load and temperature.
ii. Equipment condition-weather old or new.
iii. Compatibility of the lubricant with materials in contact.

iv. Operating environment

v. Operating condition-continuous or intermittent.

vi. Lubricants application methods, lubricant maintenance system.

vii. Clearances between moving parts

viii. Type of part to be lubricated such as gear, bearing and sliding surface (Bernald, 2006).

### 2.3.4 Important properties of lubricant

i. Good emulsifying qualities.

ii. Proper fluidity or plasticity under conditions of operation.

iii. Chemical stability

iv. Film strength commensurate with loads.

v. Non-corrosive characteristics

vi. Adhesiveness to bearing surface.

vii. Fire resistance.

viii. Resistance to the effect of nuclear radiation.

ix. Rust proofing capacity.

x. Good sealing properties

xi. High viscosities.

xii. Resistances to water wash.

xiii. Resistances to foaming (Bernald, 2006).

### 2.3.5 Method of oil lubrication

The different methods used for applying lubricating oil into moving parts are classified into three types:

i. Once through oiling/ all loss method
ii. Oil reservoirs/ reuse method
iii. Circulating oil systems

#### 2.3.5.1 *Once through oiling*

Once through oiling is so named because the oil passes through the bearing only once and is lost for further use. Method of this type includes oil can lubrication, drop feed oiling, gravity feed bottle and wick feed lubrication (Aldajah and David, 2009).

Oil can lubricator: This is the direct application of oil to a moving machine part from a hand oil cane. It is used for small bearings, chains. This method has limitations, the excess oil runs off bearing (Aldajah and David, 2009).

Drop feed oiler: When a more uniform supply of oils is required, a drop feed oiler may be used. It consists of a shut off lever, feed adjustment, oil chamber, needle valve and sight glass. The dropping of the oil through the drop feed oiler can be regulated and checked from time to time to see that the oil is continuing to feed properly (Aldajah and David, 2009).

Wick feed oiler: The wick feed oiler consists of an oil reservoir and a wool wick. The wick draws oil from an oil cup by the capillary and siphoning action of the wick and feed it into an opening in the bearing (Suraj, 2015). The amount of oil being delivered to the bearing can be regulated by changing the size of the wick. The reservoir should be kept well filled, because the rate of oil feed depends on level of the oil in the reservoir (Suraj, 2015).

The bottle oiler: The bottle oiler consists of an inverted glass mounted above the bearing and filled with a sliding pin which rests on the journal. When the journal rotates, it vibrates the pins, the vibration encourages the flow of oil from bottle to the bearing through the space between pin and its sleeves (Suraj, 2015).

#### 2.3.5.2 *Oil reservoirs/ reuse method*

In this method of lubrication, the lubricants supply to the bearings gradually leaks away and is not reused. In short, the bearing passes through the region of mix film lubrication and operate much of the time under boundary conditions (Suraj, 2015). A closer approach for maintaining a safe oils supply may be accomplished with application devices such as wick feed oilers, drop feed cups bottle oilers. Reuse method of oil application include circulating supplying lubricant for one or more machine and systems such as bath, splash, food and ring oiling (Suraj, 2015).

#### 2.3.5.3 *Circulating oil system*

This system explains a typical example, such as returning oil drains to a settling compartment, enters into reservoir. Water and heavy contaminant settle at power point from which they can be drained. Particularly purified oil overflows a baffle to a clean oil compartment. The clean oil pumps take oil through a suction strainer and pumps it to a cooler and then to bearing, gears and other lubricated parts (Suraj, 2015).

## 2.4 Principle of Lubrication

### 2.4.1 Friction

Friction is a force that resists relative motion between two surfaces in contact, it depends on the application and friction may be desirable or undesirable. Certain applications such as tire traction on pavement and braking or when feet are firmly planted to move a heavy object, rely on the beneficial effects of friction for their effectiveness (Bernald, 2006). In other applications, such as operation of engines or equipment with bearings and gears, friction is undesirable because it causes wear and generates heat, which frequently leads to premature failure (Bernald, 2006).

Two general cases of friction occur in sliding and rolling friction:

#### 2.4.1.1 *Sliding friction*

To visualize sliding friction, imagine a steel block lying on a steel table, initially a force F is applied horizontally in an attempt to move the block. If the applied force is not high enough, the block will not move because of the friction between table and block resists movement (Nassar *et al*., 2015). If the applied force is increased, eventually it will be sufficient to overcome the frictional resistance force F and the block will begin to move. At this precise instant, the applied force F is equal to the resisting friction force F and is referred to as the frictional force (Nassar *et al*., 2015).

#### 2.4.1.2 *Rolling friction*

When a body rolls on a surface, the force resisting the motion is termed rolling friction or rolling resistance, experience shows that much less force is required to roll an object than to slide or drag it because force is required to initiate and maintain reducing motion, there must be a definite but small amount of friction involved. Unlike the coefficient of rolling friction, the coefficient of rolling friction varies with conditions and has a dimension expressed in units of length (Suraj, 2015).

### 2.4.2 Wear

Wear is defined as the progressive damage resulting in material loss due to relative contact between adjacent working parts (Wang *et al*., 2017). Although some wear is to be expected during normal operation of equipment, excessive friction causes premature wear and this creates significant economic costs due to equipment failure, cost for replacement parts and downtime (Wang *et al*., 2017). Friction and wear also generate heat, which represents wasted energy that is not recoverable. Wear also causes overall loss in system efficiency (Suraj, 2015).

Ordinarily, wear is thought of only in terms of abrasive wear occurring in connection with sliding motion and friction. Wear can also result from adhesion, fatigue or corrosion. The following are types of wear (Suraj, 2015).

#### 2.4.2.1 *Adhesive wear*

Adhesive wear frequently occurs because of shearing at points of contact or asperities that undergo adhesion or cold welding. Shearing occurs through the weakest section, which is not necessarily at the adhesion plane, shearing occurs in softer material but such a comparison is based on shear tests of relatively large pure samples (Wang *et al*., 2017). The adhesion junctions are very small spot weakness or impurity that would be insignificant in a large specimen but in practice may be sufficient to permit shearing through the harder material (Wang *et al*., 2017). Theoretically, this type of wear does not remove material but merely transfer it between wearing surfaces, the transferred material is often loosely deposited and eventually flakes away in microscopic particles (Wang *et al*., 2017).

#### 2.4.2.2 *Pitting wear*

Pitting wear is due to surface failure of a material as a result of stresses that exceed the endurance (fatigue) limit of the material. Metal fatigue is demonstrated by bending a piece of metal wire, such as paper clip, back and forth until breaks, whenever a metal shape is deformed repeatedly, it eventually fails (Kalam *et al.*, 2014). A different type of deformation occurs when a ball bearing under a load rolls along its race, the bearing is flattened somewhat and the edges of contact are extended outward (Kalam *et al.*, 2014). This repeated flexing eventually results in microscopic flakes being removed from the bearing, fatigue wear also occurs during sliding motion and gear teeth often fails due to pitting (Kalam *et al*., 2014).

#### 2.4.2.3 *Abrasive wear*

Abrasive wear occurs when a hard surface slides against and cuts grooves from a surface, this condition is frequently referred to as two-body abrasion, particle cut from the softer surface or dust and dirt introduced between wearing surfaces also contribute to abrasive wear (Aldajah and David, 2009).

#### 2.4.2.4 *Corrosive wear*

Corrosive wear occurs as a result of a chemical reaction on a wearing surface, the most common form of corrosion is due to a reaction between the metal and oxygen (oxidation), and other chemicals may also contribute to corrosion (Bernard, 2006). Corrosion products, usually oxides, have shear strength different from those of the wearing surface metals from which they were formed, the oxides tend to flakes away, resulting in the pitting of wearing surfaces. Ball and roller bearings depends on extremely smooth surfaces to reduce frictional effects (Bernald, 2006).

## 2.5 Physical Properties of Lubricant

### 2.5.1 FTIR Spectrum

The intensity of an absorption bonds depends on the change in the dipole moment of the bond and the number of the specific bonds present, the bond dipole results from the bond length and charge difference between the two atoms (Bilal *et al*., 2013). When the molecule absorbs a photon, it stretches and the bond length changes and leaves the charge difference, which can be derived from the electronegativity values of the atoms involved (Bilal *et al*., 2013).

### 2.5.2 Acid/Neutralization number

The acid number or neutralization number is a measure of the amount of potassium hydroxide required to neutralize the acid contained in a lubricant, acids are formed as oils oxidize with age and service (Bilal *et al*., 2013). The acid number for an oil sample is indicative of the age of the oil and can be used to determine when the oil must be changed (Bilal *et al*., 2013).

### 2.5.3 Flash point and fire point

Oil extracted from plants without any chemical modifications will show a poor pour point value of roughly just above 0 $^{o}$C. However, in a winter climate, most lubricants are required to be able to continue to function at a few degrees below 0 $^{o}$C. (Vipin *et al*., 2017). Pour point is one of the most critical properties in determining the lubricants performances; this property is one of the main difficulties for the plant based oil used to produce the biolubricant (Kasim *et al*., 2011).

Flash point is the lowest temperature, to which a lubricant must be heated before its vapor, when mixed with air, will ignite but not continue to burn. The fire point is the temperature at which lubricant combustion will be sustained (Kasim *et al*., 2011). The flash and fire points are useful in determining a lubricants volatility and fire resistance, the flash point can be used to determine the transportation and storage temperature requirements for lubricants (Basumatary, 2013).

Manufacturer and Toll blender can also utilize the use of flash point to detect potential product contamination, a lubricant exhibiting a flash point significantly lower than normal will be suspected of contamination with a volatile product. Products with a flash point less 38 $^{o}$C will usually require special precautions for safe handling, the fire point for a lubricant is usually 8 to 10 percent above flash point (Kasim *et al*., 2011). The flash point and fire point should not be confused with the auto-ignition temperature of a lubricant, which is the temperature at which a lubricant ignite spontaneously without an external ignition source (Ashraful *et al*., 2013).

### 2.5.4 Iodine value

This is the measure of the degree of unsaturation in relation to the amount of fat or oil, iodine value is defined as the gram of iodine absorbed per 100 g sample (Ashraful *et al*., 2013). When saturated oil is heated, polymerization of the triglyceride occurs which leads to gum formation, unsaturated compounds are susceptible to oxidation when exposed to air, thereby degrading the oil quality. The iodine value is directly proportional to the degree of unsaturation, the higher the iodine value the greater the degree of unsaturation (Ashraful *et al*., 2013)

### 2.5.5 Cloud point

The cloud point is the temperature at which oil/fuel starts to crystalize, such as paraffin wax, begin to form and separate from oil. As the temperature drops, wax crystallizes and becomes visible, certain oils must be maintained at temperatures above the cloud point to prevent clogging of filters (Bilal *et al*., 2013).

### 2.5.6 Pour point

The Pour point is the lowest temperature at which oil will flow, this property is crucial for oils that must flow at low temperatures. A commonly used rule of thumb when selecting oils is to ensure that the pour point is at least $10^0$C lower than the lowest anticipated ambient temperature (Bilal *et al*., 2013).

### 2.5.7 Viscosity index

The viscosity index, commonly designated VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature (Bilal *et al*., 2013). Viscosity index can be classified as follows:

i. Low VI- below 35
ii. Medium VI- 35 to 80
iii. High VI- 80 to 110
iv. Very high VI- 110 to 125
v. Super VI- 125 to 160
vi. Super high VI- above 160 to 200

A high viscosity index indicates small oil viscosity changes with temperature, a low viscosity index indicates high viscosity changes with temperature (Bilal *et al*., 2013). Therefore, a fluid that has high viscosity index can be expected to undergo very little change in viscosity with temperature extreme and is considered to have a stable viscosity (Bilal *et al*., 2013). A fluid with a low viscosity index can be expected to undergo a significant change in viscosity as the temperature fluctuates.

Oil with a VI of 95 to 100 would change less than one with VI of 80. Knowing the viscosity index of oil is crucial when selecting a lubricant for an application and is especially critical in extremely hot or cold climates. Failure to use oil with the proper viscosity index when temperature extremes are expected may result in poor lubrication and equipment failure (Bilal *et al*., 2013).

### 2.5.8 Viscosity

Viscosity is commonly known as resistance to flow, if lubricating oil is considered as a series of fluid layers superimposed on each other, the viscosity of the oil is a measure of the resistance to flow between the individual layers (Nuhu *et al*., 2020). A high viscosity implies high resistance to flow while a low viscosity indicates low resistance to flow. Viscosity varies inversely with temperature (Nuhu *et al*., 2020). Viscosity is also affected by pressure; higher pressure causes the viscosity to increase and subsequently the land- carrying capacity of the oil also increase, this property enables use of thin oils to lubricate heavy machinery. Load-carrying capacity also increases as operating speed of the lubricated machinery is increased. There two methods for measuring viscosity which are shear and time (Nuhu *et al*., 2020).

#### 2.5.8.1 *Shear*

When viscosity is determined by directly measuring shear stress and shear rate, it is expressed in centipoise (Cp) and is referred to as the absolute or dynamic viscosity (Bilal *et al*., 2013). In the oil industry, it is more common to use kinematic viscosity, which is the absolute viscosity divided by the density of the oil being tested (Bilal *et al.*, 2013). Kinematic viscosity is expressed in centistoke (cSt). Viscosity in centistoke is conventionally given at two standard temperatures: 40 $^{o}$C and 100 $^{o}$C.

#### 2.5.8.2 *Time*

Another method used to determine oil viscosity measures the time required for an oil sample to flow through a standard orifice at a standard temperature. Viscosity is then expressed in SUS (Saybolt Universal Seconds). SUS viscosities are also conventionally given at two standard temperatures of 37 $^{o}$C and 98 $^{o}$C (Bilal *et al*., 2013).

## 2.6 Lubricant Quality Requirement

### 2.6.1 Oxidation stability

Oxidation is one of the primary causes for decreasing the stability of hydraulic fluids. Once the reaction begins, a catalytic effect takes place. The chemical reaction result in formation of acids that can increase the fluid viscosity and can cause corrosion. Polymerization and condensation produce insoluble gum, sludge and varnish that cause sluggish operation, increase wear, reduce clearances and plug lines (Ebtisam *et al*., 2017).

### 2.6.2 Demulsibility

Water that enters a hydraulic system can emulsify and promote the collection of dust, grit and dirt and this can adversely affect the operation of valves, servos and pumps, increase wear and corrosion, promote fluid oxidation, deplete additives and plug filters (Ebtisam *et al*., 2017). However, some a4dditives such as anti-rust treatments actually promote emulsion formation to prevent separate water from settling and breaking through the Anti-rust film (Ebtisam *et al*., 2017).

### 2.6.3 Air conditioning and foaming

Air enters a hydraulic system through the reservoir or through air leaks within the hydraulic system. Air entering through the reservoir contributes to surface foaming on the oil. Good reservoir design and use of foam inhibitors usually eliminate surface foaming (Ebtisam *et al.*, 2017).

### 2.6.4 Anti- wear properties

Conventional hydraulic fluids are satisfactorily for low pressure and low speed applications. However, hydraulic fluids for high- pressure (over 6900 kPa or 1000.5 lb/sq in) and high speed (over 1200 rpm) applications that use vane or gear pumps must contain anti-wear additives. (Ebtisam *et al*, 2017).

## 2.7 Biolubricant

Lubricants that are synthesized from plant oils and other environmentally friendly sources are referred to as Biolubricants and these are primarily triglyceride esters derived from plants and animals. Biolubricant production is necessary to serve as substitute lubricants due its numerous advantages over the petroleum based lubricants such as renewability, biodegradability and lower gaseous emission profile (Bilal *et al*., 2013).

### 2.7.1 Advantages of biolubricant

Numerous researchers have discussed on several merit of bio-based lubricants over petro-base lubricant. These can be discussed based on the following:

#### 2.7.1.1 *Renewable raw material*

Biolubricant can be synthesized from different crop oil producing plants. The base oil used for biolubricant production can be edible or non-edible oil (Mobarak *et al*., 2004). Some of the oil producing crops used for biolubricant production includes tallow, soybean, olive, sunflower, palm and coconut (Mobarak *et al*., 2004). Therefore, the cost of biolubricant from oil seed is relatively cheap compare to the conventional ones.

#### 2.7.1.2 *Performance*

Biolubricant have tremendous lubricity of about two to four times over mineral or conventional base corresponding lubricant. Biolubricant also possess a strong dipole moments and polar sites (Tahari *et al*., 2015). Biolubricant are known to withstand better antifriction exhibit, high pressure stability, stable film production between two surfaces, high flash point and high viscosity index when compared to conventional lubricant (Mobarak *et al*., 2004).

#### 2.7.1.3 *Environmental health benefit*

Biolubricant has the capability to contribute towards energy goal independence and security due to the biodegradability, non-toxicity and causes less harm to the environment (Ahmad-Majdi *et al*., 2018). Biolubricant causes less dermatological harm and exhibit better skin compatibility when compared to the petroleum based lubricant (Mobarak *et al*., 2004; Bilal *et al.*, 2013; Tahari *et al*., 2015). The increase in utilization of biobase lubricant will reduce the consumption petro-base lubricant which will improve the use of renewable resources and proper management of carbon cycle which may contribute to the minimizing adverse health and environmental effects (Bilal *et al.*, 2013).

#### 2.7.1.4 *Sustainability*

The environmental consideration concerning the sustainable development to attract interest of raw material for industries in time of excess production of agriculture produce (Abderrahim *et al*., 2018). The biodegradability and renewability of biolubricant is an imperative factor that determine the development of an environment. The biodegradability and low eco-toxicity are used to describe the biodegradable lubricant (Bilal *et al*., 2013).

#### 2.7.1.5 *Economy benefit*

The price stability and economic concern provide a potential edge on the use of renewable sources of biolubricants over petro-base lubricants (Ahmad-Majdi *et al*., 2018). The cost of production and disposal of biolubricant are less expensive when compare to petro-base lubricant (Ahmad-Majdi *et al.*, 2018).

### 2.7.2 Disadvantages of biolubricant

Biolubricants have bad odour if contaminants are present, they have high viscosity at low temperatures, poor oxidation stability at high temperature although additives designed specifically for plant based lubricants eliminate stability issues related to extreme high and low temperature. An untreated biolubricant lacks oxidation stability and will have high pour point (Bilal *et al.*, 2013).

#### 2.7.2.1 *Limited feedstock*

The production of biolubricant are associated with the challenge of limited availability of feedstock. It has been estimated to account for 75% of the total cost of production of biolubricant (Bilal *et al*., 2013).

#### 2.7.2.2 *Poor oxidative and thermal stability*

The presence of long unsaturated fatty acids leads to poor temperature stability while poor oxidative stability is observed when there is presence of excess of polyunsaturated fatty acids and even long monounsaturated behavior degrades the low temperature (Borugadda and Goud, 2015). The thermal stability of oil is also affected by the rise in temperature as a result of drilling process which degrades the quality of biolubricants (Borugadda and Goud, 2015). Additives are design specifically to improve the stability concern related to extreme low and high temperature and also the oxidative stability. If biolubricant is not synthesized to improve the oxidative property it leads to high pour point value (Bilal *et al.,* 2013).

### 2.7.3 Properties of biolubricant

Generally, biolubricants exhibit numerous desirable and suitable physicochemical properties. These properties include:

i. High lubricity
ii. High viscosity index (VI)
iii. High flash point, and
iv. Low evaporative losses.
v. High biodegradability (Jain and Suhane, 2020)

### 2.7.4 Factors affecting biolubricant

Lubricant production are affected by a number of factors such as temperature, time, catalyst concentration and molar ratio of the methanol which must be accurately calculated before taking any step of production to yield accurate product. This can be done using a normal chemistry calculation (that is, no of mole = mass / molar mass) in attaining the quantity of catalyst, alcohol (methanol) needed to carry out the experiments (Jain and Suhane, 2020).

## 2.8 Feedstock for Biolubricant

Feed stock for sustainable production of biolubricant include non-edible and edible vegetable oils (Jain and Suhane, 2020). The major feed stock used for the production of biolubricant include alcohol, catalyst and biodiesel.

### 2.8.1 Alcohol

Some of these alcohols are methanol, ethanol, propanol and butanol. Methanol is mostly used in the production of biodiesel commercially, because of it low boiling point compared to ethanol (Ayan, 2009). The overall process is a sequence of three consecutive and reversible reactions in which monoglycerides and diglycerides are formed as intermediates. However, excess alcohol is used to increase the yield of the alkyl esters and to allow its phase separation from the glycerol formed (Schuchardt *et al.*, 1997).

### 2.8.2 Biodiesel / fatty acid methyl ester

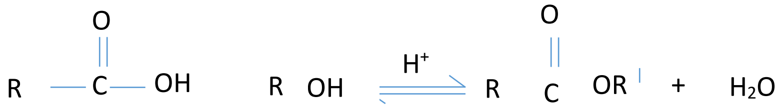
Fatty acid methyl ester also known as biodiesel is monoglycerides fatty acids derived from vegetable oil or animal fat. It is also referred to diesel equivalent for diesel engine obtained from biological source (Bilal *et al.*, 2013). Biodiesel is produce as a result of transesterification process in which involves the reaction between vegetable oil and alcohol in the presence of potassium hydroxide as a catalyst (Bilal *et al.*, 2013). Transesterification reaction of vegetable oil with methanol to produce biodiesel.

### 2.8.3 Catalyst

Catalyst is a substance introduced to a chemical mixture to speed up the rate of chemical reaction or to minimize the activation energy. Trimethylolpropane (TMP) esters are synthesized by transesterification process of fatty acids of vegetable oil with TMP in the presence of an acid catalyst (Menkiti *et al*., 2017). The acid catalyst used includes nitric acid, perchloric acid, P-toluene sulfonic acid, sulphuric acid and acid activated metakaolin. In enzymatic transesterification reaction enzyme such as lipase is commonly used. Moreover, enzymes are catalyzed transesterification reaction for synthesis of biolubricant has however attract less attention since the use of enzymes leads to high cost and low reactivity (Menkiti *et al*., 2017).

### 2.8.4 Chemistry of biolubricant

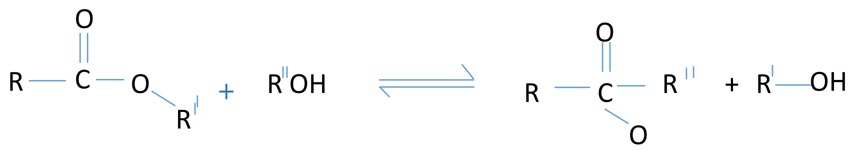
According to Jose *et al*. (2006) ester is the product that is achieve through reaction between carboxylic acid and alcohols and the process is known as Esterification process. The catalyst required to carry out the process is an acid and the reaction tends to attain equilibrium in few hours. The acid catalyst require is either sulphuric acid or hydrochloric acid. The typical mechanism required for this type of reaction is known to be nucleophilic substitution reaction in acyl-carbon (Jose *et al*., 2006).



$$R - \overset{O}{\overset{\|}{C}} - OH \qquad R\ OH \ \overset{H^+}{\rightleftharpoons}\ R\ \overset{O}{\overset{\|}{C}}\ OR' + H_2O \qquad (2.1)$$

Equation (2.1); Esterification reaction scheme between a carboxylic acid and alcohol.

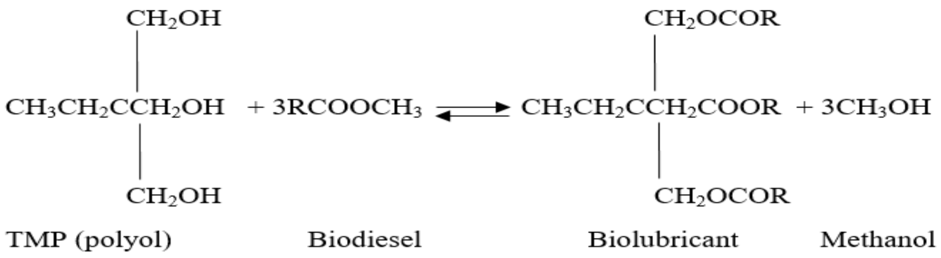
Esters are furtherly synthesis to obtained transesterification reaction. The transesterification mechanism is also similar to that of esterification process, which is acid catalyst.



(2.2)

Equation (2.2); Transesterification reaction between an ester and alcohol

The transesterification of castor oil with methanol yield methylricinoleate which is a major constituent of castor biodiesel. The transesterification of this compound with polyhydric alcohol or superior alcohols (Trimethylolpropane, pentaerythritol or Neo-pentylglycol) give rise to the production of polyesters which are important synthetic base oils precursors.



$$CH_3CH_2\overset{CH_2OH}{\underset{CH_2OH}{C}}CH_2OH + 3RCOOCH_3 \rightleftharpoons CH_3CH_2\overset{CH_2OCOR}{\underset{CH_2OCOR}{C}}CH_2COOR + 3CH_3OH$$

(2.3)

Equation (2.3); Shows the reaction between polyol (trimethylolpropane) and methyl ester (biodiesel).

### 2.8.5 Transesterification

Transesterification is also referred to general term used to describe the essential class of organic reactions where an ester is transformed into another (Schuchardt *et al*., 1997). Transesterification is referred to the chemical reaction in which three moles of alcohols react with a mole of triglyceride to give a product which are fatty acid methyl esters (biodiesel) and glycerol mixture (Bilal *et al*., 2013). The transesterification of vegetable oil derived methyl ester with polyol is essentially reverse of esterification reactions of which glycerol is replaced with commercial polyol (Bilal *et al*., 2013).

The problem faced by vegetable oil includes low thermal and oxidative stability which arise as a result of the presence of double bond and the presence of active sites in the β-hydrogen triacylglycerol ester. The problem is overcome by chemical modification (transesterification) of vegetable oil to produce better quality of biolubricant (Salimon *et al.,* 2011).

The process involves a double step, first the triglycerides is converted into methyl ester and secondly to polyol ester. In transesterification process with TMP, base catalyst is used to improve the yield of TMP esters (Akerman *et al*., 2010).

Example of catalyst used in transesterification process are potassium methoxide and sodium methoxide. The most significance advantage of using polyol instead of glycerol is the absence of β-hydrogen which enhances the thermal stability of lubricant at high temperature by preventing self-polymerization to form fatty acids (Bilal *et al*., 2013).

### 2.8.6 Parameters affecting transesterification

There are some parameters which affects the production of the production of methyl ester (biodiesel) (Momoh *et al*., 2014). The parameters include reaction temperature, catalyst concentration, molar ratio of alcohol and reaction time.

#### 2.8.6.1 *Effect of temperature on biolubricant yield*

Reaction temperature is an imperative variable that influence biolubricant yield (Akerman *et al.,* 2010). As the reaction temperature increases, the rate of reaction also increases and reaction time shortened due to the reduction in viscosity of oil (Alemayehu and Abile, 2014).

Table 2.1 shows the summary of effect of temperature on biolubricant yield from vegetable oil.

**Table 2.1: Review of Effect of Reaction Temperature**

| Feedstock | Technology method | Variation range ($^oC$) | Optimum temp. ($^oC$) | Yield (%) | Author |
|---|---|---|---|---|---|
| Fluted pumpkin seed | Transesterification | 140-160 | 160 | 81.42 | Menkiti *et al.*, 2017 |
| Castor oil | Epoxidation | 50-70 | 52.81 | 3.85 | Borugadda and Goud., 2015 |
| Palm oil | Transesterification | 80-140 | 130 | 98 | Yunus *et al.*, 2003 |
| Palm olein | Transesterification | 45-65 | 45 | 91.3 | Salimon *et al.*, 2011 |
| Palm kernel oil | Epoxidation | 30-80 | 40 | 87 | Salimon *et al.*, 2011 |
| Diesters | Esterification | 90-110 | 110 | 88.70 | Salimon *et al.*, 2011 |

### *2.8.6.2 Effect of time on biolubricant yield*

Reaction time is an imperative variable that influences the yield of biolubricant. Basically, as reaction time increases, the conversion rate of methyl ester to biolubricant increases (Sathya and Manivannan., 2013). Table 2.2 shows the summary of effect of time on biolubricant yield from vegetable oil.

**Table 2.2: Review of Effect of Reaction Time**

| Feedstock | Technology method | Variation range (hr) | Optimum time (hr) | Yield (%) | Author |
|---|---|---|---|---|---|
| Fluted pumpkin seed | Transesterification | 4-6 | 6 | 81.42 | Menkiti *et al.*, 2017 |
| Castor oil | Epoxidation | 2-4 | 2.81 | 3.85 | Borugadda and Goud., 2015 |
| Diesters | Esterification | 5-7 | 7 | 88.70 | Salimon *et al.*, 2011 |
| Methyl linoleate | Epoxidation | 4-20 | 20 | 63 | Salimon *et al.*, 2011 |

#### *2.8.6.3 Effect of catalyst concentration on biolubricant yield*

In transesterification reaction, various catalyst such as alkaline, acidic and enzymes catalyst are used to speed up the rate of conversion of methyl ester to biolubricant. Generally, homogeneous catalyst such as metal hydroxide, minerals acids and metal alkoxide are typically used in transesterification reaction. The concentration of these is an imperative factor that influences the rate of biolubricant production (Jose *et al*., 2006). Table 2.3 shows the summary of effect of catalyst concentration on biolubricant yield from vegetable oil.

**Table 2.3: Review of Effect of Catalyst Concentration**

| Feedstock | Technology method | Variation range (wt %) | Optimum catalyst. (wt%) | Yield (%) | Author |
|---|---|---|---|---|---|
| Castor oil | Epoxidation | 10-20 | 15.14 | 3.85 | Borugadda and Goud., 2015 |
| Palm oil | Transesterification | 0.7-1.2 | 0.8 | 90 | Yunus *et al*., 2003 |
| Palm olein | Epoxidation | 1.9-4.0 | 3.61 | 61.67 | Salimon *et al*., 2011 |

## 2.9 Response Surface Methodology

Response Surface Methodology (RSM) is a statistical tool use for the modeling and analysis of statistically generated data to determine the true optimal condition of a process. In recent time, response surface methodology has shown to be a valuable tool for finding solutions to problems in which a definite response of interest is affected by various processing parameters (Mohammad *et al*., 2011). The primary goal of using response surface methodology is to model a response of a process, however, response surface methodology was later used to develop models for the optimization of numerical experiments (Kathleen *et al*., 2004). When understudy treatments are based on continuous array of values, then response surface methodology can be applied to the development, improvement and optimization of response parameters which is mathematically expressed as:

$$y = f(x_1, x_2) + e \qquad (2.4)$$

In most RSM problems, the true response function f is unknown. In order to develop a proper approximation for f, the experimenter usually starts with a low-order polynomial in some small region. If the response can be defined by a linear function of independent variables, then the approximating function is a first-order model. A first-order model with 2 independent variables can be expressed as

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \varepsilon \qquad (2.5)$$

If there is a curvature in the response surface, then a higher degree polynomial should be used. The approximating function with 2 variables is called a second-order model:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} x^2{}_{11} + \beta_{22} x^2{}_{22} + \beta_{12} x_1 x_2 + \varepsilon \quad (2.6)$$

### 2.9.1 Design of experiment

An imperative part of response surface methodology is the design of experiments (DoE). These strategies were primarily developed for the model fitting of physical experiments, but can also be used for numerical experiments. The goal of design of experiment is to determine points where the response of a process should be assessed (Montgomery, 2005).

The conditions for optimal design of experiments are linked with the mathematical model of the process. Basically, these models are polynomials with an unknown structure, so the corresponding experiments are designed only for every particular problem. The choice of the design of experiments can have a large effect on the correctness of the approximation and the cost of developing the response surface (Montgomery, 2005).

### 2.9.2 Central composite design

In recent years, central composite design (CCD) has gained much consideration as the most suitable second order design for the comprehensive estimation of response surfaces based upon second order models (Mohammad *et al*., 2013). In 1951, central composite design was introduced by Box and Wilson to response surface optimization. Central composite design accounts for either a full factorial design with two levels ($2^k$) or fractional factorial designs ($2^{k-f}$) fabricated with numerous design points (Mohammad *et al.*, 2013). Central composite design involved three types of design points which are factorial points ($n_f$), central points ($n_c$) and axial points ($n_a$). Equation 2.4 gives an expression for cumulative design points:

$$n = 2^k(n_f) + 2k\,(n_a) + k\,(n_c) \qquad (2.7)$$

A second-order model can be developed effectively with CCD. Central composite design is a first-order (2N) design improved by additional centre and axial points to permit estimation of the tuning variables of a second-order model. Figure 2.4 shows a CCD for 3 design variables.

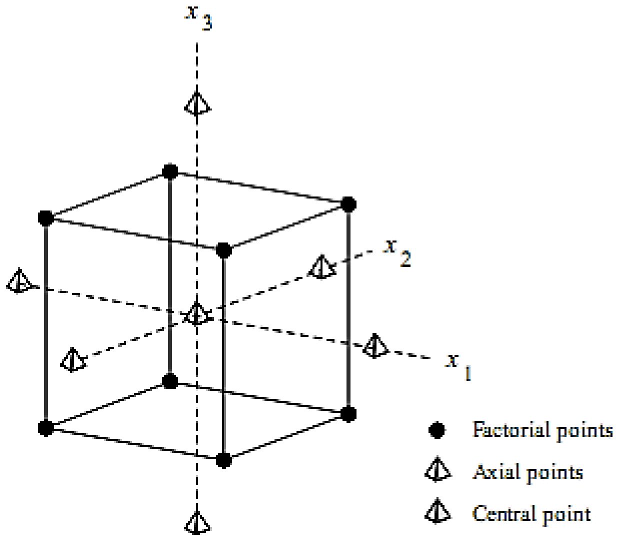


**Figure 2.1: Central composite design for 3 design variables at 2 levels**

In Figure 2.4, the design includes 2N axial points, 2N factorial points, and1central point. Central composite design can be used for 3N designs in the construction of second-order models because when compared to a full factorial design, the number of experiments is reduced, for example, 27 number of experiment in the case of full-factorial design compared to 15 number of experiment in the case of central composite design. In recent time, central composite design has been used for multi objective design of a flywheel, but as the number of designs variables increases, the experiments becomes tedious even with the use of central composite design (Montgomery, 2005).

Mohammad *et al*., (2011) reported a study on the optimization of transesterification reaction of TMP with Jatropha oil via response surface methodology studying the effect of reaction temperature, reaction time and catalyst concentration. The Jatropha oil was extracted on a laboratory scale and analyzed to determine its physical and chemical properties. The author reported 0.1722 kg/$m^3$s yield at optimum reaction condition of reaction temperature (150 °C), reaction time (80 mins) and 0.8% catalyst concentration.

Salimon *et al*., (2011) reported a study on the optimization of esterification reaction of rubber seed oil (RSO) with trimethylolpropane (TMP). In the study, optimization of esterification of rubber seed oil fatty acid with TMP was achieved via $H_2PO_3$ acting as the catalyst. RSO was successfully converted to biolubricant with 78% yield at reaction temperature (150 $^oC$), sulphuric acid (2 %wt/wt) and at reaction time (5 hours). The composition and structure of ester formed was determined using gas chromatography and FTIR respectively (Mohammad *et al*., 2011).

# CHAPTER THREE

## 3.0 MATERIALS AND METHOD

### 3.1 Materials and Equipment

Various types of materials and equipment were used in the course of this research work, the lists are as follows:

### 3.1.1 List of Reagents

**Table 3.1 shows the list of Chemical Reagents**

| S/NO | Chemicals | Grade | Availability |
|---|---|---|---|
| 1 | Trimethylolpropane | TMP Trioleate 46 | Purchased |
| 2 | Methanol | Grade A 99.0% | Purchased |
| 3 | Phenolphthalein | Lab Grade, 100g | WAFT LAB |
| 4 | Deionized water | Type 2 water | CHE LAB |
| 5 | n-Hexane | 98 % purity | Purchased |
| 6 | Sodium thiosulphate | Reagent Grade (500g) | WAFT LAB |
| 7 | Acetic acid | Reagent Grade (99%) | WAFT LAB |
| 8 | Chlorofoam | Laboratory Grade (99 %) | WAFT LAB |
| 9 | Tetraoxosulphate (VI) acid | Laboratory Grade (97%) | CHE LAB |

### 3.1.2 List of Equipment

**Table 3.2 List of equipment**

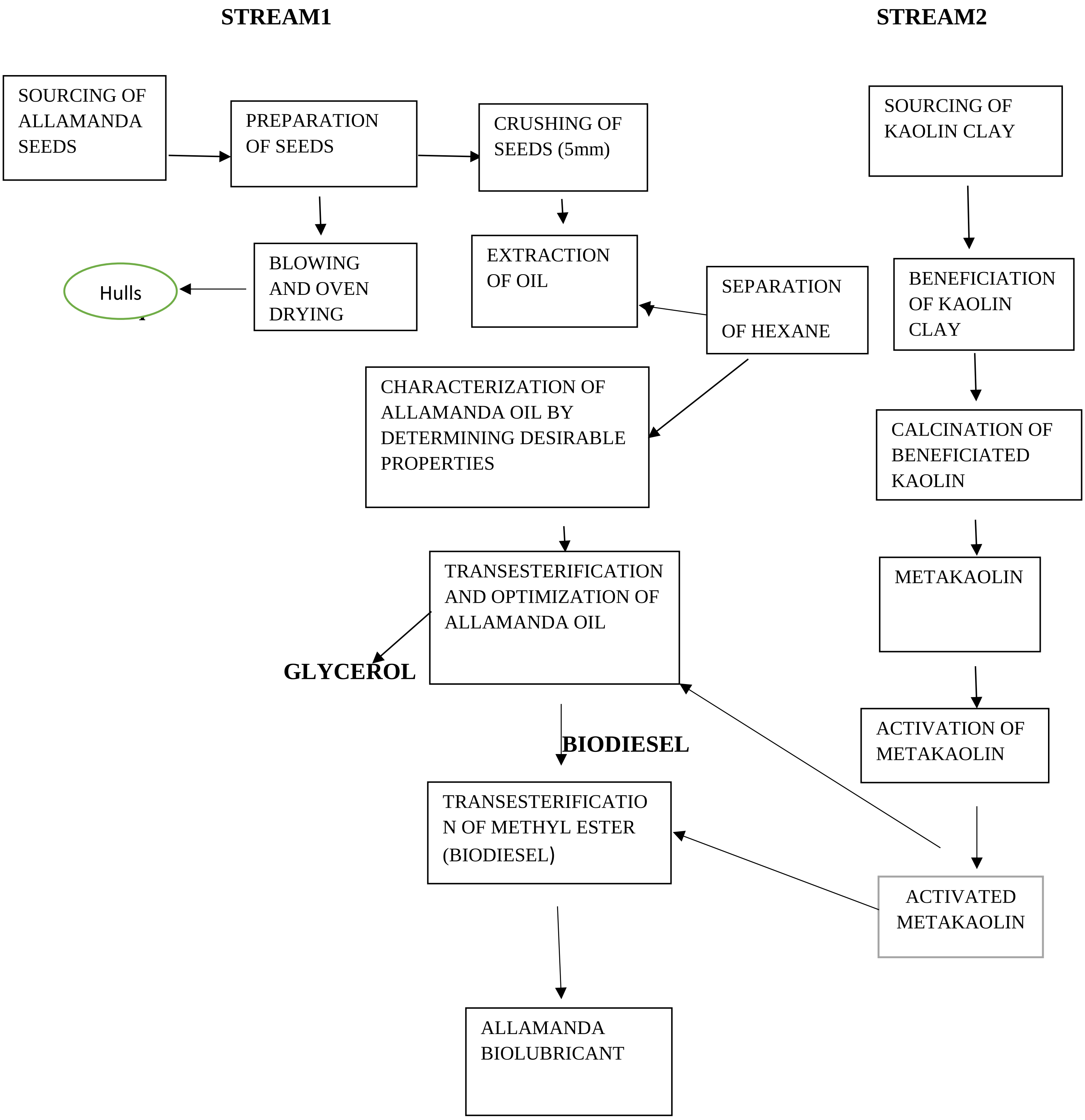
| S/NO | Equipment and instrument | Model | Manufacturer | Source |
|---|---|---|---|---|
| 1 | Density bottle | | PYREX | CHE LAB |
| 2 | Digital Weighing Balance | SNR-8728416524 | Adventurer | CHE LAB |
| 3 | Magnetic Stirrer | | | ABE LAB |
| 4 | Measuring Cylinder | | PYREX | CHE LAB |
| 5 | Beaker | | PYREX | CHE LAB |
| 6 | Conical Flask | | PYREX | CHE LAB |
| 7 | Thermometer | | | CHE LAB |
| 8 | Separating Funnel | | PYREX | CHE LAB |
| 9 | Oven | PBS118SF | GEN LAB | CHE LAB |
| 10 | Flash point tester | | | ABE LAB |
| 11 | pH meter | | | ABE LAB |
| 12 | Miller | | | |
| 13 | Syringe | | | Purchased |
| 14 | Burrette | | PYREX | CHE LAB |
| 15 | Pipette | | PYREX | CHE LAB |
| 16 | Dessicator | | | CHE LAB |
| 17 | Heating mantle | | | CHE LAB |
| 18 | Soxhlet extractor | | | CHE LAB |

### 3.1.3 List of Materials

**Table 3.3 shows the list of materials**.

| S/NO | Material | Availability |
|---|---|---|
| 1 | Kaolin Clay | Kutigi, Niger State. |
| 2 | Allamanda seed | Ciromawa Estate, Niger State. |
| 3 | Thimble | Purchased |
| 4 | Filter Paper | Purchased |
| 5 | Transparent Bucket | Purchased |
| 6 | Spatula | CHE LAB |

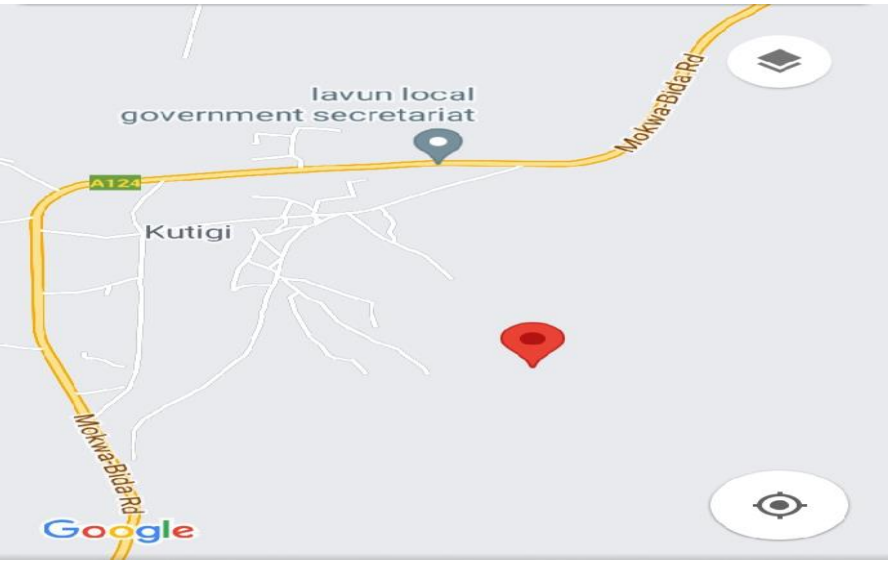
## 3.2 Experimental Procedure



### 3.2.1 Raw Materials and Reagent Collection

Allamanda seeds was sourced at Ciromawa estate, along Bosso Road, Minna, Niger state, Nigeria and other nearby gardens. The kaolin clay was procured from Kutigi, Lavun Local Government Area, Niger state, Nigeria. Some of the chemicals and reagents were purchased from outlet retailers and others were collected from the Department of Chemical Engineering, Federal University of Technology Minna, Niger state, Nigeria.

3.2.1.1 Geographical location of Kutigi on google map



Source; Google.

Plate I: Geographical location of Kutigi.

### 3.2.2 Seed Preparation

The following steps were employed in the seed preparation to make the Allamanda seeds suitable for solvent penetration into the oil cells as well as for best percolation.

The Allamanda seeds were cracked manually to obtain the kernels, the kernels were covered with hulls, the hulls were blown off with air. The dehulled Allamanda kernels was kept under the sun for 6 hours, the kernels were oven dried at a temperature of 85 $^{o}$C to 100 $^{o}$C for 2 hours, the dried kernels were crushed to a size of 5mm to reduce the size and increase the interfacial area for proper extraction of oil. The crushed Allamanda seeds was kept in an air tight container to prevent intake of moisture into the crushed seeds (Nadia *et al*., 2013).

The raw Allamanda Oil Seeds is as shown on Plate II, the kernel of the Allamanda Seeds is as shown on plate III and the Crushed Allamanda Seeds is as shown on plate IV.

Plate II: Allamanda seeds

Plate III: Allamanda kernels

Plate IV : Crushed Allamanda Kernel

### 3.2.3 Oil extraction

Oil extraction was carried out by weighing 50 g of the crushed Allamanda seeds and was placed into the center of the extractor through the thimble, the round bottom flask was filled with 250 $cm^3$ of hexane, the heating mantle was set at a temperature of 68 $^oC$ and the time for each batch of extraction was 6 hours (Blin *et al*., 2013). The round bottom flask containing the hexane was heated until the hexane boils, during the steady extraction, the extract seeped through the pore of the thimble and filled the siphon tube, where it flows back into the round bottom flask. This process was repeated for several batches until the needed quantity of oil was extracted from the crushed Allamanda kernels, the extracted oil was heated with rotary evaporator to separate the little amount of hexane and water from the oil (Blin *et al*., 2013).

The setup of the soxhlet extractor apparatus for the extraction of the Allamanda oil is shown on plate V and some of the extracted oil is shown on plate VI.

Plate V: Soxhlet extractor apparatus set up

Plate VI: Extracted Allamanda oil

### 3.2.4 Characterization of allamanda crude oil

#### *3.2.4.1 Percentage (%) yield*

The percentage oil yield was calculated using equation (3.1);

$$Percentage\ oil\ yield\ = \frac{Weight\ of\ Oil}{Weight\ of\ sample} \times 100 \qquad (3.1)$$

#### 3.2.4.2 *Density*

An empty beaker was weighed and the weight was recorded, 50 $cm^3$ of the sample (Allamanda oil) was transferred into the beaker and weighed. From the sample weight recorded, the density was determined by taking the ratio of the weight of the oil to the known volume (50 $cm^3$) in SI units according to equation (3.2);

$$Density = \frac{Weight\ of\ sample}{Voliume\ of\ Sample} \quad (3.2)$$

### 3.2.4.3 *Saponification value*

Saponification value is the measure of the molecular weight of the fatty acid. 2 g of the Allamanda oil was weighed and transferred into a 250 $cm^3$ conical flask. 50 $cm^3$ of 0.5 ethanoic KOH was added to the sample and mixture was heated to saponify the oil. The unreacted KOH was back titrated with 0.5 N HCl acid using 2-3 drops of phenolphthalein indicator. The saponification value (SV) was determine using equation (3.3) ;

$$SV = \frac{(V0 - V1)\times 0.5\times 56.10}{M}\frac{mgKOH}{g} \quad (3.3)$$

Where $V_0$= the volume of the solution used for blank test

$V_1$ = the volume of the solution used for determination

N = Actual normality of the HCl used

M = Mass of the oil used.

### 3.2.4.4 *Percentage free fatty acid (% FFA)*

Percentage free fatty acid is the percentage by weight of the specified fatty acid in the oil, the method employed for this analysis is the American Oil Chemists Society (AOCS) method, 1 g of Allamanda oil was weighed and poured into conical flask, 25 $cm^3$ of isopropyl alcohol and 3 drops of phenolphthalein indicator solution was added. The mixture was titrated against 0.1 N sodium hydroxide shaken constantly until a pink colour persisted for 30 seconds. The acid value was determined using equation (3.4);

$$\%FFA = \frac{(mL\ of\ titrant)(Normality\ of\ NaOH)+28.2}{Weight\ of\ sample}\times 100 \quad (3.4)$$

### 3.2.4.5 *Acid value*

The acid value of the Allamanda oil was determined by weighing 1 g of the oil and was poured into a conical flask and the weight was recorded. 25 $cm^3$ of isopropyl alcohol and 3 drops of the phenolphthalein indicator solution was added. It was titrated with 0.1 N potassium hydroxide solution with constant stirring until a faint pink end point appears and persists 30 seconds. The volume of the titrant used to reach this endpoint was recorded and from the value obtained, the acid value is evaluated using equation (3.5);

$$Acid\ Value = \frac{56.10 \times V \times C}{Y} \tag{3.5}$$

Where V = Volume of potassium hydroxide used for titration ($cm^3$),

C = Concentration of potassium hydroxide used for titration (mol/l) and

Y = mass of oil sample used for analysis (g)

### 3.2.4.6 *Determination of peroxide value*

This was carried out in accordance to the method specified by AOCS official method Cd 8-53. 1 g of the oil sample was weighed and transferred into the flask and 20 $cm^3$ of the acetic acid – chloroform (2:1) solution was then added to the oil. The flask was gently warmed using water bath and swirled until the sample was completely dissolved. This was followed by the addition of 0.5 $cm^3$ of saturated potassium iodide solution and 30 $cm^3$ of distilled water. The flask was shaken vigorously to liberate the iodine from the chloroform layer. The resulting solution was titrated with 0.002N sodium thiosulphate using starch indicator until the blue gray colour disappeared in the aqueous upper layer. This same procedure was followed for the blank test. The volume of titrant used for determination and blank test were recorded.

Peroxide value was calculated from expression (3.6);

$$Peroxide\ value = \frac{(S - B) \times Nof\ thiosulphate \times 1000}{Weight\ of\ sample} \frac{meq}{Kg} \tag{3.6}$$

S=titrant of sample, B= titrant of the blank.

#### 3.2.4.7 *Determination of iodine value*

The iodine value was determined in accordance to the method specified by AOCS cd3-25. 0.5 g of oil sample was weighed and transferred into a flask. Carbon tetrachloride, 25 cm$^3$ added to dissolve the oil and 25 cm$^3$ of the wijs solution was added into the flask the stopper was inserted and the mixture was shaken gently and kept in the dark for 1 hour. At the end of 1 hour, 20 cm$^3$ of potassium iodide KI, 10 % solution and 125 cm$^3$ of water was added. The mixture was titrated with 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solution until yellow colour due to iodine had almost disappeared. 1 cm$^3$ of the starch, 1 % indicator solution was added, and titration was continued with very vigorous shaking until the blue colour just disappeared. This same procedure was followed for the blank test.

The iodine value (I.V) is given by expression (3.7);

$$IV = \frac{(V1 - V2.) \times 0.1269 \times C \times 100}{M} \text{ (gl}_2\text{/100g oil)} \tag{3.7}$$

Where C = Concentration of sodium thiosulphate used

$V_1$ = Volume of sodium thiosulphate used for blank test

$V_2$ = Volume of sodium thiosulphate used for determination

M = Mass of the sample

### 3.2.4.8 *Determination of specific gravity*

This was carried out as specified by ASTM D1250 (2008). Density bottle was used to determining the density of the oil. A clean and dry bottle was weighed (A) and then filled with water, stopper inserted and reweighed to give (B). The bottle was dried in an oven and the oil was substituted with water and weighed to give (C).

The expression for specific gravity (Sp.gr) is given by equation (3.8);

$$Sp.gr = \frac{C-A}{B-A} = \frac{Mass\ of\ substance}{Mass\ of\ equal\ volume\ of\ water} \tag{3.8}$$

A=mass of empty bottle,

B= mass of bottle + mass of water,

C=mass of bottle + mass of oil

### 3.2.4.9 *Determination of viscosity*

An NDJ-5S Rotary Viscometer was used to determine the viscosity of the oil. The viscosities of the oil sample were determined at temperatures of 40 $^{o}$C and 100 °C, following the procedure specified by the manufacturer. Rotor 2 and 1 with speed of 60 revolutions per minute (60 RPM) were selected for bio lubricant, crude oil and biodiesel respectively. The oil sample was then transferred into a 250 cm$^3$ beaker and was heated to raise the temperature to the desired value using water bath heater. The rotor was attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the rotor counter clockwise. The rotor was immersed in the centre of the sample up to the middle of the indentation in the shaft. The viscometer was then turned on and allowed to run until a constant reading was display; this reading was taken as the viscosity of the sample in cSt.

#### 3.2.4.10 *Determination of pH value*

The pH of the oil was determined with a digital pH meter, it was dipped into the oil and the pH was recorded (Dave *et al*., 2014).

### 3.2.5 Kaolin beneficiation

Kaolin was sourced from Kutigi, Niger state, Nigeria. 10 kg of the sourced kaolinite clay was soaked in a transparent bucket with 20 liters of deionized water, it was stirred for 3 minutes and the floated dirt was decanted and discarded. Wet sieving and sedimentation method was adopted for the beneficiation process of the kaolin clay (Colina and Costa, 2005).

The soaked kaolin in the transparent bucket undergoing sedimentation process as shown on plate VII and the wet sieving process is shown on plate VIII.

Plate VII: Beneficiation of kaolinite clay

Plate VIII: Wet Sieving process

The dissolved kaolinite clay was first sieved with a sieve of mesh size 2.8 mm, secondly sieved with sieve of 1.0 mm mesh size and was finally sieved with a sieve of mesh size 500 micro metre. The sieved dissolved kaolin was allowed to settle for 12 hours, after settling three layers was observed, the first layer was a clear liquid, the second layer was the beneficiated kaolin, the third layer contained some amount of the beneficiated kaolin and sand. The first layer was decanted and discarded, the second layer which is the beneficiated kaolin was decanted into another bucket and water was added into the third layer in the transparent bucket for further separation between the little beneficiated kaolin remaining and sand left in the third layer (Aderemi *et al.*, 2010). This process was repeated until infinitesimal amount of beneficiated kaolin was left in the third layer.

The beneficiated kaolin was poured in a metallic bucket and placed in the oven for dryness at 150 $^{o}$C – 200 $^{o}$C for 48 hours. After drying, the kaolin was grounded, sieved and poured into well labelled sample bottles and was calcined at 650 $^{o}$C for 90 minutes (Aderemi *et al.*, 2010).

The muffle furnace used for the calcination of the beneficiated kaolin is shown on plate IX and plate X shows the sample of the beneficiated kaolin clay in the muffle furnace.

Plate IX: Muffle Furnace (SX-5-12 USA)

Plate X: Calcination of the beneficiated kaolin.

#### 3.2.5.1 *Activation of metakaolin*

The activation of metakaolin was carried out by dividing 200 g of the metakaolin (calcined kaolin) into four beakers, 2M of $H_2SO_4$ was prepared by diluting 103 $cm^3$ of 98 wt% $H_2SO_4$ in 100 $cm^3$ of deionized water, after which the volume was increased to 500 $cm^3$. This solution was added to the metakaolin in the four beakers, the beakers were placed in the bath shaker and it was set to operate for 3 hours at 100 $^oC$ for proper agitation. The acid activated metakaolin in the beaker was then washed until it reached a pH value of 7, it was oven dried, ground and sieved to a very fine particle (Aderemi *et a*l., 2010).

### 3.2.6 Transesterification of allamanda oil

Box-Behnken module of response surface methodology available in “Design Expert® Software” was used to evaluate the number of runs needed with their operating conditions. In this experiment, the oil to methanol ratio was kept constant while the reaction time, temperature and catalyst weight was varied with the design expert.

Fifty $cm^3$ of Allamanda oil was measured and poured in a conical flask, the conical flask was placed on the magnetic stirrer, after heating the oil for 2 minutes, 10 $cm^3$ of methanol was added into the conical flask, amount of catalyst was added as shown on various combinations of run according to Response Surface Methodology “Design Expert® software” and the mixture was stirred for the stipulated reaction time and temperature as shown on Table 3.4 (Goyal *et al*., 2013). After completion of each run, the mixture was poured into separating funnel and allowed to settle for 24 hours, after 24 hours the mixture in the funnel resulted into two layers of liquids which was separated and the top layer was washed with warm water severally until the amount of soap present in it was reduced to an infinitesimal amount (Goyal *et al*., 2013). The top layer of the liquid is the Allamanda methyl ester and bottom layer is the glycerol, the methyl ester (biodiesel) was further placed in the oven for 2 hours at 60 $^oC$ for drying/evaporating any available methanol. After carrying out the complete numbers of run, they were characterized to obtain the run with the optimum operating condition and the highest yield.

The number of runs carried out to optimize the biodiesel production and their various operating conditions are as shown on Table 3.4.

**Table 3.4: Surface response methodology (Box-Behnken)**

| | **Factor 1** | **Factor 2** | **Factor 3** | **Response 1** |
|---|---|---|---|---|
| **Run** | A:Time | B:Temperature | C:Catalyst | Yield |
| | Mins | $^{o}$C | % | |
| **1** | 120 | 52.5 | 2.75 | |
| **2** | 120 | 52.5 | 2.75 | |
| **3** | 60 | 65.0 | 2.75 | |
| **4** | 120 | 52.5 | 2.75 | |
| **5** | 60 | 52.5 | 5.00 | |
| **6** | 120 | 40.0 | 0.50 | |
| **7** | 180 | 52.5 | 5.00 | |
| **8** | 120 | 52.5 | 2.75 | |
| **9** | 120 | 40.0 | 5.00 | |
| **10** | 180 | 52.5 | 0.50 | |
| **11** | 60 | 52.5 | 0.50 | |
| **12** | 60 | 40.0 | 2.75 | |
| **13** | 120 | 65.0 | 5.00 | |
| **14** | 120 | 52.5 | 2.75 | |
| **15** | 180 | 40.0 | 2.75 | |
| **16** | 120 | 65.0 | 0.50 | |
| **17** | 180 | 65.0 | 2.75 | |

The produced biodiesel can be seen as shown on plate XI in the separating funnel and the biodiesel production in runs is as shown on Plate XII.

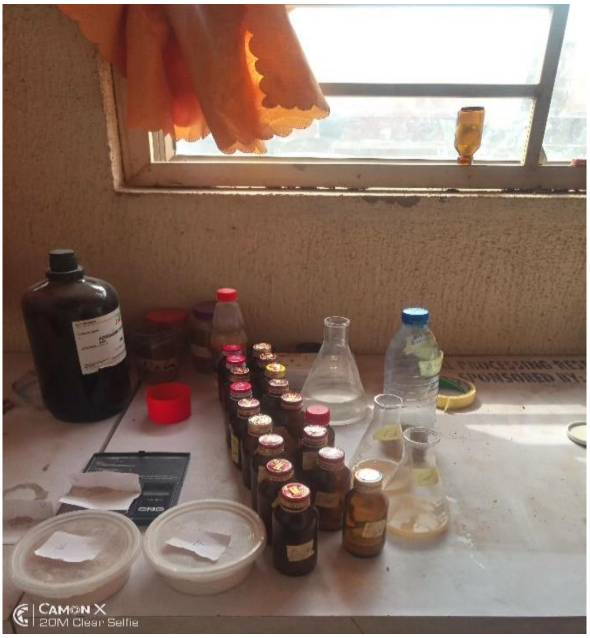


Plate XI: Biodiesel Production

Plate XII: Biodiesel Production in runs

### 3.2.7 Transesterification of allamanda methyl ester

Similar experimental set up was also used for the biolubricant production as shown on plate XII, the produced biodiesel (allamanda methyl ester) was transesterified with trimethyolpropane (TMP), the TMP was measured, melted and it was added while stirring the mixture. The amount of TMP required was determined by molar ratio of 4:1 of Allamanda methyl ester (AME) to trimethyolpropane (TMP), 0.5 % wt of the acid activated metakaolin catalyst was added to the solution and the reaction was conducted at a temperature of 120 $^{o}$C for 2 hours 30 minutes (Bilal *et al*., 2013). The synthesized Allamanda oil based biolubricant was taken as sample and it was analyzed to obtain it properties.

The set up for the biolubricant production is as shown on plate XII and the produced biolubricant can be seen on plate XIII

**Plate XIII:** Biolubricant production process

**Plate XIV:** Allamanda oil based biolubricant

# CHAPTER FOUR

## 4.0 RESULT AND DISCUSSION

### 4.1 Results

The properties of Allamanda oil was compared with standards; ASTM and AOCS to ascertain its quality. Table 4.1 shows the comparism of the Allamanda oil properties with ASTM and AOCS.

### 4.1: Physiochemical Properties of Allamanda Oil in Comparism with ASTM and AOCS

The extracted Allamanda oil was dark brown in colour with a yield of 64 %, the physiochemical properties of Allamanda seed oil can be seen as shown on Table 4.1. The physiochemical properties of Allamanda seed oil was compared with American standard for testing material (ASTM) and American oil chemists' society (AOCS) standard values. From the experimental result obtained, the saponification value of Allamanda oil is 158.483 mgKOH/g, the value falls below the range of values given by ASTM and AOCS which indicates the presence of less unsaturated fatty acid characteristics of foaming ability. The free fatty acid value of Allamanda oil is 2.60 %, this is in the range of values given by ASTMD6751, this indicates that the Allamanda oil will not be corrosive when used for biodiesel production, which can affect fuel pumps and tanks (Dave *et al*., 2014). According to Edward *et al*., (2001) oils with high fatty acid value are liable to form soap and difficult to separate during biodiesel production which will result to low biodiesel yield.

**Table 4.1: Physiochemical Properties of Allamanda Seed Oil**

| Property | Unit | Test Method | ASTM | AOCS | Allamanda oil Value |
|---|---|---|---|---|---|
| Specific gravity | | ASTM D1250 | 0.957-0.968 | 0.88-0.915 | 0.928 |
| Saponification Value | MgKOH/g | ASTM D558-95 | 175-187 | 174-184 | 158.483 |
| Iodine Value | $gI_2$/100g oil | AOCS cd 3.25 | 82-88 | 83-88 | 40.659 |
| Acid Value | mgKOH/g | ASTM D664 | 0.4-4.0 | 2.0 | 5.20 |
| Viscosity @40 $^0$C | Cst | ASTM D445 | 35max | - | 20.5 |
| Viscosity @100 $^0$C | Cst | ASTM D446 | - | - | 1.45 |
| Viscosity @25$^o$C | Cst | ASTM D2270 | -21.7 | - | 48.9 |
| Pour Point | $^0$C | ASTM D97 | -21.7 | - | -5.6 |
| Refractive Index | | AOCS cc7.75 | - | 1.467-1.470 | - |
| Peroxide Value | meq/kg | AOCS cd8.53 | 5.00 | - | 5.36 |
| PH Value | - | | - | - | 5.96 |
| % FFA | % | ASTM D6571 | 25 max | <1 | 2.60 |
| Density | g/cm$^3$ | ASTM D6710 | 0.7-0.95 | - | 0.924 |
| % Oil Yield | % | - | | | 64 |
| Smoke Point | $^0$C | ASTM D97 | | | 149.0 |
| Flash Point | $^0$C | ASTM D94 | | | 215 |
| Fire Point | $^0$C | ASTM D901 | | | 270 |

The viscosity of Allamanda oil at 40 $^o$C is greater than the cited literature but tallies with that of ASTM value, which indicate that Allamanda oil is suitable for the production of biodiesel

(Dave *et al*., 2014), viscosity increases with molecular weight and decreases with increasing unsaturated level and temperature (Edward *et al.*, 2001). The iodine value of Allamanda oil falls below the ASTM and AOCS standard, this indicates that the oil has a low degree of unsaturation, according to (Mittelbach, 1996) oils with low iodine value are better for biodiesel production due to the fact that heating oil of higher degree of unsaturation will lead to polymerization of glycerides and causes formation of deposit or deterioration of the biodiesel.

The peroxide value of Allamanda oil (5.36 meq/kg) is slightly above the ASTM standard, this proves that the extracted Allamanda oil has a good oxidative stability (Eromosele, 2002).

The density of Allamanda oil (0.924 g/cm$^3$) falls within the range given by ASTM6710 but lesser than the density of water, generally oils have density lesser than that of water. According to Gunstone (2004). The density of oil decreases with molecular weight but increases with unsaturation level.

### 4.1.2 Brunauer- Emmett- Teller (BET) for calcined and acid activated kaolin

Table 4.2 shows the surface area, pore volume and pore size of the raw kaolin, calcined kaolin and activated metakaolin was determined, the results shows a drastic increase in surface area of the raw kaolin and calcined kaolin (154.819 m$^2$/g and 636.531 m$^2$/g) and there was also increase of surface area in the calcined kaolin and acid activated metakaolin (636.531 m$^2$/g and 954.405 m$^2$/g) these increase in surface area can be attributed to the beneficiation, calcination and activation process, the results correspond with those reported by (Mudi *et al*., 2018), which stated that any porous material with surface area is above 100

$m^2g$ is considered a good material for catalyst. The surface area of the acid activated metakaolin is 954.405 $m^2/g$, the pore volume is 0.6279 cc/g and the pore size is 2.399 nm.

**Table 4.2: Result of Brunauer –Emmett – Teller (BET) for Calcined and Acid Activated Kaolin**

| Sample | Surface area ($m^2/g$) | Pore volume (cc/g) | Pore size (nm) |
|---|---|---|---|
| Raw Kaolin | 154.819 | 0.0857 | 2.126 |
| Calcined Kaolin | 636.531 | 0.3244 | 2.139 |
| Acid activated metakaolin | 954.405 | 0.6279 | 2.399 |

### 4.1.3 X-Ray Fluorescence Result (XRF) for Raw and Calcined Kaolin

The X-ray florescence (XRF) analysis was conducted on the raw and calcined kaolin clay, Table 4.3 indicated that the kaolinite clay is rich in silicon oxide, and aluminum oxide but contains a lower composition of other oxides such as sodium, potassium, magnesium, manganese, iron, tritium, lead, calcium and Barium. From the obtained result on Table 4.3 there was decrease in Silicon and Aluminum oxide after beneficiation and calcination, this can be attributed to removal of impurities such as quartz and feldspar. The high content of $K_2O$, $Fe_2O_3$ and CaO in the calcined sample suggested their presence in crystalline form with relatively small particle sizes which could freely pass through mesh size of the used sieve.

**Table 4.3: Result for X-ray fluorescence for raw and calcined kaolin**

| Component | Raw kaolin (%) | Peak (cps/mA) | Calcined kaolin(metakaolin) ( %) | Peak (cps/mA) |
|---|---|---|---|---|
| $SiO_2$ | 58.409 | 57014 | 57.960 | 56142 |
| $Al_2O_3$ | 32.248 | 25283 | 31.786 | 24878 |
| $Na_2O$ | 0.5701 | 620 | 0.5176 | 615 |
| $K_2O$ | 0.4900 | 671 | 0.4829 | 665 |
| CaO | 0.04481 | 92 | 0.04129 | 90 |
| MgO | 0.730 | 162 | 0.696 | 155 |
| $TiO_2$ | 1.6753 | 7053 | 1.6703 | 7032 |
| $Fe_2O_3$ | 1.4245 | 4381 | 1.4054 | 4217 |
| MnO | 0.00667 | 81 | 0.00664 | 80 |
| $P_2O_5$ | 0.2609 | 479 | 0.2510 | 468 |
| $Cr_2O_3$ | 0.01316 | 92 | 0.01271 | 89 |
| PbO | 0.01448 | 7 | 0.01361 | 6 |
| SrO | 0.1128 | 29 | 0.1117 | 30 |
| BaO | 0.1527 | 403 | 0.1410 | 395 |
| $ZrO_2$ | 0.6602 | 904 | 0.6590 | 895 |
| $Ga_2O_3$ | 0.00622 | 91 | 0.00610 | 87 |
| LOI | 3.1812 |  | 4.24175 |  |

### 4.1.4 Scanning electron microscopy result for raw and calcined kaolin

The SEM micrograph for the raw kaolin shows different layers of different sizes which indicates the disorder of silica and alumina layers in kaolinite (Teku *et al*., 2017). The SEM micrograph for the calcined kaolin (metakaolin) shows larger plates and stacks which indicated the ordering of silica and alumina layers in kaolinite. The level of impurities can be seen in SEM micrographs for the raw kaolinite clay in between the silica –alumina stacks, the micrograph for the calcined sample shows layers of uniform size with ordering in the plates. The SEM for result for raw and calcined kaolin is as shown on plate XV and plate XVI.

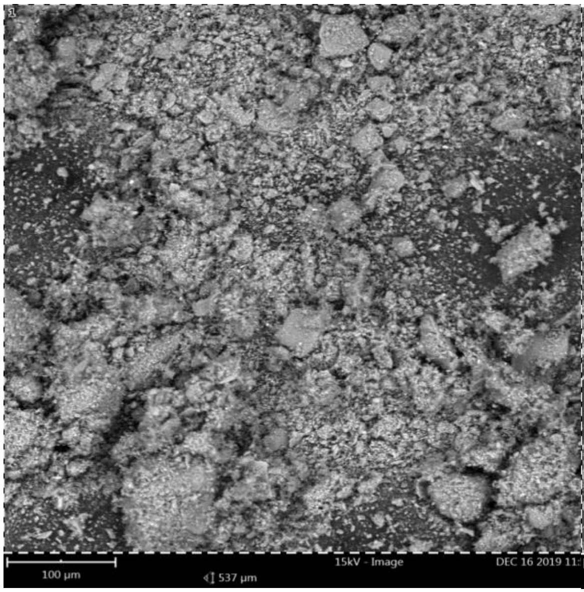
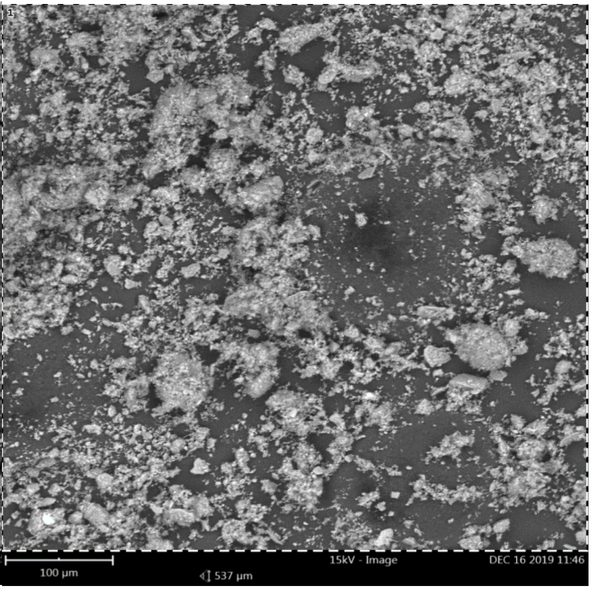


**Plate XV:** SEM for raw kaolin



**XVI** 4.2: SEM for calcined kaolin(metakaolin)

#### 4.1.4.1 Scanning Electron Microscopy EDX for raw kaolin

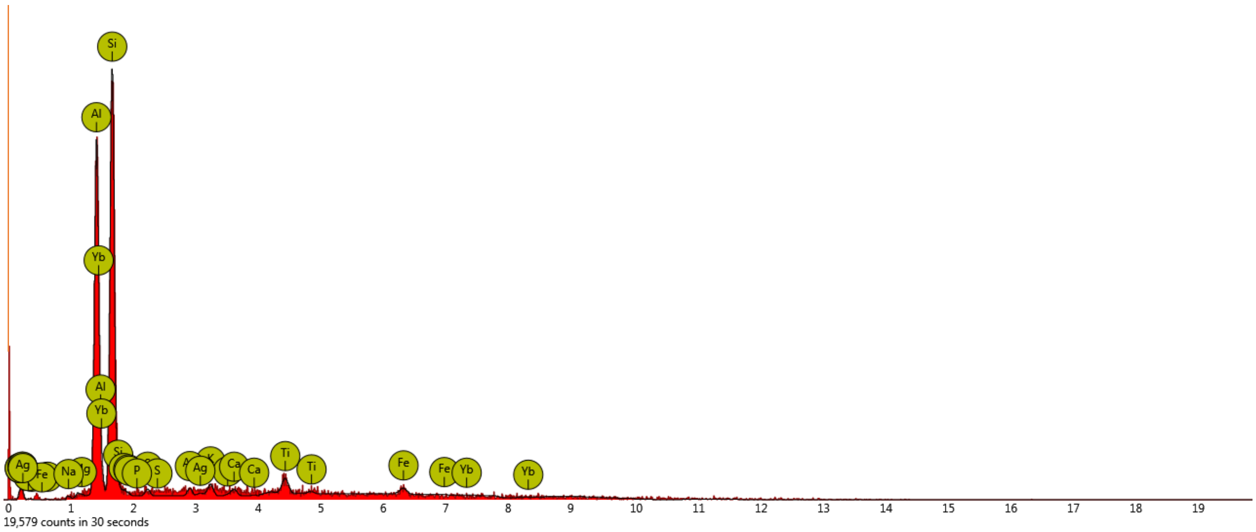


**Figure 4.1:** Scanning Electron Microscopy EDX for raw kaolin

#### 4.1.4.2 Scanning Electron Microscopy EDX for calcined kaolin

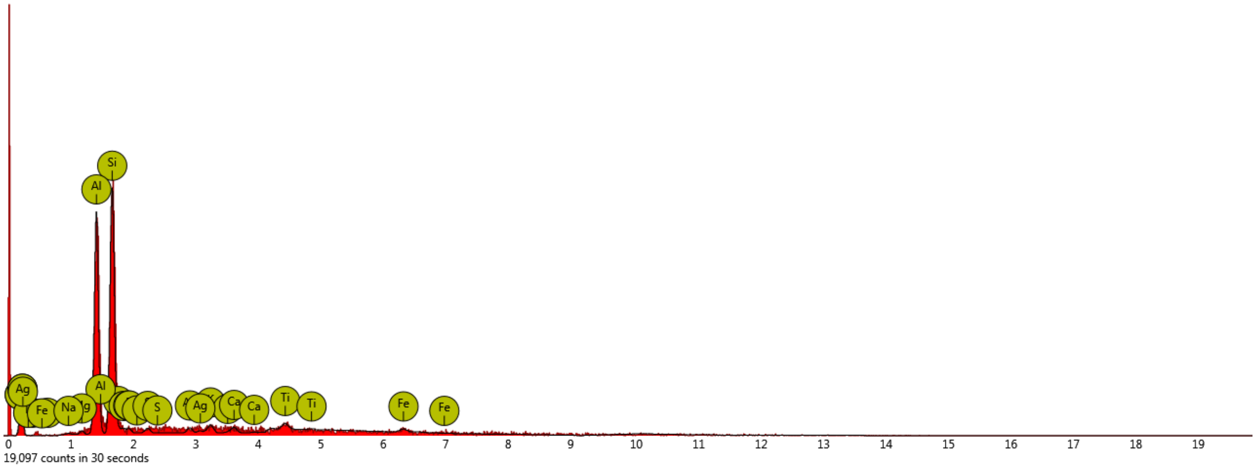


**Figure 4.2:** Scanning Electron Microscopy EDX for calcined kaolin

The SEM-EDX for the raw kaolin shows high content of silicon and aluminum oxides compared to the SEM-EDX for calcined kaolin, this can be attributed to the beneficiation process. The SEM-EDX result for the raw and calcined kaolin is in correlation with the XRF result for the raw and calcined kaolin.

The pore size is a measure of the void spaces in a material and is a fraction of the volume of voids over the total volume while the pore volume is the total volume of very small opening in a bed of adsorbent particles (Teku *et al*., 2017).

Figures 4.3 and 4.4 show the plot for XRD result for the raw kaolin and calcined kaolin (metakaolin) sample, the peaks of 2 theta values at 12.46$^o$, 24.99$^o$, 26.72$^o$, 38.62$^o$ and 62.36$^o$ on the XRD graph for raw kaolin, represents the crystalline structure of the kaolinite with quartz and feldspar as major impurities. The peaks on the XRD graph for calcined kaolin was observed to have reduced drastically due to the beneficiation and calcination process which led to the disappearance of crystalline high peaks thereby transforming the crystalline kaolin to amorphous metakaolin (Teku *et al*., 2017). The peaks on XRD graph for calcined kaolin was observed at 20.92$^o$, 26.64$^o$, 36.57$^o$, 50.17$^o$ and 60.01$^o$.

### 4.1.5 X-Ray Diffraction for Raw Kaolin

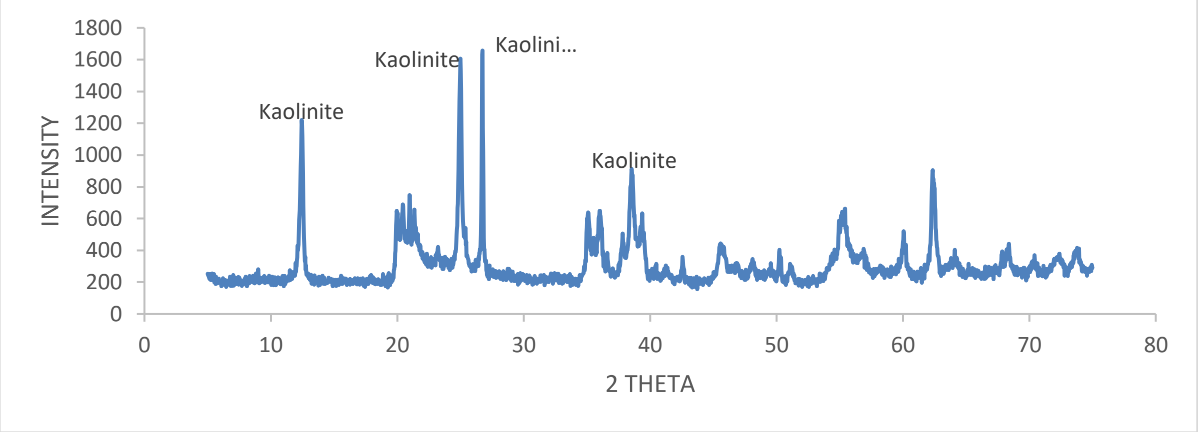


**Figure 4.3:** X-ray Diffraction Characterization for raw kaolin.

### 4.1.6 X-Ray Diffraction for Calcined Kaolin.

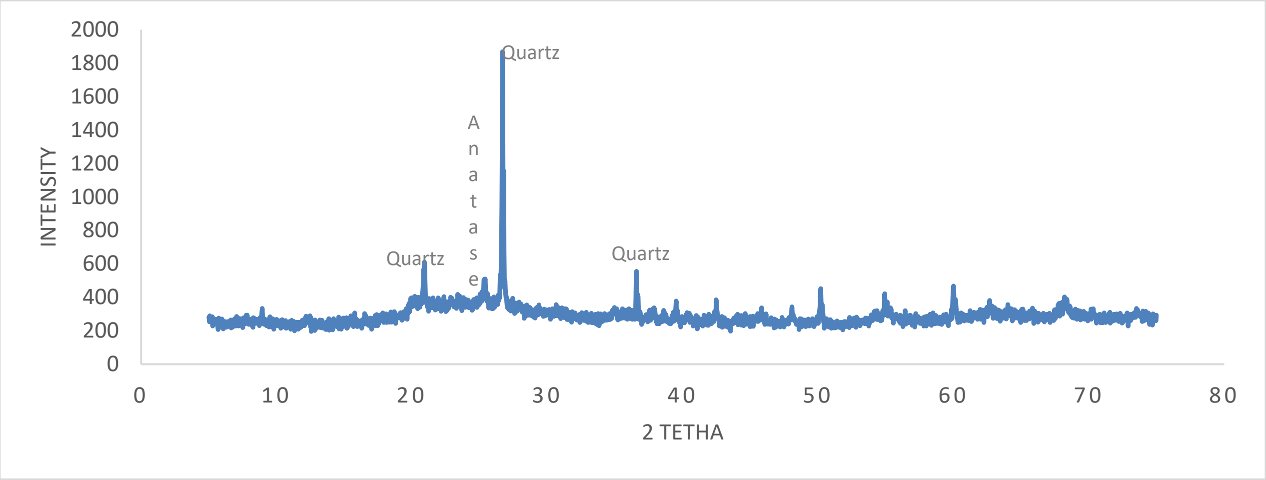


**Figure 4.4:** X-ray Diffraction characterization for calcined kaolin.

### 4.1.7 X-ray Diffraction for Acid Activated Metakaolin

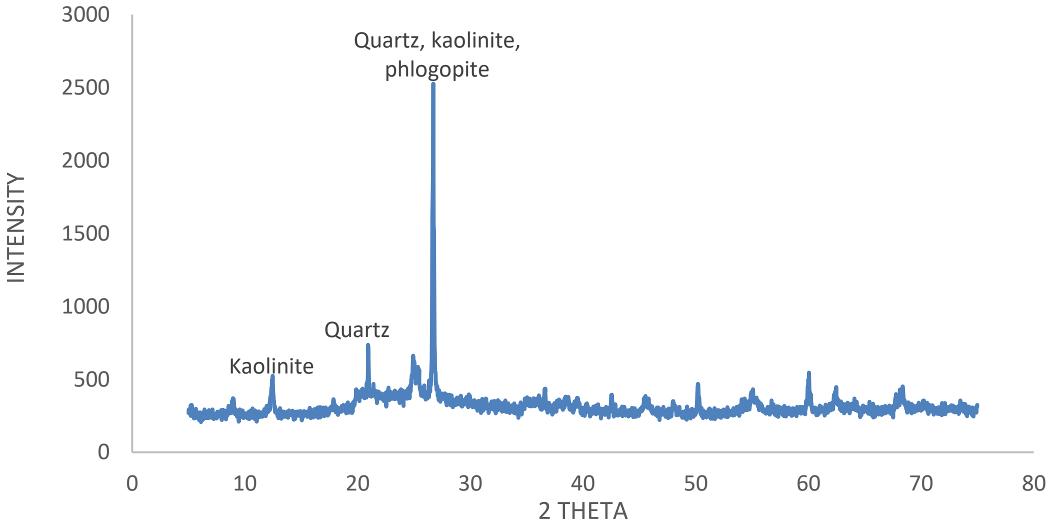


**Figure 4.5:** X-ray Diffraction for the Acid Activated Metakaolin.

The X-ray diffraction of the acid activated metakaolin shows the presence of quartz, kaolinite and phlogopite, it can be observed from the result that a little percentage of anatase was remaining in the metakaolin after activation. The percentage of quartz present in the activated metakaolin was 47.5%, kaolinite was 34.3%, phlogopite was 13.1% and anatase was 5.1%.

## 4.2 Experimental Design for Biodiesel Production

Table 4:4 shows the derived operating conditions using the surface response methodology (Box-Behnken), 17 runs were carried out, the optimum operating condition was obtained at the 16th runs with a reaction time of 120 minutes, temperature of 65 °C, catalyst concentration of 0.5 wt % and a yield of 91.3%.

**Table 4.4: Experiment Design for the Production of Allamanda oil based Biodiesel.**

|  | Factor 1 | Factor 2 | Factor 3 | Response 1 |
|---|---|---|---|---|
| Run | A:Time | B:Temperature | C:Catalyst | Yield |
|  | Mins | $^{o}$C | Wt % |  |
| 1 | 120 | 52.5 | 2.75 | 64.0000 |
| 2 | 120 | 52.5 | 2.75 | 65.3333 |
| 3 | 60 | 65.0 | 2.75 | 76.6667 |
| 4 | 120 | 52.5 | 2.75 | 66.6667 |
| 5 | 60 | 52.5 | 5.00 | 63.3333 |
| 6 | 120 | 40.0 | 0.50 | 60.0000 |
| 7 | 180 | 52.5 | 5.00 | 66.6667 |
| 8 | 120 | 52.5 | 2.75 | 62.0000 |
| 9 | 120 | 40.0 | 5.00 | 57.3333 |
| 10 | 180 | 52.5 | 0.50 | 58.6667 |
| 11 | 60 | 52.5 | 0.50 | 76.6667 |
| 12 | 60 | 40.0 | 2.75 | 61.6667 |
| 13 | 120 | 65.0 | 5.00 | 56.0000 |
| 14 | 120 | 52.5 | 2.75 | 58.0000 |
| 15 | 180 | 40.0 | 2.75 | 66.6667 |
| 16 | 120 | 65.0 | 0.50 | 91.3333 |
| 17 | 180 | 65.0 | 2.75 | 58.0000 |

## 4.3 Statistical Analysis of the Biodiesel Production Process

Table 4.5 shows the effect of reaction temperature, reaction time, catalyst concentration and their interactions on the yield of the produced biodiesel. From the analysis of the produced biodiesel, the reaction time does not have significant effect on the yield of the biodiesel at p-value= 0.087, this negates (Mathiyazhagan and Ganapathi, 2011) which state; that increase in reaction time increases the conversion rate of Jatropha biodiesel.

**Table 4.5 shows ANOVA for Response Surface Model**

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 1020.67 | 6 | 170.11 | 6.09 | 0.0065 | Significant |
| A-Time | 100.35 | 1 | 100.35 | 3.59 | 0.0873 | |
| B-Temperature | 165.01 | 1 | 165.01 | 5.91 | 0.0354 | |
| C-Catalyst | 234.72 | 1 | 234.72 | 8.40 | 0.0159 | |
| AB | 140.03 | 1 | 140.03 | 5.01 | 0.0491 | |
| AC | 113.78 | 1 | 113.78 | 4.07 | 0.0712 | |
| BC | 266.78 | 1 | 266.78 | 9.55 | 0.0114 | |
| Residual | 279.28 | 10 | 27.93 | | | |
| Lack of Fit | 233.59 | 6 | 38.93 | 3.41 | 0.1277 | not significant |
| Pure Error | 45.69 | 4 | 11.42 | | | |
| Cor Total | 1299.95 | 16 | | | | |

The reaction temperature has a great effect on the biodiesel yield, this is in agreement with (Barnwal and Mahendra, 2005) which state; that a higher reaction temperature can decrease the viscosity of the oil and result in an increase in reaction rate as more energy is been supplied for the reaction to occur and as a result the yield of the biodiesel is improved. According to Barnwal and Mahendra, (2005) reaction temperature is effective on biodiesel yield as it escalates the catalyst activity, accelerate movement of molecules so that the frequency of collision from one and another molecule is bigger and reaction proceed faster.

The catalyst concentration has significant effect on the yield of the produced biodiesel, this is in agreement with (Atadashi *et al*., 2010) which stated that when the catalyst concentration increases above it optimum value, it won't increase the biodiesel conversion rate but will increase the cost of biodiesel production. The optimum catalyst weight obtained was 0.5 wt %.

From the ANOVA Table 4.5, the interaction between time and temperature (AB) shows significant effect on the biodiesel yield, according to (Atadashi *et al*., 2010) increase in the temperature and time will increase the conversion and biodiesel yield, which corresponds with the result on the ANOVA Table 4.5.

The interaction between time and catalyst is not significant on the yield of the produced biodiesel as shown on the ANOVA Table 4.5. According to (Oghenejoboh, 2013) if the reaction time is increased and catalyst concentration is increased beyond the optimum catalyst concentration, this will not lead to an increased biodiesel yield but will reduce the conversion, lead to unwanted side reactions, reduce biodiesel yield and also increase cost of production arising from post production processes and product purification such as biodiesel washing.

From the ANOVA Table 4.5, the interaction between temperature and catalyst has a great significant effect on the biodiesel yield as shown on the table where (p-value = 0.0114). This agrees with (Gordian and Ndidi, 2013), which states that in transesterification reaction interaction between catalyst and temperature, significantly affect the yield of biodiesel.

### 4.4 Regression Analysis of Percentage Yield Against Time, Temperature and Catalyst Concentration.

$$\%\,Yield = -18.72119 + 0.246497X + 2.10852Y + 8.09630Z - 0.007889XY + 0.039506XZ - 0.290370YZ \tag{4.1}$$

The above equation is the final equation in terms of actual factor, which is also the model equation for the optimization process of the synthesized Allamanda oil based biodiesel, the equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. In the model equation, X represents time, Y represents temperature and Z represents catalyst concentration.

### 4.5: Effect of Interactive Process Parameters On Biodiesel Yield

In the course of biodiesel production, several process parameters interacted with one other, the interaction of these parameters are discussed in section 4.5.1

### 4.5.1: Effect of interaction between reaction time and catalyst concentration on biodiesel yield.

Figures 4.5 and 4.6, shows the effect of interaction between reaction time and catalyst concentration on biodiesel yield when the reaction temperature was kept fixed at 52.5 °C. The result shows that interaction between reaction time and catalyst concentration does not have a significant effect on the biodiesel yield. A simultaneous increase in reaction time and catalyst concentration will lead to reduction in biodiesel yield. Figure 4.5 shows that the highest biodiesel yield of 75 % was obtained at a reaction time of 80 minutes, catalyst concentration of 1.1 wt% and reaction temperature of 52.5 °C, this indicated that increase in reaction time favors the biodiesel yield but when the catalyst concentration is increased above 1.1 wt % the biodiesel yield started reducing. A continuous increase in catalyst concentration will only increase the cost of production and higher tendency of soap formation.

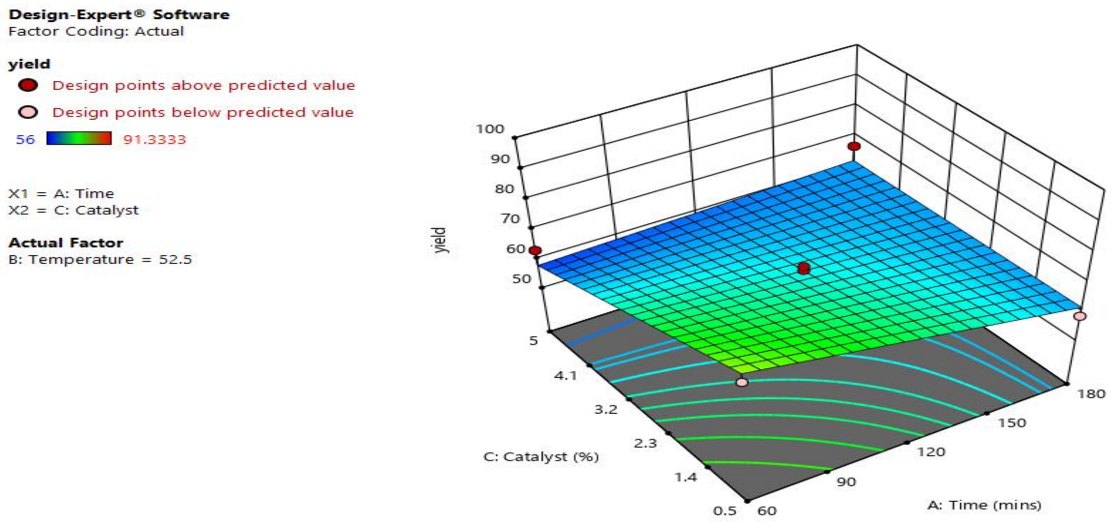


**Figure 4.6**: The 3D Surface representation of the effect of interaction between reaction time and catalyst concentration on biodiesel yield.

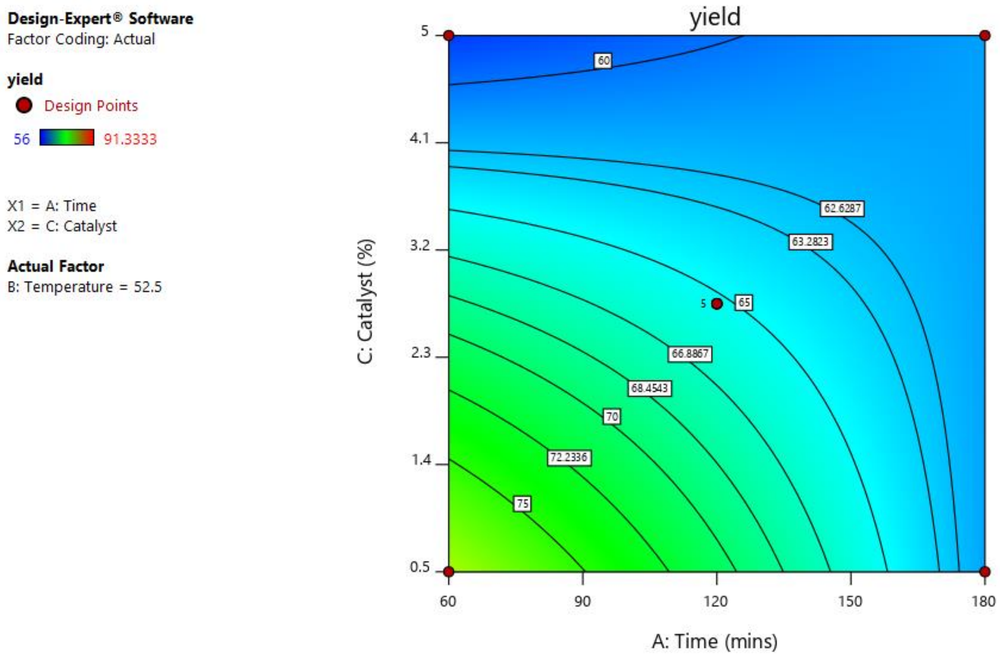


**Figure 4.7:** Shows the contour line representation of the effect of interaction between reaction time and catalyst concentration on biodiesel yield.

### 4.5.2 Effect of interaction between catalyst concentration and reaction temperature on biodiesel yield.

Figures 4.7 and 4.8 shows the interaction between catalyst concentration and reaction temperature at fixed time of 120 minutes, from the obtained result it was shown on figure 4.7 and 4.8, that the interaction between catalyst concentration and reaction temperature has significant effect on the biodiesel yield, this statement was confirmed by (Gordian and Ndidi 2013). The highest biodiesel yield of 75 % was obtained at a reaction temperature of 61 $^0$C, at catalyst concentration of 1.3 wt % and at reaction time of 120 minutes, this shows that increase in temperature and decrease in catalyst concentration favors the reaction.

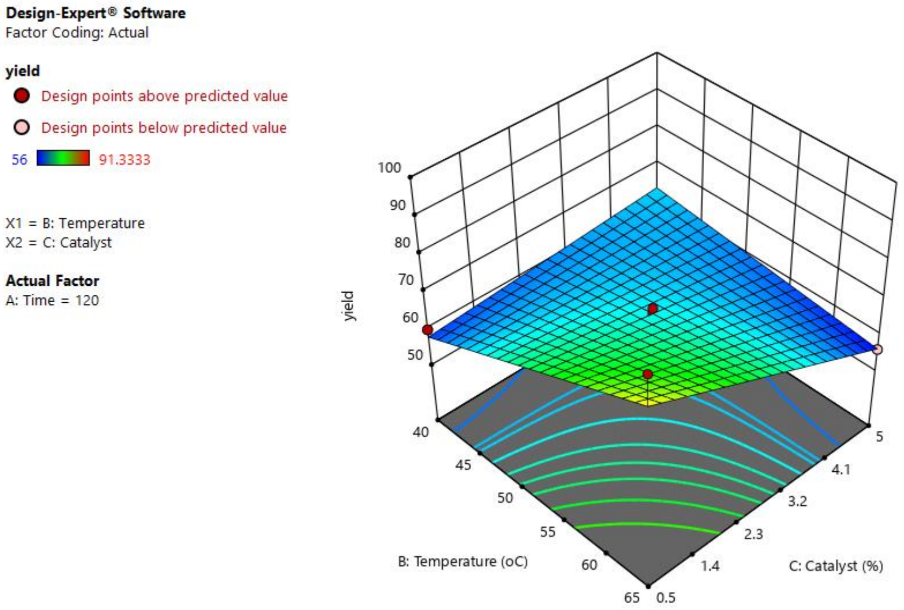


**Figure 4.8**: 3D Surface Representation of the interaction between catalyst concentration and reaction temperature.

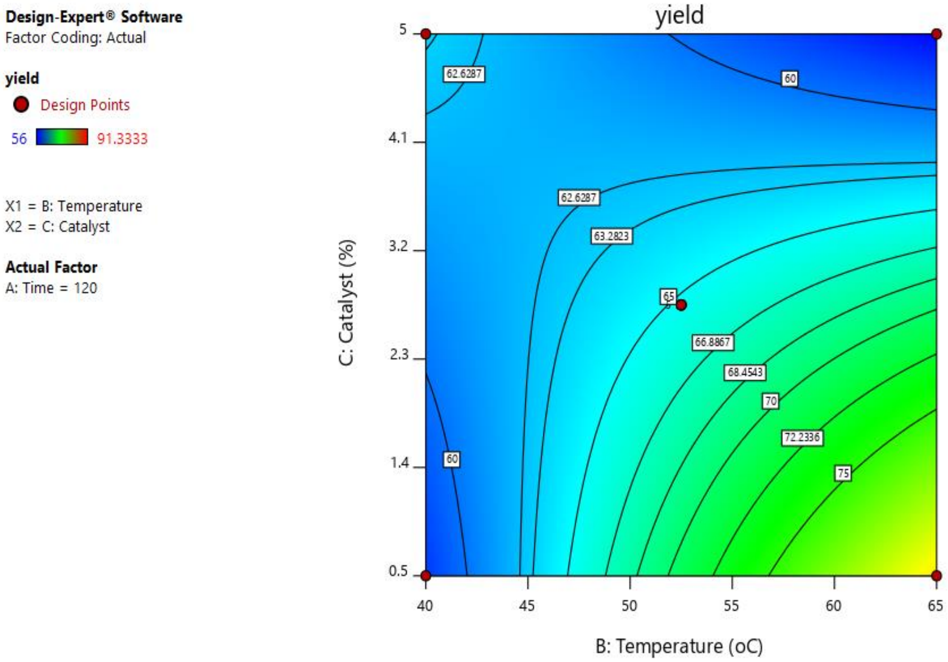


**Figure 4.9:** The Contour line representation of the interaction between catalyst concentration and reaction temperature on biodiesel yield.

### 4.5.3 Effect of interaction between reaction temperature and reaction time on biodiesel.

Figure 4.9 shows the interaction between reaction time and reaction temperature, the interaction of these process parameters have significant effect on the biodiesel yield. According to Atadashi *et al*., (2010) increase in temperature and time will increase the biodiesel yield. From figure 4.9, the highest yield was obtained at reaction time of 90 minutes, at reaction temperature of 60 $^{o}$C and catalyst concentration of 2.75 wt %.

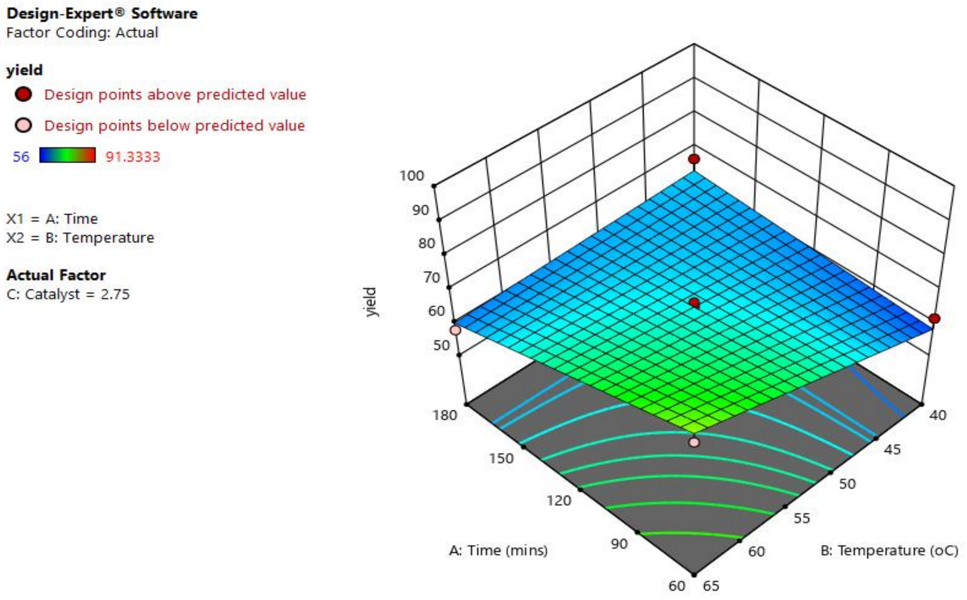


**Figure 4.10:** Effect of interaction between reaction time and reaction temperature on biodiesel yield.

## 4.6 Physiochemical Properties of the Allamanda Oil Biodiesel

Table 4.6 Shows the physiochemical properties of Allamanda oil based biodiesel, which was compared with American Standard for tools and equipment with other literatures (Ayan *et al*., 2016, Abdulkareem *et al.,* 2012, and Mohamad *et al*., 2014).

**Table 4.6 shows the physiochemical properties of the Allamanda oil based biodiesel.**

| Property | Unit | Test Method | Allamanda Biodiesel | ASTM | X | Y | Z |
|---|---|---|---|---|---|---|---|
| Smoke Point | $^0$C | ASTM D1250 | 123.10 | 120-130 | 121.00 | 125.00 | 127.00 |
| Acid Value | | ASTM D664 | 0.62 | 0.50 | - | - | - |
| Viscosity @ 40$^0$C | Cst | ASTM D445 | 19.00 | 19-25 | 23.00 | 25.00 | 23.50 |
| Viscosity @ 100 $^0$C | Cst | ASTM D448 | 0.99 | 1.50 | - | - | - |
| Viscosity @ RT | Cst | ASTMD450 | 36.50 | 38.50 | - | - | - |
| Flash Point | $^0$C | ASTM D97 | 186.50 | <130.00 | 140.90 | 65.56 | 152.00 |
| %FFA | % | ASTM D664 | 0.31 | - | - | - | - |
| Cloud Point | $^0$C | ASTM D2600 | 1.83 | -3-12 | - | 8.00 | 12.00 |
| Fire Point | $^0$C | ASTM D2140 | 196.00 | - | - | - | - |
| Pour Point | $^0$C | ASTM D84 | -7.00 | - | - | - | - |

X= Ayan *et al.,* 2016. Y= Abdulkaareem *et al*., 2012. Z= Mohamad *et al*., 2014.

### 4.6.1 Determination of acid value

The acid value of the Allamanda oil methyl ester was determined to be 0.62 mgKOH/g, which exceeds the value specified by ASTM standard. There was a drastic reduction from 5.20 mgKOH/g for initial Allamanda oil sample which improved the biodiesel quality for biolubricant production. The acid value of the Allamanda oil methyl ester indicates that soap formation reduced during transesterification, which made the Allamanda oil based biodiesel a good biodiesel for biolubricant synthesis.

### 4.6.2 Determination of percentage free fatty acid

The percentage free fatty acid of Allamanda methyl ester was determined, from the analysis the percentage free fatty acid as obtained was 0.31 %. There was a remarkable improvement from 2.60% for initial Allamanda oil sample which is desirable for biodiesel. This indicates that soap formation reduced during transesterification for biolubricant synthesis.

### 4.6.3 Viscosity

Viscosity of the Allamanda oil ethyl ester was determined at 40 $^{o}$C and was found to be 19.0 cSt which falls within the specified range given by the ASTM standard but lesser than the values reported by other cited literatures. This implies that the synthesized Allamanda methyl ester has a higher flow capability and can easily undergo further transesterification for the synthesis of biolubricant, as well as low tendency of forming deposits on engines and therefore suitable as fuel.

### 4.6.4 Determination of flash point

Flash point indicates the minimum temperature at which fuel ignites on application of an ignition source under specified conditions, it varies inversely with fuel's volatility. The flash point of the Allamanda methyl ester is 186.5 $^{o}$C, which also satisfied the ASTM standard (>130 $^{o}$C) but higher than other cited literatures shown in Table 4.6 and this is desirable. This higher value obtained shows the safety of the biodiesel during usage and storage (Busamatary, 2013).

### 4.6.5 Determination of cloud point

The cloud point is the temperature at which fuel starts to form crystals, with further decrease in temperature these crystals increase in size and quantity until the fuel gel does not move again (Bilal *et al.*, 2013). From this analysis the cloud point of Allamanda methyl ester was 1.83 $^{o}$C, which satisfied the requirement of ASTM standard (-3-12 $^{o}$C) but lower than 12 $^{o}$C reported by (Mohamad *et al.*, 2014) and this means that the Allamanda methyl ester has low tendency to crystallize in cold temperature.

## 4.7 Properties of the Produced Allamanda Oil Based Biolubricant.

Table 4.8 shows the properties of Allamanda oil based biolubricant produced by using an acid activated metakaolin, the result was compared with other seed oil based biolubricants including Allamanda oil based bilolubricant with base activated catalyst. The viscosity of the Allamanda oil based biolubricant was determined to be 77 $^{o}$C at 40 $^{o}$C, this result shows that there was an improvement in the viscosity of Allamanda oil methyl ester (biodiesel), the obtained value shows the synthesized biolubricant met ISO VG 32, ISO VG 46, and ISO VG 68 viscosity grade requirement.

**Table 4.7 The Properties of the Produced Allamanda Oil Based Biolubricant**.

| Properties | Pour point<br>0C | Flash point<br>0C | Viscosity at 40 oC<br>CSt | Viscosity at 100 oC<br>CSt | Viscosity index |
|---|---|---|---|---|---|
| This study | -11.2 | 261.0 | 77.0 | 26.0 | 376.15 |
| ISO VG32 | <-10 | 220.0 | >41.40 | >4.10 | >90.00 |
| ISO VG46 | <-10 | - | >41.4 | >4.10 | >90.00 |
| ISO VG68 | <-10 | 226.0 | >61.40 | >4.10 | >198.00 |
| ISO VG100 | <-10 | 246.0 | >90.00 | >4.10 | >216.00 |
| ISO VG220 | -6 | 265.0 | >12.00 | >4.10 | >50.00 |
| A | -12 | - | 35.43 | 7.93 | 206.00 |
| B | -35 | 290.0 | 60.83 | 10.21 | 290.00 |
| C | -7 | - | 55.17 | 10.96 | 195.22 |
| D | -27 | 211.0 | 6.39 | 2.28 | 207.00 |
| E | -66 | - | 40.50 | 7.80 | 204.00 |
| F | -12.8 | 249.0 | - | 64.00 | 28.00 |

[A] Jose *et al.*, (2020), [B] Menkiti *et al.*, (2017), [C] Bilal *et al.*, (2013), [D] Musa *et al*, (2015) [E] Francis (2014), [F] Khadijat, (2021)

LEGEND

A= Rape Seed Oil

B= Jatropha Seed Oil

C= Jatropha Seed Oil

D= Castor Oil

E= Moringa Oleifera Oil

F= Allamanda Seed Oil

The viscosity of the Allamanda oil based biolubricant (base activated) has it viscosity at 40 $^{o}$C to be 64 cSt which is lesser than that of acid activated Allamanda oil based biolubricant, it met the viscosity grade requirement by ISO VG 32, ISO VG 46, ISO VG 68 and ISO VG 220.

The viscosity of Allamanda biolubricant (acid activated) at 100 $^{o}$C was lesser than the base activated Allamanda oil based biolubricant, both biolubricants (acid and base activated) met the viscosity grade requirement by ISO VG 32, ISO VG 46, ISO VG 68, ISO VG 100 and ISO VG 220. Viscosity is a very important property of biolubricant, it holds a vital key in which lubricants are graded, lubricants with low viscosity can be used in small machines like chain-saw or small pumps while lubricants with high viscosity like Allamanda oil based biolubricant can be used in automobile engines and hydraulics (Ghazi, 2009).

Flash point of a lubricant is the lowest temperature by which the lubricant gives off adequate amount of vapour capable of mixing with air and be ignited. It is used to measure the safety of lubricant during usage and storage, the flash point of Allamanda oil based biolubricant (acid activated) was 261.0 $^{o}$C, this flash point is above that of ISO VG 32, ISO VG 68 but in proximity with ISO VG 220 (265 $^{o}$C) and the flash point of Allamanda oil based biolubricant (base activated) was determined to be 249.0 $^{o}$C. The synthesized Allamanda oil based biolubricant can be used as motor gear oil as it has a flash point in proximity with ISO VG 220 requirement for lubricant.

The pour point of the synthesized Allamanda oil based biolubricant (acid activated) was determined to be -11.2 $^{o}$C, this corresponds with the pour point of ISO VG 32, ISO VG 46, ISO VG 68 and ISO VG 100, the pour point of Allamanda oil biolubricant (base activated) also corresponds with the ISO VG 32, ISO VG 46, ISO VG 68 and ISO VG 100, this implies that both biolubricants (acid and base activated) can be used both in humid and temperate regions of the world. Pour point which is the minimum temperature at which a fluid and other liquid remains pourable, the pour point of Allamanda oil biolubricant (base activated) is -12.5 $^{o}$C, the difference in pour point between the acid and base activated Allamanda oil based biolubricants can be attributed to their difference in catalyst activation.

# CHAPTER FIVE

## 5.0 CONCLUSION AND RECOMMENDATION

### 5.1 Conclusion

1. Acid activated catalyst was developed from kaolinite clay and was characterized using the following analysis; X-ray Diffraction, X-ray Fluorescence, Scanning Electron Microscopy and Braunauer Emmett Teller.
2. Allamanda seed oil was extracted from Allamanda seeds and characterized to determine the physiochemical properties, which shows it ability as a good feedstock for biolubricant production.
3. The Allamanda oil base Fatty Acid Methyl Ester (Biodiesel) was synthesized, optimized and characterized.
4. The Allamanda oil base Biolubricant was synthesized and characterized to obtain it properties and compared to standard, which shows that Allamanda oil base Biolubricant can serve as substitute for the conventional petroleum base lubricant.

### 5.2 Recommendations

1. Combinations of metallic oxides with kaolin could be used to investigate further the production of biolubricant.
2. The Nigerian government should provide more fund and promote researches in this area, as the world is gradually transiting towards bio based source of energy because of it numerous advantages.
3. It is important that research in this area should be scaled up from laboratory to industrial scale, so it can be of national benefit.

4. Optimization of the synthesized Allamanda oil base biolubricant.

## 5.3 Contribution to Knowledge

Acid activated metakaolin was prepared from Kutigi kaolin clay in Niger State, using 2 moles of $H_2SO_4$, calcined at 650 $^0$C for 90 mins, for the production of Allamanda oil based biodiesel and biolubricant.

Allamanda oil was extracted from it seeds using Soxhlet extractor and was characterized, the free fatty acid of the oil was 5.20 mgKOH/g. Based on this study, the optimum biodiesel yield obtained was 91.3%, 5:1 oil to methanol ratio, reaction time of 120 mins, reaction temperature of 65 $^0$C and catalyst weight of 0.5wt%.

Allamanda oil based biolubricant was produced using transesterification process with a molar ratio of 4:1 of allamanda methyl ester to trimethylopropane (TMP), reaction temperature of 120 $^0$C, reaction time of 2 hours 30 mins and catalyst weight of 0.5 wt%. The pour point obtained was 11.2 $^0$C, flash point was 261.0 $^0$C, viscosity at 40 $^0$C was 77.0 Cst, viscosity at 100 $^0$C was 26.0 Cst and the viscosity index was 376.15.

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# APPENDICES

## APPENDIX A

SPECIFIC GRAVITY

The expression for specific gravity (Sp.gr) is:

Sp.gr = = $\frac{C-A}{B-A}$ = Mass of the substance / Mass of an equal volume of water.

A=mass of empty bottle,

B= mass of bottle +mass of water,

C=mass of bottle + mass of oil

A=mass of empty bottle= 45.562 g

B=mass of bottle + mass of water = 45.562+49.998 = 95.560 g

C=mass of bottle + mass of oil = 45.562+46.384 = 91.946 g

Sp.gr = = $\frac{91.946-45.562}{95.560-45.562}$ = 0.928

DENSITY

Density = $\frac{weight\ of\ sample}{volume\ of\ sample}$

Weight of allamanda oil = 46.205 g

Volume of allamanda oil = 50 $cm^3$

Density = $\frac{46.205\ g}{50\ cm3}$ = 0.924 $g/cm^3$

SAPONIFICATION VALUE

The saponification value (S.V.) is given by: S.V = $\frac{(V0-V1)\times 0.5\times 56.10}{M}$ (mgKOH/g)

Where V0 = the volume of the solution used for blank test

VI = the volume of the solution used for determination

N = Actual normality of the HCl used

M = Mass of the oil used.

V0 = 27.5 $cm^3$

VI = 16.2 $cm^3$

N= 0.5

M= 2.0 g

S.V = $\frac{(27.5-16.2)\times0.5\times56.10}{2.0}$ (mgKOH/g) = 158.483 mgKOH/g

ACID VALUE

Acid value = $\frac{56.10\times V\times C}{Y}$

Where V = Volume of potassium hydroxide used for titration (ml),

C = Concentration of potassium hydroxide used for titration (mol/l) and

Y = mass of oil sample used for analysis (g)

V= 1.9 $cm^3$

C= 0.1 M

Y= 2.05 g

Acid value = $\frac{56.10\times1.9\times0.1}{2.05}$ = 5.20 mgKOH/g

FREE FATTY ACID

FFA = = $\frac{Acid\ value}{2}$= $\frac{5.20}{2}$= 2.60 %

PEROXIDE VALUE

Peroxide value = $\frac{(S-B)\times N\ of\ thiosulphate\times1000}{weight\ of\ sample}$ (meq/kg)

S=titrant of sample, B= titrant of the blank.

N of thiosulphate = 0.025 M

S= 0.75

B= 0.3

Weight of oil = 2.1 g

Peroxide value = $\frac{(0.75-0.3)\times 0.025\times 1000}{2.1}$ (meq/kg) = 5.36 meq/kg

IODINE VALUE

I.V = $\frac{(V1-V2.)\times 0.1269\times C\times 100}{M}$ ($gI_2$/100g oil) (3.5)

Where C = Concentration of sodium thiosulphate used

$V_1$ = Volume of sodium thiosulphate used for blank test

$V_2$ = Volume of sodium thiosulphate used for determination

M = Mass of the sample

$V_1$ = 87.4 $cm^3$

$V_2$ = 23.0 $cm^3$

M = 2.01 g

I.V = $\frac{(87.4-23.0.)\times 0.1269\times 0.1\times 100}{2.01}$ ($gI_2$/100g oil) = 40.659 $gI_2$/100g oil

# APPENDIX B

This tables shows the 100 Solutions found during the optimization of the Allaamanda oil based Biodiesel.

| **Number** | **Time** | **Temperature** | **Catalyst** | **Yield** | **Desirability** | |
|---|---|---|---|---|---|---|
| **1** | **63.559** | **61.773** | **0.609** | **91.757** | **1.000** | **Selected** |
| 2 | 60.458 | 60.770 | 0.545 | 91.431 | 1.000 | |
| 3 | 60.780 | 64.306 | 0.853 | 94.042 | 1.000 | |
| 4 | 60.000 | 64.167 | 0.650 | 95.685 | 1.000 | |
| 5 | 71.812 | 64.579 | 0.677 | 93.266 | 1.000 | |
| 6 | 83.344 | 64.647 | 0.502 | 91.921 | 1.000 | |
| 7 | 69.407 | 62.619 | 0.622 | 91.564 | 1.000 | |
| 8 | 66.570 | 63.159 | 0.552 | 93.492 | 1.000 | |
| 9 | 68.369 | 62.805 | 0.558 | 92.530 | 1.000 | |
| 10 | 64.022 | 63.052 | 0.768 | 92.265 | 1.000 | |
| 11 | 60.738 | 63.795 | 1.010 | 92.084 | 1.000 | |
| 12 | 61.067 | 64.317 | 0.980 | 92.954 | 1.000 | |
| 13 | 67.720 | 64.762 | 0.695 | 94.344 | 1.000 | |
| 14 | 63.164 | 62.604 | 0.581 | 93.247 | 1.000 | |
| 15 | 66.446 | 64.916 | 0.789 | 94.091 | 1.000 | |
| 16 | 71.728 | 64.913 | 0.662 | 93.860 | 1.000 | |
| 17 | 80.180 | 64.391 | 0.568 | 91.861 | 1.000 | |
| 18 | 63.122 | 62.295 | 0.655 | 92.256 | 1.000 | |
| 19 | 62.903 | 62.993 | 0.679 | 93.109 | 1.000 | |
| 20 | 74.741 | 63.625 | 0.531 | 92.401 | 1.000 | |
| 21 | 66.001 | 61.973 | 0.575 | 91.762 | 1.000 | |
| 22 | 65.291 | 64.032 | 0.755 | 93.427 | 1.000 | |
| 23 | 60.098 | 60.468 | 0.502 | 91.367 | 1.000 | |
| 24 | 69.763 | 64.330 | 0.683 | 93.365 | 1.000 | |
| 25 | 63.417 | 64.794 | 1.107 | 92.022 | 1.000 | |
| 26 | 60.483 | 60.617 | 0.502 | 91.506 | 1.000 | |
| 27 | 68.431 | 64.874 | 0.762 | 93.786 | 1.000 | |
| 28 | 67.456 | 63.571 | 0.541 | 93.951 | 1.000 | |
| 29 | 65.051 | 64.096 | 0.949 | 92.032 | 1.000 | |
| 30 | 66.927 | 63.608 | 0.793 | 92.184 | 1.000 | |
| 31 | 70.662 | 63.783 | 0.754 | 91.876 | 1.000 | |
| 32 | 72.969 | 64.430 | 0.502 | 94.151 | 1.000 | |

| | | | | | |
|---|---|---|---|---|---|
| 33 | 61.971 | 64.738 | 0.969 | 93.410 | 1.000 |
| 34 | 63.190 | 64.845 | 1.177 | 91.559 | 1.000 |
| 35 | 81.400 | 64.225 | 0.509 | 91.788 | 1.000 |
| 36 | 70.536 | 63.559 | 0.639 | 92.472 | 1.000 |
| 37 | 71.563 | 62.809 | 0.617 | 91.380 | 1.000 |
| 38 | 64.673 | 62.875 | 0.549 | 93.540 | 1.000 |
| 39 | 62.422 | 62.453 | 0.725 | 92.101 | 1.000 |
| 40 | 68.816 | 63.728 | 0.774 | 92.064 | 1.000 |
| 41 | 64.101 | 62.634 | 0.737 | 91.901 | 1.000 |
| 42 | 84.579 | 64.891 | 0.546 | 91.611 | 1.000 |
| 43 | 61.382 | 63.024 | 0.659 | 93.654 | 1.000 |
| 44 | 66.293 | 64.900 | 0.995 | 92.434 | 1.000 |
| 45 | 63.672 | 62.871 | 0.618 | 93.237 | 1.000 |
| 46 | 64.465 | 63.048 | 0.786 | 92.022 | 1.000 |
| 47 | 65.827 | 64.477 | 0.574 | 95.368 | 1.000 |
| 48 | 65.215 | 63.752 | 0.972 | 91.354 | 1.000 |
| 49 | 73.172 | 64.974 | 0.832 | 92.252 | 1.000 |
| 50 | 60.330 | 63.828 | 1.069 | 91.745 | 1.000 |
| 51 | 87.508 | 64.998 | 0.500 | 91.367 | 1.000 |
| 52 | 80.972 | 64.305 | 0.551 | 91.684 | 1.000 |
| 53 | 71.515 | 64.500 | 0.653 | 93.418 | 1.000 |
| 54 | 64.158 | 64.405 | 1.081 | 91.574 | 1.000 |
| 55 | 63.590 | 61.808 | 0.506 | 92.558 | 1.000 |
| 56 | 65.709 | 64.989 | 0.774 | 94.491 | 1.000 |
| 57 | 75.240 | 64.984 | 0.850 | 91.643 | 1.000 |
| 58 | 61.166 | 63.327 | 0.559 | 94.927 | 1.000 |
| 59 | 70.904 | 64.726 | 0.670 | 93.739 | 1.000 |
| 60 | 77.554 | 63.855 | 0.610 | 91.466 | 1.000 |
| 61 | 66.328 | 63.921 | 0.947 | 91.532 | 1.000 |
| 62 | 71.187 | 63.208 | 0.692 | 91.454 | 1.000 |
| 63 | 63.743 | 64.326 | 0.743 | 94.286 | 1.000 |
| 64 | 60.840 | 63.635 | 1.034 | 91.662 | 1.000 |
| 65 | 84.716 | 64.682 | 0.504 | 91.619 | 1.000 |
| 66 | 68.688 | 63.639 | 0.741 | 92.229 | 1.000 |
| 67 | 74.488 | 64.672 | 0.835 | 91.534 | 1.000 |
| 68 | 71.201 | 64.179 | 0.535 | 93.970 | 1.000 |
| 69 | 65.814 | 64.444 | 0.737 | 94.014 | 1.000 |

| | | | | | |
|---|---|---|---|---|---|
| 70 | 63.307 | 63.707 | 0.787 | 93.175 | 1.000 |
| 71 | 60.253 | 63.093 | 0.816 | 92.776 | 1.000 |
| 72 | 65.525 | 62.887 | 0.552 | 93.339 | 1.000 |
| 73 | 82.657 | 64.896 | 0.588 | 91.774 | 1.000 |
| 74 | 73.944 | 64.748 | 0.860 | 91.561 | 1.000 |
| 75 | 72.675 | 63.907 | 0.648 | 92.385 | 1.000 |
| 76 | 73.697 | 63.824 | 0.617 | 92.270 | 1.000 |
| 77 | 66.258 | 64.033 | 0.675 | 93.836 | 1.000 |
| 78 | 62.532 | 63.119 | 0.509 | 94.692 | 1.000 |
| 79 | 62.657 | 63.817 | 0.693 | 94.224 | 1.000 |
| 80 | 76.016 | 63.479 | 0.571 | 91.606 | 1.000 |
| 81 | 74.391 | 64.777 | 0.649 | 93.141 | 1.000 |
| 82 | 72.073 | 64.956 | 0.534 | 94.847 | 1.000 |
| 83 | 67.680 | 63.987 | 0.675 | 93.442 | 1.000 |
| 84 | 61.905 | 61.908 | 0.577 | 92.552 | 1.000 |
| 85 | 69.896 | 64.369 | 0.699 | 93.259 | 1.000 |
| 86 | 79.382 | 64.417 | 0.615 | 91.736 | 1.000 |
| 87 | 69.741 | 63.536 | 0.785 | 91.519 | 1.000 |
| 88 | 64.483 | 62.370 | 0.643 | 92.156 | 1.000 |
| 89 | 61.385 | 63.019 | 0.736 | 93.043 | 1.000 |
| 90 | 83.563 | 64.777 | 0.512 | 91.963 | 1.000 |
| 91 | 77.408 | 64.506 | 0.584 | 92.557 | 1.000 |
| 92 | 71.136 | 64.320 | 0.612 | 93.586 | 1.000 |
| 93 | 60.000 | 58.969 | 0.500 | 89.166 | 0.939 |
| 94 | 98.231 | 65.000 | 0.500 | 88.727 | 0.926 |
| 95 | 60.000 | 57.716 | 0.500 | 87.298 | 0.886 |
| 96 | 97.969 | 65.000 | 0.944 | 85.723 | 0.841 |
| 97 | 127.338 | 65.000 | 0.500 | 81.551 | 0.723 |
| 98 | 180.000 | 40.000 | 5.000 | 71.152 | 0.429 |
| 99 | 179.057 | 40.000 | 5.000 | 71.031 | 0.425 |
| 100 | 180.000 | 40.268 | 5.000 | 70.948 | 0.423 |

# APPENDIX C

**Summary of previous research works that had been carried out in biolubricant production are shown in this table.**

| S/NO | TITLE | FEEDSTOCK & CONDITION | YIELD | STRENGTH | LIMITATION | REFERENCE |
|---|---|---|---|---|---|---|
| 1 | Production of biolubricant from jatropha curcas seed oil.<br>Potassium hydroxide (KOH) and Sodium methoxide was used as catalyst. | Jatropha curcas oil seed.<br>Methanol and oil sample in water bath was heated at 60$^0$C<br>Stirred at 700rpm for 1hr and titrated against 0.1N solution of KOH, repeated for 5times with an hour interval to determine the FFA content in the oil.<br>Catalyst used was 0.5 % w/w of the oil and the reaction was conducted at a temperature of 60$^0$C for 2 hrs.<br>Oil to methanol ratio used was 3:1<br>The weight ratio of oil to methanol used was 3.5:1<br>0.8 % w/w of the total reactant | 85 % | Non edible and waste<br>High yield<br>Hexane was used as solvent for oil extraction. | Expensive catalyst.<br>Alkaline Catalyst.<br>Temperature of mixture didn't exceed 60$^0$C. | Bilal *et al.*, 2013 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | was used as catalyst.<br>Reaction was conducted at a temperature of 120$^0$C for 2hr 30min | | | | |
| 2 | Manufacturing of enironment friendly biolubricants from vegetable oil.<br>Sodium methoxide was used as catalyst | Palm oil and jatropha oil<br>Reaction time was 4hours at 130$^0$C<br>Palm/jatropha biodiesel was treated with silica gel for 30min to remove soap, filtered and dried overnight in an oven at 105$^0$C.<br>Sodium methoxide catalyst (0.9-1w%)<br>was added according to the type of methyl esters. | Palm oil base biolubricant had yield of 97.8% while jatropha oil based biolubricant had yield of 98.2% | High yield<br>Non edible and waste(jatropha)<br>Pretreatment test was carried out.<br>The feedstock was characterized.<br>Weight percent of the biolubricants was determined. | Expensive catalyst<br>Reaction time did not exceed 4hours and temperature did not exceed 130$^0$C<br>Alkaline catalyst | Ebtisam *et al*., 2017 |
| 3 | Process optimization and kinetics of biolubricants synthesis from fluted pumpkin seed.<br>Ca(OH)$_2$ was | Fluted pumpkin seed<br>Optimum condition for the yield of TMP trimester were 160$^0$C, 6hours was reaction time and mole ratio (MME:TMP) of 6:1 | Biolubricant yield was 81.42% | Pretreatment was carried out on the oil.<br>High yield<br>Hexane was used as solvent for extraction. | Expensive catalyst.<br>Alkaline catalyst.<br>Optimum condition for the yield of TMP tiester did not exceed 160$^0$C and the reaction time did not exceed 6 hours. | Menkiti *et al*., 2017. |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | used as catalyst. | Gas chromatography analysis was carried out<br>Fluted pumpkin based biolubricant was held in a gas chromatographer at $80^{0}$C for 2 minutes then heated at $340^{0}$C for $5^{0}$C/min and finally held at $340^{0}$C for 5 minutes. |  |  |  |  |
| 4 | Synthesis of environmental friendly biolubricant: A novel approach.<br>Catalyst used was perchloric acid. | Oleic acid and i-amyl alcohol.<br>Molar ratio of reactant was 1:2<br>Reaction temperature was $70^{0}$C<br>Catalyst used was 1 % w/w with respect to the fatty acid. | Oil yield was not determined. | Descent characterization result.<br>Acidic catalyst. | Yield was not determined.<br>Expensive catalyst<br>Reaction temperature didn’t exceed $70^{0}$C<br>Expensive feed stock | Mobarak *et al*., 2014. |
| 5 | Synthesis of palm oil based trimethylolpropane ester as potential biolubricant: chemical kinetics modelling | Palm oil<br>Palm oil methyl esters was fractionated at $170^{0}$C – $180^{0}$C<br>Under vacuum pressure of 1.0-1.5 Mbar<br>POME was dried overnight at $105^{0}$C in an oven. | 27% | The reaction was a reversible reaction.<br>The transesterification between POME and TMP occurs in step mechanism. | Alkaline catalyst<br>Expensive catalyst<br>Edible catalyst<br>Low oil yield<br>Homogenous catalyst. | Yunus *et al*., 2003. |

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|  | Liquid sodium methoxide was used as catalyst. | Ratio of palm oil methyl esters to trimethylolpropane POME:TMP is 10:1<br>Catalyst weight used was 2% w/w based on total mass of the reactant.<br>Reaction equilibrium was achieved and stabilized after 1 hour. |  |  |  |  |
| 6 | Production of biolubricant from allamanda seed oil using acid activated metakaolin. | Allamnda seeds<br>Methanol to oil ratio was kept constant at 1:5, reaction temperature, catalyst weight and reaction time.<br>AME:TMP at a molar ratio of 1:4 in presence of catalyst. | 93 % | Feed stock is a waste and non edible oil.<br>Catalyst is not expensive.<br>Operating conditions were optimized. |  | Sunday *et al*., 2021 |