SYNTHESIS OF BIOLUBRICANT FROM VEGETABLE OILS

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DECLARATION

I, declare that the work in this thesis entitled “Synthesis of Biolubricant from Vegetable Oils” has been carried out by me in the Department of Chemical Engineering, Ahmadu Bello University, Zaria, under the supervision of Dr. I. A. Mohammed-Dabo, Dr O.R Momoh and Dr. S. M. Warizi of the Department of Chemical Engineering ABU, Zaria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously been presented for another degree or diploma at this or any other institution.

Nuhu Mohammed

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Name of Student	Signature	Date

CERTIFICATION

This thesis entitled "SYNTHESIS OF BIOLUBRICANT FROM VEGETABLE OILS" meets the regulations governing the award of the degree of Master of Science (M.Sc) in Chemical Engineering, Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This project work is dedicated to my beloved father and mother Dr. Nuhu Mohammed Usman and Amina Musa Mohammed, my beloved sisters and brothers and my beloved wife Amina Magaji Samaila. May Almighty bless them all ameen.

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My sincere gratitude goes to Almighty Allah for his guidance in keeping me up to this level of academic discipline and my family for their support.

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ABSTRACT

This thesis aimed at the production of biolubricant from vegetable oils. The first stage produced methyl ester of the oil and in the second stage; the methyl ester was transesterified with Trimethylolpropane (TMP) in a ratio of 3.5:1 at 150^0C to produce the biolubricant. The pour points biolubricant and its blend were significantly improved when compared to that of raw oils. The pour point for Jatropha oil improved from 6.5 to -8 to -13, Moringa oil from 6 to -8 to -15, Castor oil from 5 to -4 to -30 and Cotton seed oil from 4°C to -6°C to -16°C respectively. Similarly the viscosity index of Jatropha oil reduced from 220.70 to 216, Moringa oil from 224.70 to 197.75, Castor oil from 96.42 to 88.32, and Cotton seed oil from 213.12 to 198.57 respectively. As the temperature increased from 30^0C to 100 the viscosity reduces by 37.97, 53.46, 69.58 and 39.32 cSt. The GC-MS result shows that the oils contained more of unsaturated ricinoleic, and linoleic acid than saturated fatty acid of caproic, capric, palmitic and stearic acid. It was found that the biolubricant produced was comparable to the ISO VG-32 and VG-46 commercial standards for light and industrial gears applications respectively.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations/Symbols	Unit	Meaning
ISO		International Standards Organization
VG		Viscosity Grade
TMP		Trimethylolpropane
FTIR		Fourier Transform Infrared Spectrometer
GC-MS		Gas Chromatography - Mass Spectrometry
API	^{0}C	American Petroleum Institute
VI		Viscosity index
SN		Straight Neutral Oil
BS		Base Straight Oil
ASTM		American Standard Test Method
KOH		Potassium Hydroxide
f	N	Frictional Force
SUV		Saybolt Universal Second
BCI		Bio Corrosion Inhibitors
PPD		Pour Point Depressants
VII		Viscosity Index Improvers
SAE		Society of Automotive Engineers
AGMA		American Gear Manufacturers Association

NARICT		National Research Institute for Chemical Technology
NLGI		National Lubricating Grease Institute
TE		Triester
ME		Monoester
DE		Diester
JME		Jatropha Methyl Ester
M		Methanol
Max.		Maximum
n_D		Refractive Index
N	N	Normality
HCl		Hydrochloric Acid
CCl_4		Carbon Tetrachloride
KI		Potassium Iodide
Avg.		Average Value
B	ml	Blank Titer Value
S	ml	Sample Titer Value

CHAPTER ONE

INTRODUCTION

1.1 PREAMBLE

The environmental threats posed by the fossil fuels are currently a major global concern. Fossil fuels are increasingly associated with the emissions of greenhouse gases, majorly CO_2, leading to climate change, emergence of drought, spread of diseases and variation in population sizes of both plant and animal species (Lashof and Ahuja, 1990). The depletion of the world's crude oil reserve, increasing crude oil prices, and issues related to conservation have brought about renewed interest in the use of bio-based materials. Fossil fuels such as petroleum, coal and natural gas, which have been used to meet the energy needs of man, are associated with negative environmental impacts such as global warming (Munack *et al*., 2001; Saravanan *et al.,* 2007). Supply of these non-renewable energy sources is threatening to run out in a foreseeable future (Sambo, 1981; Munack *et al.,* 2001). It has been widely reported that not less than ten major oil fields from the 20 largest world oil producers are already experiencing decline in oil reserves.

The contact pressures between devices in close proximity and moving relative to each other are usually sufficient to cause surface wearing, frictions and generation of excessive heat without protector (Hassan *et al*. 2006). These friction, wear and excessive heat have to be controlled by a process or technique called lubrication. Lubrication is the process or technique employed in reducing wear or tear of one or both surfaces in close proximity and moving relative to each other by interposing a substance called lubricant between the

surfaces to carry the load between the opposing surfaces (Hassan *et al*. 2006; Parsons, 2007).

Synthetic biolubricant based on renewable resources are important in developing environmentally acceptable lubricating oils. Currently, lubricant-based petroleum worldwide end up in the environment via total loss applications, spills, or major accidents. A fact remains that about 3million tonnes are lost in the European environment every year originating from loss of high-risk lubricants mostly based on mineral oil. Modern approaches have been adopted to solve the problems associated with application of vegetable oils in biolubricants, and some of them used for chemical modification and additive treatment (Erhan, 2005).

Emphasis on the development of renewable, biodegradable, and environmentally friendly industrial fluids, such as diesel, lubricants and other fuels has resulted in the widespread use of natural oils and fats for non-edible purposes. A lubricant is a substance (often a liquid) introduced between two moving surfaces to reduce the friction between them, improving efficiency and reducing wear. Biodegradable lubricants have been formulated from crude plant oil to chemically modified plant oil with properties better than mineral oil lubricants (Ghazi *et al.,* 2010). These ecological friendly lubricants are obtained from either edible or non-edible plant among which are castor, moringa, cotton and Jatropha curcas.

Many studies have confirmed that the monounsaturated fatty acids in plants oils, such as oleic and palmitic, are considered as the best candidates for lubricants and hydraulic oils (Rudnick, 2006). Any plant oils with a high concentration of saturated linear fatty acids are not desirable for lubricant production because they generally appear as solid form at room temperature. Oleic acid has been proved by many studies as the most ideal mono-saturated fatty acid for biolubricant application. Many studies have also confirmed that the plant oils extracted from the

crops with a high concentration of oleic acid, such as canola/rapeseed and castor seeds, are the most desirable plants oils for biolubricant production (Rudnick, *2006*).

Jatropha is a non-edible plant that was recently discovered to have great potential as feedstock for biodiesel and biolubricant (Banerji, 1985). The oil is considered non-edible oil due to the presence of toxic esters (Shah *et al.*, 2004). Thus, it provide an alternative of sufficient supplies of low cost feedstock for fuel oil and its derivatives with no competition with food uses (Ghazi *et al.*, 2010).Cottonseed oil like any other vegetable oil such as sunflower oil, palm oil could be used as an alternative to mineral lubricant but no record has been found on it lubricant properties to critically exploit it for this purpose. Castor is a nonedible plant that was recently discovered to have great potential as feedstock for biodiesel and also biolubricant (Banerji, 1985). Eckey (1954) reported that the moringa oil is unusually resistant to the development of rancidity and recommended it as suitable for effleurage and as a lubricant.

The present work sought into production of biolubricant from vegetable oils source (Jatropha, Moringa, Castor, and Cotton seed oil) with improved physico-chemical properties such as pour point, viscosity index, and temperature stability.

1.2 RESEARCH PROBLEM

Lubricants derived from petroleum base are widely used in almost all applications. However its non-biodegradable properties have made a serious problem in terms of environmental pollution. This aroused the need to develop lubricants from non-fossil sources. Low-temperature studies have shown that most vegetable oils undergo cloudiness, poor flow, and solidification at cold temperatures.

1.3 RESEARCH AIM

This research is aimed at the production of bio-lubricant from Jatropha, Moringa, Castor and Cotton seed oil using two stage transesterification reaction.

1.4 RESEARCH OBJECTIVES

The aim will be realized through the following objectives:

1. To produce the biolubricants.
2. To determine the physico-chemical properties of the synthesized biolubricant and compare with ISO VG requirement.
3. To study the fatty acid composition of the synthesized biolubricant produced and infrared spectrum of the trimethylolpropane (TMP) used for the polyol ester synthesis.
4. To investigate the effect of temperature on viscosity of the synthesized biolubricant blend with mineral base oil.

1.5 JUSTIFICATION

Lubricant with higher viscosity index tends to exhibit less viscosity change with temperature. Less emission due to higher boiling temperatures ranges of esters. Biodegradability and high cleanliness at the working place with higher wetting tendency of polar esters which lead to friction reduction.

1.6 **SCOPE OF THE RESEARCH**

The scope of this research work covered collection of materials, production of biolubricants, physic-chemical determination and chemical modification in order to enhance their suitability for ISO viscosity grades requirement by adopting the following;

i. Esterification reaction

ii. Methyl ester and polyol ester synthesis

iii. Characterization of the raw oils, synthesized biolubricant and trimethylolpropane (TMP) using:

   a. Qualitative measurement

   b. Fourier Transform Infrared Spectrum (FTIR)

   c. Gas Chromatography - Mass Spectrometry (GC-MS)

iv. Effect of temperature on viscosity

.

CHAPTER TWO

LITERATURE REVIEW

This chapter discus on lubricant and lubricating properties. It also talks about biolubricant synthesis methods and source of raw material sources. Some of the biolubricant properties are viscosity and viscosity index, pour and flash point, fatty acid compositions etc.

2.1 LUBRICANT

Lubricant is a substance introduced to reduce friction between moving surfaces. It may also have the function of transporting foreign particles. The property of reducing friction is known as lubricity (Jeffrey, 2007).

A good lubricant possesses the following characteristics:

1. High boiling point
2. Low freezing point
3. High viscosity index
4. Thermal stability
5. Corrosion prevention
6. High resistance to oxidation.

One of the single largest applications for lubricants, in the form of motor oil, is protecting the internal combustion engines in motor vehicles and powered equipment.

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 polyolefins, esters, silicones, fluorocarbons and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination, etc.

Lubricants such as 2-cycle oil 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 (Jeffrey, 2007).

2.1.1 Purpose

Lubricants perform the following key functions.

1. Keep moving parts apart
2. Reduce friction
3. Transfer heat
4. Carry away contaminants & debris
5. Protect against wear
6. Prevent corrosion

2.1.1.1 Keep moving parts apart

Lubricants are typically used to separate moving parts in a system. This has the benefit of reducing friction and surface fatigue, together with reduced heat generation, operating noise and vibrations. Lubricants achieve this by several ways. The most common is by forming a physical barrier i.e., a thin layer of lubricant separates the moving parts. This is analogous to hydro-planning, 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. 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 (Jeffrey, 2007).

2.1.1.2 Reduce friction

Typically the lubricant-to-surface friction is much less than surface-to-surface friction in a system without any lubrication. Thus use of a lubricant reduces the overall system friction. 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, e.g. protecting the valve train in a car engine at start up (Jeffrey, 2007).

2.1.1.3 Transfer heat

Liquid lubricants are much more effective on account of their high specific heat capacity. Typically the liquid lubricant is constantly circulated to and fro from the cooler part of the system, although lubricants may be used to warm as well as to cool when regulate temperature is required. This circulating flow also determines the amount of heat that would be carried away in any given unit of time. High flow systems can carried 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. Their disadvantage was the larger sumps and bigger cooling units needed. Another disadvantage 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. An automotive oil-cooled turbocharger is a typical example. Turbochargers get red hot during operation and the oil that is cooling them only survives as its residence time in the system is very short i.e. high flow rate. If the system shut down suddenly the oil in the turbo charger will immediately oxidizes and clog the oil ways with deposits. Over time these deposits can completely block the oil ways and reduced the cooling which result to failure of the turbo charger with seized bearings. Non-flowing lubricants such as greases and pastes are not effective

at heat transfer although they do contribute by reducing the generation of heat in the first place (Jeffrey, 2007).

2.1.1.4 Protect against wear

Lubricants prevent wear by keeping the moving parts apart. Lubricants may also contain anti-wear or extreme pressure additives to boost their performance against wear and fatigue.

2.1.1.5 Prevent corrosion

Good quality lubricants are typically formulated with additives that form chemical bonds with surfaces, or exclude moisture, to prevent corrosion and rust.

2.1.2 Types of Lubricant

Lubricants are generally composed of base oil plus a variety of additives to impart desirable characteristics. Although generally lubricants are based on one type of base oil, mixtures of the base oils also are used to meet performance requirements.

2.1.2.1 Base oil groups

Mineral oil term is used to encompass lubricating base oil derived from crude oil. The American Petroleum Institute (API) designates several types of lubricant base oil. Table 2.1 gives the classification of mineral base oil groups. Most of the commercial lubricants sold in the market are obtained from the blend of group I mineral base oil with additives using company formulations (Jeffrey, 2007).

Table 2.1: API Classification of lubricant base oils

Property	**Group I**	**Group II**	**Group III**
Saturates, %	65 – 85	93 - 99+	95 - 99+
Aromatics, %	15 – 35	1 - 5	1 - 7
Sulfur, ppm	300 - 3000	5 – 300	0 - 30
Viscosity index (VI)	95 - 105	123 - 150	120 - 135
Example	SN150,500 and BS150	SN60,100,600 and BS150	Polyalpha olefins

Source: Anonymous[(A)], 2013

However, the group I mineral base oil were characterized using American Standard Test Method as shown in Table 2.2. These properties are important during the lubricant blend formulation.

Table 2.2: Physico-chemical properties of SN150 and SN500

Property	**SN150**	**SN500**	**ASTM-D**
Kinematic vis. @ 100^0C, cSt	5.5	10.5	D-445
Kinematic vis. @ 40^0C, cSt	38	101	D-445
Viscosity index (VI)	100	95	D-2270
Flash point, ^{0}C	198	240	D-92
Pour point, ^{0}C	- 9	-6	D-97
Specific gravity @15^0C	0.872	0.880	D-4052
Sulfur content , wt%	0.2	0.4	D-2622
Color	0.5	1.5	D-1500
Total Base Number, mgKOH/g	<0.05	<0.05	D-664
Carbon residue, wt%	0.04	0.12	D-189

Source: Anonymous [(A)], 2013

2.2 PRINCIPLES OF LUBRICATION

2.2.1 Friction

Friction is a force that resists relative motion between two surfaces in contact. Depending on the application, 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. 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. Two general cases of friction occur which sliding and rolling friction (Anonymous [(A)], 2013).

2.2.1.2 Sliding friction

To visualize sliding friction, imagine a steel block lying on a steel table. Initially a force F (action) is applied horizontally in an attempt to move the block. If the applied force F is not high enough, the block will not move because the friction between the block and Table resists movement. 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 force of friction (Anonymous [(A)], 2013).

2.2.1.3 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 rolling motion, there must be a definite

but small amount of friction involved. Unlike the coefficient of sliding friction, the coefficient of rolling friction varies with conditions and has a dimension expressed in units of length.

A certain amount of slippage (which is the equivalent of sliding friction) occurs in rolling friction. If the friction of an un-housed rolling object is measured, slippage effects are minimal. However, in practical applications such as a housed ball or roller bearing, slippage occurs and contributes to rolling friction. Neglecting slippage, rolling friction is very small compared to sliding friction.

2.2.2 Wear

Wear is defined as the progressive damage resulting in material loss due to relative contact between adjacent working parts. 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. Friction and wear also generate heat, which represents wasted energy that is not recoverable. In other words, wear is also responsible for overall loss in system efficiency (Anonymous [(A)], 2013).

2.2.2.1 Types of Wear

Ordinarily, wear is thought of only in terms of abrasive wear occurring in connection with sliding motion and friction. However, wear also can result from adhesion, fatigue, or corrosion.

2.2.2.1Abrasive 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. Particles cut from the softer surface or dust and dirt introduced between wearing surfaces also contribute to abrasive wear.

2.2.2.2 Adhesive wear

Adhesive wear frequently occurs because of shearing at points of contact or asperities that undergo adhesion or cold welding, as previously described. Shearing occurs through the weakest section, which is not necessarily at the adhesion plane. In many cases, shearing occurs in the softer material, but such a comparison is based on shear tests of relatively large pure samples. The adhesion junctions, on the other hand, are very small spots of weakness or impurity that would be insignificant in a large specimen but in practice may be sufficient to permit shearing through the harder material. In some instances the wearing surfaces of materials with different hardness can contain traces of material from the other face. Theoretically, this type of wear does not remove material but merely transfers it between wearing surfaces. However, the transferred material is often loosely deposited and eventually flakes away in microscopic particles; these, in turn, cause wear.

2.2.2.3 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 a paper clip, back and forth until it breaks. Whenever a metal shape is deformed repeatedly, it eventually fails. 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. This repeated flexing eventually results in microscopic flakes being removed from the bearing. Fatigue wear also occurs during sliding motion. Gear teeth frequently fail due to pitting (Anonymous [(A)], 2013).

2.2.2.4 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); however, other chemicals may also contribute. Corrosion products, usually oxides, have shear strengths different from those of the wearing surface metals from which they were formed. The oxides tend to flake away, resulting in the pitting of wearing surfaces. Ball and roller bearings depend on extremely smooth surfaces to reduce frictional effects. Corrosive pitting is especially detrimental to these bearings (Anonymous [(A)], 2013).

2.3 PHYSICAL PROPERTIES

2.3.1 Viscosity

Viscosity is more 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. A high viscosity implies a high resistance to flow while a low viscosity indicates a low resistance to flow. Viscosity varies inversely with temperature (Anonymous [(A)], 2013).

Viscosity is also affected by pressure; higher pressure causes the viscosity to increase, and subsequently the Load-carrying Capacity of the oil also increases. 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. Two methods for measuring viscosity are commonly employed: Shear and Time (Anonymous [(A)], 2013).

2.3.1.1 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. 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. Kinematic viscosity is expressed in centistokes (cSt). Viscosity in centistokes is conventionally given at two standard temperatures: 40 °C and 100 °C (104 °F and 212°F) (Anonymous [(A)], 2013).

2.3.1.2 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 °C and 98 °C (100 °F and 210 °F). As previously noted, the units of viscosity can be expressed as centipoise (cP), centistokes (cSt), or Saybolt Universal Seconds (SUS), depending on the actual test method used to measure the viscosity (Anonymous [(A)], 2013).

2.3.2 Viscosity Index

The Viscosity Index, commonly designated VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. Viscosity index can be classified as follows (Anonymous [(A)], 2013):

1. Low VI - below 35
2. Medium VI - 35 to 80
3. High VI - 80 to 110
4. Very High VI - 110 to125

5. Super VI - 125 to 160
6. 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. Therefore, a fluid that has a high viscosity index can be expected to undergo very little change in viscosity with temperature extremes and is considered to have a stable viscosity. A fluid with a low viscosity index can be expected to undergo a significant change in viscosity as the temperature fluctuates. For a given temperature range, say -18 to 370 °C (0 - 100 °F), the viscosity of one oil may change considerably more than another.

Oil with a VI of 95 to 100 would change less than one with a 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 (Anonymous [(A)], 2013).

2.3.3 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 °C (20 °F) lower than the lowest anticipated ambient temperature.

2.3.4 Cloud Point

The Cloud Point is the temperature at which dissolved solids in the oil, such as paraffin wax, begin to form and separate from the 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 (Anonymous [(A)], 2013).

2.3.5 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°C (Asadauskas and Erhan, 1999). However, in a winter climate, most lubricants are required to be able to continue to function at a few degrees below zero (Ghazi *et al.,* 2010). Pour point is one of the most critical properties in determining the lubricants performance. This particular property is one of the main difficulties for the plant based oil used to produce the biolubricant.

The 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.

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. Manufacturers and Toll Blenders can also use the 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 than 38 °C (100 °F) will usually require special precautions for safe handling. The fire point for a lubricant is usually 8 to 10 percent above the flash point. 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 will ignite spontaneously without an external ignition source.

2.3.6 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. 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 (Anonymous [(A)], 2013).

2.3.7 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 100g sample. When unsaturated oil is heated, polymerization of the triglyceride occurs which leads to gum formation. Also, unsaturated compounds are susceptible to oxidation when exposed to air, thereby degrading the oil quality. Hence, the higher the iodine value, the greater the degree of unsaturation.

2.3.8 FTIR Spectrum

The intensity of an absorption bands 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 the charge difference between the two atoms. 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.

2.4 LUBRICANT QUALITY REQUIREMENTS

2.4.1 Oxidation Stability

Oxidation is one of the primary causes for decreasing the stability of hydraulic fluids. Once the reactions begin, a catalytic effect takes place. The chemical reactions 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 and valves (Jeffery, 2007).

2.4.2 Rust and Corrosion Prevention

Rust is a chemical reaction between water and ferrous metals. Corrosion is a chemical reaction between chemicals (usually acids) and metals. Water condensed from entrained air in hydraulic system causes rust if the metal surfaces are not properly protected. In some cases water reacts with chemicals in a hydraulic fluid to produce acids that cause corrosion. The acids attack and remove particles from metal surfaces allowing the affected surfaces to leak. To prevent rust, biohydraulic fluids use Bio Corrosion Inhibitors (BCI) those deposit a protective film on metal surfaces. The film is virtually impervious to water and completely prevents rust once the film is established throughout the hydraulic system (Jeffery, 2007).

2.4.3 Air Containment 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.

2.4.4 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. Bio Hydraulic Fluids made from stabilized high oleic base stocks permit water to separate or demulsify readily. However, some additives such as anti-rust treatments actually promote emulsion formation to prevent separated water from settling and breaking through the Anti-Rust Film (Jeffery, 2007).

2.4.5 Anti-Wear Properties

Conventional hydraulic fluids are satisfactory 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. These applications do not permit the formation of full fluid film lubrication to protect contacting surfaces - a condition known as boundary lubrication (Jeffery, 2007).

2.4.5.1 Pour Point Depressants (PPD)

An oil pour point is the temperature at which the oil ceases to flow under the influence of gravity. In cold weather, oil with a high Pour Point makes startup of machinery difficult or impossible. Pour point depressants reduce the size and cohesiveness of the crystal structures, resulting in reduced pour point and increased cold flow at reduced temperatures.

2.4.5.2 Viscosity Index Improvers (VII)

The Viscosity Index is an indicator of the change in viscosity as the temperature is changed. The higher the VI, the less the viscosity of an oil changes for a given temperature change. Viscosity Index Improvers are used to limit the rate of change of viscosity with temperature. These

improvers have little effect on oil viscosity at low temperatures. However, when heated, the improvers enable the oil viscosity to increase within the limited range permitted by the type and concentration of the additive. This quality is most apparent in the application of multi-grade motor oils (Jeffery, 2007).

2.5 SELECTION OF LUBRICANTS

Proper selection of a lubricant depends on understanding the lubricating regime (i.e., Film, Mixed, and Boundary), established conventions of classifications, and an ability to interpret and apply the producer's product data specifications to the equipment.

2.5.1 Lubricant Classification

Professional societies and organizations have established classifications for oil and grease. Figure 1 give the comparative viscosity classification base on the following organizations, such as Society of Automotive Engineers (SAE), American Petroleum Institute (API), American Gear Manufacturers Association (AGMA), International Standards Organization (ISO), and National Lubricating Grease Institute (NLGI).

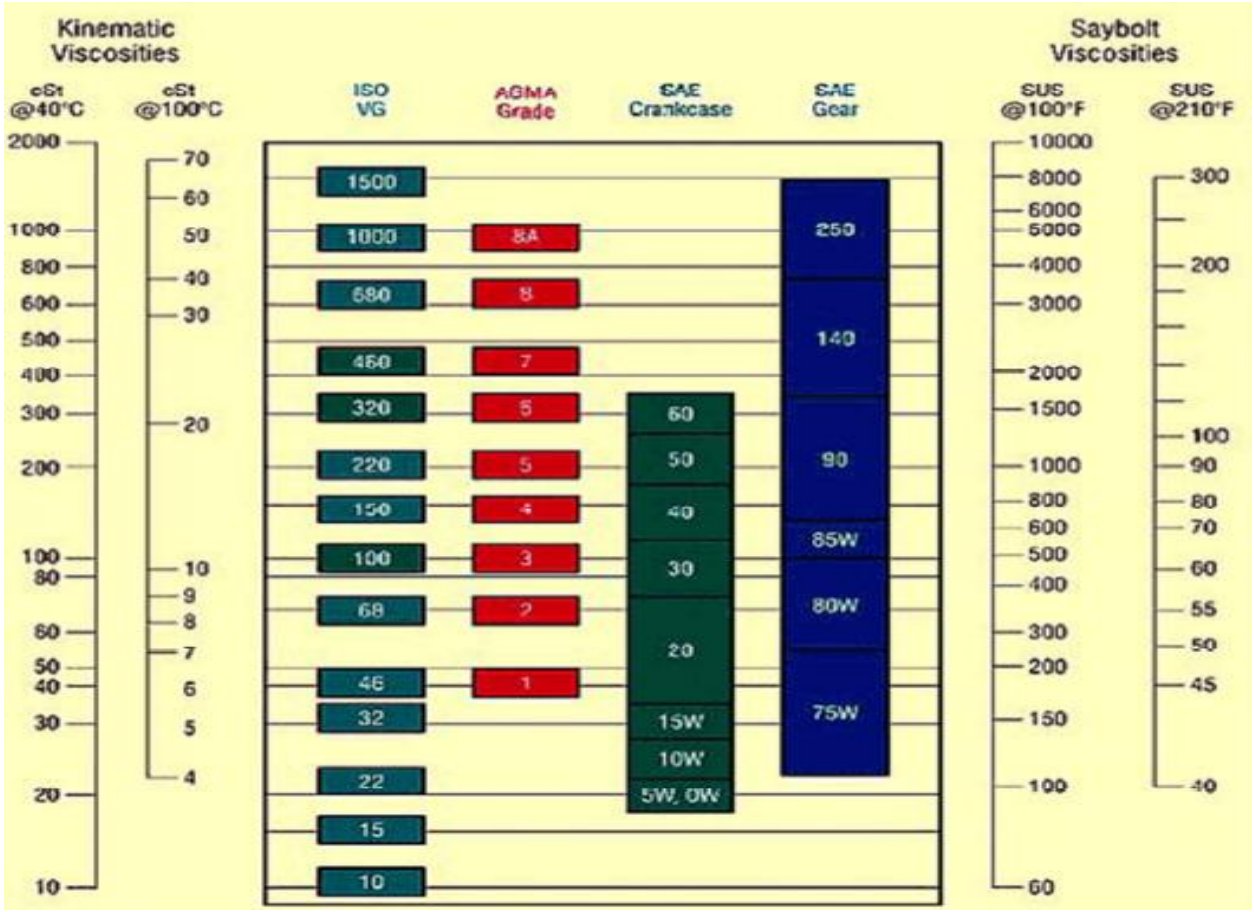


Figure 2.1: Comparative viscosity classification (Ashley, 2007)

2.6 BIOLUBRICANT

Bio-lubricants are primarily triglyceride esters derived from plants and animals. The plant derived materials are preferred. Bio-lubricants provide environmental and health benefits over petroleum-based products (Adam, 2009). Table 2.3 gives the ISO various viscosity grades requirement. The grades are majorly classified base on their viscosity index and pour point.

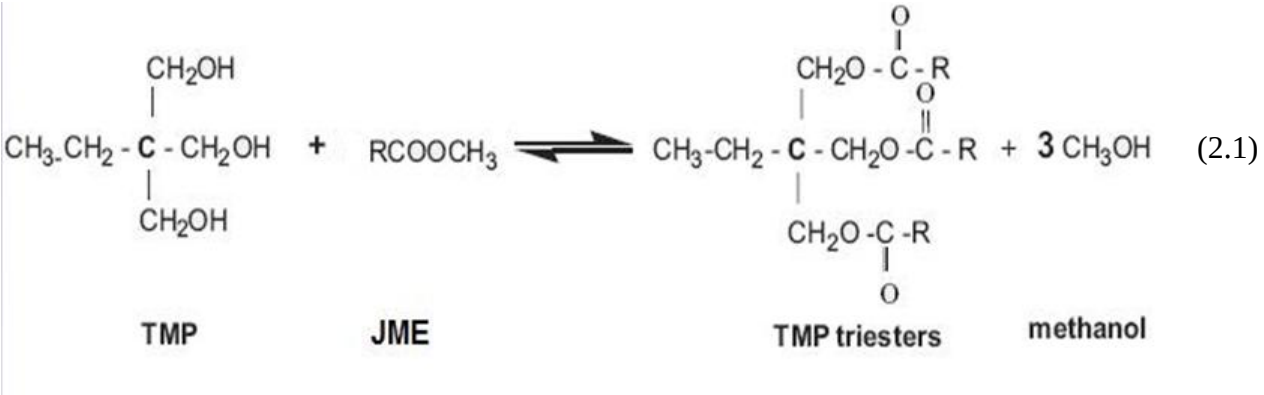
Table 2.3: ISO viscosity grades requirement

Fluid	ISO VG32[a]	ISO VG46[a]	ISO VG68[a]	ISO VG100[a]
Kinematic viscosity (cSt)				
40 °C	>28.8	>41.4	>61.4	>90.0
100 °C	>4.1	>4.1	>4.1	>4.1
Viscosity Index (VI)	>90	>90	>198	>216
Pour point (°C)	<–10	<–10	<–10	<–10

Source: [a]Rudnick, 2006

2.6.1 Biolubricant Synthesis Reaction

This involves the cleavage of alcohol group in polyol and replaced by fatty acids derived from methyl esters. The synthesized esters would have polyol backbone rather than the glycerol (triglycerides).Equation (1) describe the transesterification of jatropha methyl ester (JME) with common polyol trimethylolpropane (TMP) produced the TMP based ester which exhibits improved temperature properties. The optimum temperature was found to be at 150°C. The molar ratio of JME to TMP was optimized at 3.5:1 and the optimum catalyst loading was found to be 0.8% of the weight of the total reactants (Ghazi *et al.*, 2010).



(2.1)

2.6.2 Intermediate Reactions

Intermediates would likely be formed prior to the desired product, which is the Triester (TE). The intermediate reaction involves with the formation of Monoester (ME) and Diester (DE) (Ghazi *et al.,* 2010). Equation (2.2) to (2.4) gives the possible intermediate while Equation (2.5) represents the overall polyol ester synthesis (biolubricant synthesis).

$$JME + TMP \Leftrightarrow ME + M \quad (2.2)$$

$$JME + ME \Leftrightarrow DE + M \quad (2.3)$$

$$JME + DE \Leftrightarrow TE + M \quad (2.4)$$

Overall reaction:

$$3JME + TMP \Leftrightarrow TE + 3M \quad (2.5)$$

2.6.3 Vegetable Oils

2.6.3.1 Jatropha oil

Jatropha oil is non-edible oil that has a great potential feedstock for biodiesel and bio-lubricant production (Banerji, 1985). The oil is considered non-edible oil due to the presence of toxic esters (Shah *et al.,* 2004). The physico-chemical properties of jatropha oil were presented in Table 2.4 as reported by Shah *et al.,* (2004).

Table 2.4: Physico-chemical properties of jatropha curcas oil

Parameter	Value
Color	Golden-yellow
R	0
Y	5
Total lipid content (%)	59.32±0.09
Free fatty acid as oleic acid (%)	1.89±0.10
Acid value (mg KOH/g)	3.76±0.07
Iodine value (wijs)	104.90±0.25
Saponification value (mg/g)	203.36±0.36
Unsaponifiable matter (%)	1.76±0.03
Viscosity at room temperature (cp)	32

Source: Shah *et al., 2004*

2.6.3.2 Cotton seed oil

Cottonseed Oil is the refined fixed oil obtained from the seed of cultivated plants of various varieties of *Gossypiumhirsutum Linn*, or of other species of *Gossypium (FamMalvaceae).*The physico-chemical properties of cotton seed oil were presented in Table 2.5.

Table 2.5: Physico-chemical properties of cottonseed oil

Parameters	Values (%)
Free fatty acid	5.75mgKOH/g
Acid value	11.50mgKOH/g
Iodine value	94.7gI_2/100g
Saponification value	189mgKOH/g
Peroxide value	9.25mEq/kg
Refractive index	1.464
Specific gravity	0.92
Colour	Reddish brown colour
pH	4.82
Taste	Mild taste
Viscosity	74

Source: Jumat, 2010

2.6.3.3 Castor oil

Castor oil can be used in many industrial and nonindustrial applications such as: agriculture, plastics and rubber, food, cosmetics and perfumeries, paper and pharmaceutical, paints, inks and additives, textile chemicals, lubricants because of it high flash point castor oil is useful in the field where high temperature occurs. It also has high oxy-rich property it will be beneficial in the vehicle engine and gear box as a lubricant (Chinchkar, 2012). Table 2.6 present the commercial grade castor oil with high iodine content which indicate the level of unsaturation.

Table 2.6: Physico-chemical properties of commercial grade castor oil

Property	Value
Appearance	Pale dark yellow
Color	30 unit max
Iodine value	82 – 90
Saponification value	177 – 187
Hydroxyl value	160min
Acid value	2.0max
Specific gravity	0.954 – 0.967

Source: (Chinchkar, 2012)

2.6.3.4 Moringa oil

Moringa oleifera seeds contain about 35–40% oil. This oil is of excellent quality, similar to olive oil, and is slow to become rancid. It is used as a fuel for cooking purposes and burnt for light in developing countries. It is also used in perfumes, as a lubricant in watches and other fine machinery, and for making soap. Table 2.7 report some of the physico-chemical properties of raw moringa oil.

Table 2.7: Physico-chemical properties of moringa oil

determination	*M. oleifera*[a]	literature
iodine value (g of I/100 g of oil)	69.45 ± 1.20 (68.00–71.80)	66.83 (*30*)
refractive index (n_D 40 °C)	1.4608 ± 0.001 (1.459–1.4625)	1.4549 (*30*)
density (24 °C) (mg/mL)	0.9057 ± 0.001 (0.9036–0.9080)	0.8809 (*30*)
saponification value (mg of KOH/g of oil)	186.67 ± 2.01 (180.6–190.5)	178.11 (*30*)
unsaponifiable matter (%)	0.90 ± 0.09 (0.70–1.10)	present work
acidity (% as oleic acid)	0.40 ± 0.04 (0.27–0.48)	0.85 (*30*)
smoke point (°C)	200 ± 1.80 196–203	198 (*30*)
color (red units)	1.00 ± 0.04 (0.95–1.10)	0 (*30*)
color (yellow units)	29.00 ± 3.00 (20.00–35.30)	40 (*30*)

Source: Farooq and Bhanger, 2003.

2.8 RELATED WORKS

Belafi, *et al.*, (2004) on his work entitle "Manufacture of an environmental-safe biolubricant from fusel oil by enzymatic esterification in solvent-free system". He observed that the oleo-chemical ester produced doesn't have aquatic toxicity and also the determined tribologycal and physico-chemical properties of the lubricant proved biodegradability and an environmental friendliness although enzymatic esterification processes are quite complex and expensive.

Smith *et al.*, (2010) discus on some of the benefits of bio-based lubricants.After his findings he conclude that petroleum-based oils get lubricity from additives such as chlorine and sulfur. Bio-based products don't need these additives due to the much higher natural lubricity.

Francis, (2012) on his study on the extraction and characterization of soybean oil based bio-lubricant.His finding was the flash/fire point (310^0C/320^0C) of the crude soybean oil obtained is in line with those obtained from both light duty oil (SAE 30) and heavy duty oil (SAE 40) with flash/fire points of 243^0C/290^0C and 260^0C/ 300^0C, respectively.

Ghazi *et al.* (2012) study the kinetics of jatropha biolubricant from transesterification of jatropha curcas oil. He studied in details the effects of temperature on the synthesis at a range between 120 ^{0}C and 200 ^{0}C with pressure kept at 10 mbar. The conversion of JME to jatropha biolubricant was found to be the highest (47%) at 200 ^{0}C.

However, this research aims at exploring more on the synthesis of biolubricant using four different vegetable oils. Unlike previous research that used sodium hydroxide as catalyst in the methyl ester synthesis which resulted to high glycerol formation, the used of calcium oxide gives almost 100% vegetable oil to methyl ester conversion with no phase separation after the reaction. The pour point would also be improved by blending the synthesis biolubricant with mineral oil.

CHAPTER THREE

MATERIALS AND METHOD

Details of research procedures employed are discussed in this chapter. The materials and equipment used are first listed.

3.1 MATERIALS AND EQUIPMENT

Different types of material and equipment were used to carry out the experimental work of this research are listed as follows:

3.1.1 List of Materials

1. Anhydrous methanol (Haddiz Chemical Ltd, 85% w/v)

2. Sodium hydroxide (Haddiz Chemical Ltd, analytical grade)

3. Potassium hydroxide (Haddiz Chemical Ltd, analytical grade)

4. Sodium methoxide (Chemical Engineering Department, ABU Zaria, 30% w/w in methanol)

5. Tetraoxosulphate (IV) acid (Haddiz Chemical Ltd, 95% w/v)

6. Hydrochloric acid (Haddiz Chemical Ltd, 95% w/v)

7. Trimethylolpropane (TMP) (Hefei TNJ Chemical Industry Co.,Ltd China, 99.5% w/w)

8. Isopropyl alcohol (Haddiz Chemical Ltd, 95% w/v)

9. Phenolphthalein (Haddiz Chemical Ltd)

10. Calcium Oxide (NARICT Basawa Zaria, 99.5% w/w)

3.1.2 List of Apparatus

1. Beakers (50-500ml) (Chemical Engineering Department, ABU Zaria)

2. Burette (50ml) (Chemical Engineering Department, ABU Zaria)

3. Pipette (25ml) (Chemical Engineering Department, ABU Zaria)

4. Glass funnel (Chemical Engineering Department, ABU Zaria)

5. Thermometer (Chemical Engineering Department, ABU Zaria)

6. Retored stand (Chemical Engineering Department, ABU Zaria)

7. Measuring cylinder (50-250ml) (Chemical Engineering Department, ABU Zaria)

3.1.3 List of Equipment

1. FTIR Spectrophotometer (FTIR-8400S, Shimadzu, Japan)

2. GC-MS Analysis (GCMS-QP2010 plus, Shimadzu, Japan)

3. Pour Point Analyzer (SETA – LEC Cloud and Pour Point Refrigerator)

4. Multiflash Flash Point Tester (Model: 34000)

5. Brookfield® (Synchro-lectric Viscometer: RVT)

6. Weighing balance (OHAUS Adventurer Pro Model: AV264)

7. Oil bath (HAAKE FISON: DC3)

3.2 EXPERIMENTAL PROCEDURE

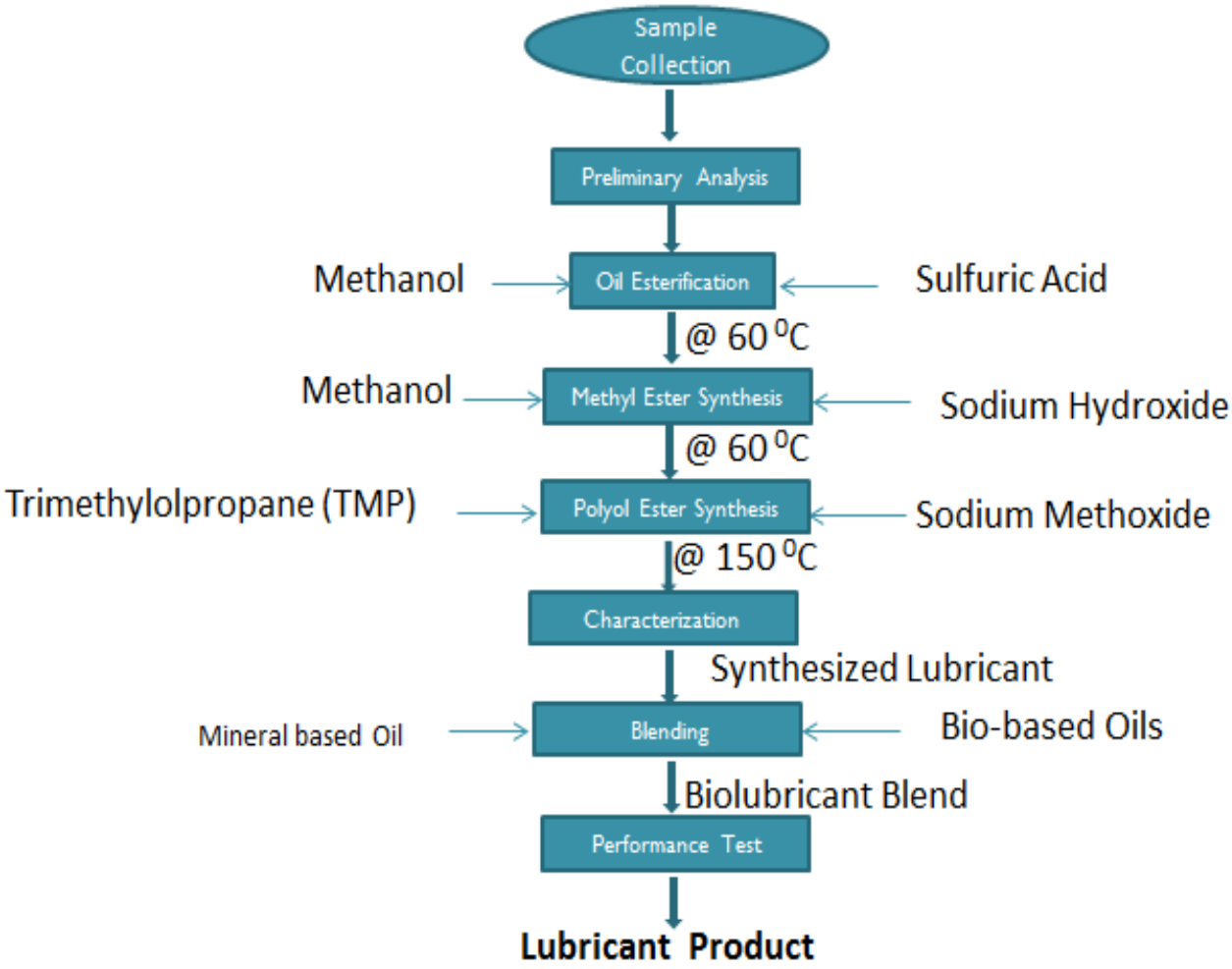


Figure 3.1: Research methodology

3.2.1 Raw Materials and Reagents Collection

Jatropha curcas and Castor seed were obtained from NARICT Basawa Zaria while Moringa and Cotton Seed Oils were procured from Zaria city market. The chemicals were sourced from the chemical engineering department and outlet retailers. These chemicals include anhydrous methanol, sodium hydroxide, potassium hydroxide, sodium methoxide (30% in methanol),

tetraoxosulphate (IV) acid, hydrochloric acid, Trimethylolpropane (TMP), isopropyl alcohol, phenolphthalein indicator.

3.2.2 Preliminary Analysis

The preliminary analysis gives the basis for the oil characterization to determine whether the oil could be used as lubricant base. The analysis was done for jatropha, castor, moringa, and cotton seed oil. This analysis includes; density, pour and flash point, viscosity index, saponification value, iodine value and free fatty acid reduction (esterification reaction).

3.2.3 Oil Esterification

This is informed by the need to reduce the free fatty acid (FFA) content of the oil as it may lead to high saponification. The high FFA content of the oil was reduced by the esterification of the oils with methanol using sulphuric acid as catalyst. 100g of the oil samples was weighed and transferred into a three necks round bottom flask. 20 % w/w methanol and 5% w/w sulphuric acid were also weighed and mixed in a conical flask. The methanol-acid mixture and the oil sample were placed in a water bath and heated to a temperature of 60 ^{0}C. Mechanical stirrer was inserted through one of the necks while the other two necks were stoppered by the stirrer rotating at 700 rpm. The temperature of the bath was maintained at 60 ^{0}C for homogeneity. At this moment, timing started. After 60 minutes, a picking pipette was used to withdraw the sample and was titrated against 0.1 N solution of KOH to determine the free fatty acid content of the oil. The titration was repeated for 60 min intervals up to the 240 min.

The free fatty acid value was calculated according to Equation 3.1:

$$\% \text{ Free Fatty Acid} = \frac{(\text{mL of titrant})(\text{N of titrant}) * 28.2}{(\text{sample wt.})} \times 100 \qquad (3.1)$$

3.2.4 Transesterification

Production (synthesis) of biolubricant involves a two stage transesterification; the first one is aimed at producing an intermediate product- methyl ester of the oils, while the second uses the methyl ester as reactant to produce the desired product- a polyol ester. The two processes proceed as follows:

3.2.4.1 Methyl ester synthesis

89.36 g (100 ml) of the oil was transesterified with methanol using potassium hydroxide as catalyst. The weight ratio of oil-to-methanol was 3:1; the amount of catalyst used was 0.5% w/w of the oil. The reaction was conducted at a temperature of 60 ^{0}C for two hours (2 hrs).

3.2.4.2 Polyol ester (Biolubricant) synthesis

This was achieved by transesterification of the methyl ester with timethylolpropane (TMP) in 50 ml batches using sodium methoxide (in 30% methanol) as catalyst. The weight ratio of vegetable oil methyl ester-to-trimethylolpropane was 3.5:1, the amount of catalyst used was 0.8% w/w of the total reactants and the reaction was conducted at a temperature of 150 ^{0}C for three hours (3 hours) (Ghazi and Resul, 2010). The reaction was carried out under vacuum condition to promote a forward reaction by ensuring the entire methanol produced was removed from the reaction mixture.

3.2.5 Blending

The blend was prepared by mixing 30% (135 ml) of the synthesized biolubricant with 70% mineral base oil (315 ml) to make up 450 ml of the blend for each of the four oil samples. The blend was prepared in order to determine if there will be a significant change in lubricating

properties. Phase separation was observed while blending the castor oil biolubricant with the mineral oil which was later settled and harmonized.

3.2.6 Characterization

The synthesized and blended biolubricant were characterized for physico-chemical properties, such as: density, pour and flash point, viscosity index, saponification value, iodine value and temperature viscosity test.

3.2.6.1 Density

An empty beaker was weighed and recorded. 50cm^3 of the oil sample was then poured into the beaker and weighed again. From the sample weight obtained, the density was determined by taking the ratio of the weight of the oil to the known volume (50cm^3) according to Equation 3.2

$$\text{Density} = \frac{\text{Sample Weight}}{\text{Sample Volume}}\ , g/cm^3 \qquad (3.2)$$

3.2.6.2 Pour point

The pour point is defined as the lowest temperature at which a liquid is still able to pour. This particular property is one of the main problems for the use of plant based oil as a lubricant. Normally, oil extracted from plants without any chemical modifications will show a poor pour point value of roughly just above 0◦C (Asadauskasand Erhan, 1999). However, in a winter climate, most lubricants are required to be able to continue to function at a few degrees below zero. This limitation would be overcome by applying chemical modifications as proposed in this work. The pour point was measured using ASTM D 97. The pour point was determined by placing a test jar filled with the processed oil in a cooling media (water bath) and was measured in 3^0C increments until the oil stops to pour.

3.2.6.3 Viscosity

The viscosity was measured at two different temperatures 40^{o}C and 100^{o}C respectively. At the start a proper viscometer spindle (3) was chosen. The sample was transferred to a beaker large enough to hold the viscometer spindle. The beaker was placed on a heating mantle which was set to a desired temperature, while the temperature of the sample was raised. The temperature of the sample was checked using a thermometer. When the desired temperature reached, the sample was then removed from the heat source and the viscosity was read. The spindle was attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the spindle counterclockwise. The knob was set to the minimum speed which includes the centipoise range on of the material that will be tested. The uppermost number on the knob indicates the revolutions per minute (rpm). The spindle was immersed into the sample up to the middle of the identification in the shaft. The viscometer was turned on and allowed to run until a constant reading (usually 5 to 10 revolutions) was attained. The viscosity of the sample was determined using Equation 3.3.The viscosity was reported to two decimal place accuracy for viscosities under 100 and to the nearest whole number for viscosities over 100.

$$\text{Viscosity} = \text{reading obtained} \times (\text{factor for the spindle/speed comb.}) \quad (3.3)$$

3.2.6.4 Viscosity index

The viscosity index is an empirical number; its value was determined using the value of viscosities obtained in section 3.2.6.3. The viscosities obtained were converted to kinematic viscosities by dividing with their densities from which the viscosity indexes were determined using ISO viscosity grade viscosity index calculator.

3.2.6.5 Saponification value

2g of the oil sample was weight and poured into a 250ml conical flask. 50cm^3 of 0.5 ethanolic KOH was added to the sample and the mixture was then heated to saponify the oil. The unreated KOH was then back-titrated with 0.5N HCl acid using 2-3 drops of phenolphthalein indicator. Saponification value is the measure of the molecular weight of the fatty acid. The values were calculated using Equation 3.4.

$$\text{Saponification value} = \frac{(\text{Sample titer value}) \times \text{Normality of HCl} \times 56.1}{weight\ of\ oil\ sample}\text{, mgKOH/g} \qquad (3.4)$$

3.2.6.6 Iodine value

The method employed was AOCS method. 1g of the sample was weighed and poured into a 250ml conical flask, 10cm^3 of CCl_4 was then added to dissolve the sample by swirling, 20cm^3 of wij's solution was added and stoppered immediately. The mixture was swirled and allowed to stand in the dark at ambient temperature for 30 minutes. 15cm^3 of 10% KI solution was then added with 100cm^3 of distilled water to rinse the flask and the solution was then titrated with a solution of sodium thiosulphate using starch indicator. A blank sample was prepared and back titrated accordingly. The iodine value was calculated using the formula

$$\text{Iodine value} = \frac{(\text{Sample Titer Value} - \text{Blank Titer Value}) \times \text{Normality} \times 12.69}{weight\ of\ oil\ sample} \qquad (3.5)$$

3.2.6.7 Flash point

The cup was filled at any convenient temperature (not more than 56^{0}C below the expected flash), so that the top of the meniscus is expected at the filling line. The light test flame would be on and adjusted to 3.2 - 4.8mm. The heat was applied initially to the sample to give a change in temperature of 14 – 17^{0}C per minute. When the sample was about 56^{0}C below the anticipated flash, the heat source was decreased to the rate of 5

– 6^{0}C per minute. Starting with at least 28^{0}C below the flash point, the test flame was also applied when the temperature reache each successive 2 ^{0}C mark. The test flame was passed across the center of the cup at right angles to the diameter and not more than 3mm above the upper edge of the cup in one direction. At the time of the next flame application, it was passed in opposite direction. The time taken to pass the test flame across the cup was about 1 sec. The flash point was recorded as the temperature at which an instantaneous flash occurs on application of the flame.

3.2.6.8 Temperature effect on viscosity

The viscosity of the synthesized lubricant and biolubricant blend sample were determined at temperatures of 30, 40, 50, 60, 70, 80, 90 and 100^{o}C. First, spindle 3 was selected; the sample is transferred to a 250ml beaker. The temperature of the oil sampled was raised to the desired value by heating on a heating mantle with constant stirring. The spindle was immersed into the sample up to the middle of the indentation in the shaft. They were attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the spindle anticlockwise. The spindle was immersed into the sample up to the middle of the indentation in the shaft. The viscometer was turned on and allowed to run until a constant reading was attained, this was taken as the viscosity of the sample. A plot of viscosity against temperature was done to study the effect of temperature on viscosity.

3.2.6.9 Gas Chromatography

Gas chromatography (GC) analyses involved the separation of the sample according to the molecular mass and thus, provided the necessary data of the sample composition. The column used in this GC was (GCMS-QP2010, Shimadzu) from NARICT, Zaria. The GC column used was calibrated by injecting methyl ester standards. Good separations were achieved by diluting

the sample in a small amount of ethyl acetate. The carrier gas used was hydrogen and its flowrate was regulated at 41.27 ml/min while the column flows at 1.82 ml/min. The oven temperature was set at 80°C before ramping up at 6°C/min until 340°C.

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents all the results generated from the investigations and discussion. These includes; free fatty acid contents, physico-chemical property determination for both raw, synthesized and blended lubricants, temperature effect on viscosity, FTIR spectrum and GC-MS analysis.

4.1 DETERMINATION OF FREE FATTY ACID

Table 4.1 shows the results of the free fatty acid (FFA) content for the oils before and after esterification. Detail evaluation of data is presented in Appendix A.

Table 4.1: FFA Content (wt.%) of the Vegetable Oils

Run	Time (min)	Jatropha , wt.%	Moringa,wt.%	Castor,wt.%	Cotton seed,wt. %
1	0	9.870	7.050	12.408	13.82
2	60	7.050	5.640	5.640	6.050
3	120	2.820	2.256	2.820	4.230
4	180	1.692	1.128	1.692	1.692
5	240	0.564	0.508	0.649	0.733

The free fatty acid (FFA) content of the crude vegetable oils prior to the production of the methyl ester was above 1% for all the four oils investigated. From Table 4.1 the FFA content of Jatropha, Moringa, Castor and Cotton seed oil were 9.87, 7.05, 12.408 and 13.820 wt.% respectively at zero minute. These values were reduced to 0.564, 0.508, 0.649 and 0.733 wt.% respectively after 240 minute of reaction. This is in-line with the specified ASTM standard limit (<1%) and also in consistent with work reported by Singh, (2011).

4.2 DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES

Table 4.2 shows the results of the pysico-chemical properties for both the crude vegetable oils and synthesized biolubricants. Detail evaluation of data is presented in Appendix A.

Table 4.2: Pyhsico-chemical properties of crude vegetable oils and synthesized bioluricants

	Jatropha		**Moringa**		**Castor**		**Cotton**	
Properties	Crude	Biolube	Crude	Biolube	Crude	Biolube	Crude	Biolube
Density, kg/m^3	920.4	917.8	907.8	896.3	900	826	926	917
Kinematic Viscosity @ 40 ^0C, cSt	66.74	64.7	64.7	56.27	36.9	35.13	62.37	54.94
Kinematic Viscosity @ 100 ^0C, cSt	14.28	14.26	14.26	11.24	12.32	11.2	12.93	11.06
Viscosity Index	220.7	216	224.7	197.75	96.42	88.32	213.12	198.57
Saponification Value, mgKOH/g	198.76	193.15	193.04	186.11	196.35	182.75	194.75	191.2
Iodine Value	29.06	17.49	24.30	18.56	19.10	10.21	27.41	11.78
Pour Point, ^0C	6.5	-8	6	-8	5	-4	4	-6

The Moringa, Jatropha, Castor and Cotton seed methyl esters were initially dried in an oven at slightly above 100°C overnight before the experimentation to reduce the moisture content. Since

Trimethlyolpropane (TMP) is hygroscopic or prone to absorb moisture, TMP was added to the reaction mixture very carefully (Yunus *et al.,* 2003).

The density of the lubricant was observed to decrease when compared with that of the crude oil sample. This may be attributed due to the series of modifications it undergoes through the esterification and transesterification processes.

The values in Table 4.2 are found comparable to previous studies by Ghaza *et al.,* (2010) and Bilal *et al.,* (2013) using the Jatropha oil.

The saponification value results for the crude vegetable oils were 198.76, 193.04, 196.3 and 194.75mg KOH/g oil for Jatropha, Moringa, Castor and Cotton seed oil respectively, which are comparable to the work of Mohammed-Dabo *et al.,* (2012) and Bilal *et al.,* (2013) with saponification values of 202.34 and 198.76 mgKOH/g respectively. These values are very much close to that of soybean oil and it is an indication that the oil will not be good for soap making (Abitogun *et al.,* 2009). However, there is little decrease in saponification value when oils were synthesized. This is due to esterification reaction for the FFA reduction.

The unsaturated glycerides of oil have the ability to absorb a definite amount of iodine (Morris and Jacobs, 1999). The determined iodine values were high, owing to the fact that the oil contain unsaturated hydrocarbon (Prevot, 1986).

The pour points of the synthesized biolubricants were significantly improved when compared to those of vegetable crude oils as shown in Table 4.2. This was due to the presence of polyol group present in the TMP during the polyol synthesis and the absence of beta-hydrogen in the final biolubricant produced. It is also comparable to the pour point value of 5 to -7 reported by Bilal *et al.,* (2013).

The produced biolubricant was subjected to performance requirement since more applications require specific lubricant properties. These properties include pour point, flash point, viscosity and viscosity index. Synthetic esters normally possess superior thermal stability and low-temperature properties compared to the original crude oil (Ghazi *et al.*, 2010). Table 4.3 gives the physico-chemical properties of synthesized biolubricant and its blends. The blend was formulated using 70% mineral base oil (SN500) and 30% synthesized bioluricant. Biolubricant tend to performed up to BL30 (30% biolubricant blended with 70% mineral base oil) as reported by Imran *et al*, (2013).

Table 4.3: Physico-chemical properties of synthesized biolubricant and its blends

	Jatropha		Moringa		Castor		Cotton seed	
Properties	BL30	Biolube	BL30	Biolube	BL30	Biolube	BL30	Biolube
Density, kg/m^3	885.3	917.8	893.3	896.3	918.1	826.0	891.0	917
Viscosity @40 ^{0}C, cSt	45.57	64.7	62.73	56.27	82.44	35.13	46.46	54.94
Viscosity @100 ^{0}C, cSt	7.6	14.26	9.27	11.24	12.86	11.2	7.14	11.06
Viscosity Index	134	216	127	197.75	157	88.32	113	198.57
Flash Point, ^{0}C	212	175	272	265	85	83	215	188
Pour Point, ^{0}C	-13	-8	-15	-8	-30	-4	-16	-6

BL30 = 30% Synthesize biolubricant + 70% Mineral oil

The pour points of the synthesized biolubricants were significantly improved when compared to those of vegetable crude oils. The same was observed when the synthesized lubricants were blended with 70% mineral based oil (SN500) due it high saturated property. This was shown in Table 4.2 and 4.3. This might be due to the effects of the unsaturated fatty acid chains and also due to the absence of beta-hydrogen when the methyl ester reacted with Trimethylolpropane (TMP).

There was significantly dropped in viscosity index after the blend due to the inherently lower viscosity index of mineral oils without chemical modification. The VI of the SN500 used was found to be 98 which was comparable with the work of Rudnick, (2006) VI 62. However, different trend was observed for the case of Castor oil blend. This was due to the phase separation observed during oil blending which was later harmonized. The flash points of the synthesized biolubricant blends were found to be relatively lower than that of the synthesized biolubricant. This is due the higher flash point value of mineral oil (280^0C) used.

Bioluricant are widely used in automotive gear and transmission applications (Lakes, 1991). Requirements for such applications were high viscosities and viscosity index and pour point. Biolubricant has some certain advantages owing to their polarity of esters molecule. The strong dipole moment caused them to be attracted to each other hence, lowering the volatility and the vapour pressure. It also attracts them to the oxide layer of a metal during lubricity, making them good lubricants. Furthermore, Viscosities Index (VI) of esters is superior to mineral oil and thus making it suitable for many applications (Ghazi *et al.,* 2009).

ISO Viscosity Grades (VG) 32 and 46 are two of the many grades requirements based on the viscosity range of the lubricants. They represents over 80% of all fluid consume (Lauer, 1995). It is shown that the synthesized Jatropha, Moringa, Castor and Cotton seed oil biolubricant blend fulfill the requirements of the ISO VG 32 and 46 since their viscosity index were within the range given in Table 4.4 and 4.5. The ISO VG 32 and 46 serves the requirement of light gear oil and also industrial gear oils use for low temperature applications (Ghazi *et al.,* 2009).

Table 4.4: Synthesized biolubricant properties and comparison with ISO VG32, 46, 68, 100 and literature standard

	ISO Viscosity Grade	**Biolubricants base oil**	**Rudnick (2006)**

Properties	32	46	68	100	Jatropha	Moringa	Castor	Cotton Seed	Mineral oil
Viscosity @40^{0}C, cSt	>28.80	>41.40	>61.40	>90	64.70	56.27	35.13	54.94	56.80
Viscosity @100^{0}C, cSt	>4.10	>4.10	>4.10	>4.10	14.28	11.24	11.20	11.06	27.80
Viscosity Index	> 90	> 90	>198	>216	216	197.75	88.32	198.57	62
Pour Point, ^{0}C	< -10	< -10	< -10	< -10	-8	-8	-4	-6	-4

Table 4.5: Synthesized biolubricant blend properties and comparison with ISO VG32, 46, 68, 100 and SN500 mineral oil

	ISO Viscosity Grade				**BL30**				**Mineral Oil**
Properties	32	46	68	100	Jatropha	Moringa	Castor	Cotton Seed	SN500
Viscosity @40 ^{0}C, cSt	>28.80	>41.40	>61.40	>90	45.57	62.73	82.44	46.46	95.76
Viscosity @100^{0}C, cSt	> 4.10	> 4.10	> 4.10	>4.10	7.6	9.27	12.86	7.14	10.86
Viscosity Index	> 90	> 90	> 198	>216	134	127	157	113	98
Pour Point, ^{0}C	< - 10	< - 10	< - 10	<-10	-13	-15	-30	-16	-31

4.3 EEFECT OF TEMPERATURE ON VISCOSITY

The noise level of an engine will rise as it experiences small decrease in viscosity when the working engine speed increase due to many factors. Temperature increases more in oil with a lower VI (Paul, 2006). Part of the noise produced is mainly caused by the engine oils with low viscosity of say 10 cSt at 100°C, while noise reduction can be achieved by oil with high viscosity of approximately 10,000 cSt at 0°C. Thus, the change of only 100°C in temperature can cause the noise generated by the impact of the piston to a thousand-fold change in viscosity (Zuidema,

1958).The effect of temperature on the viscosity of the lubricant as shown in Figure 4.1, indicates an inverse relationship.

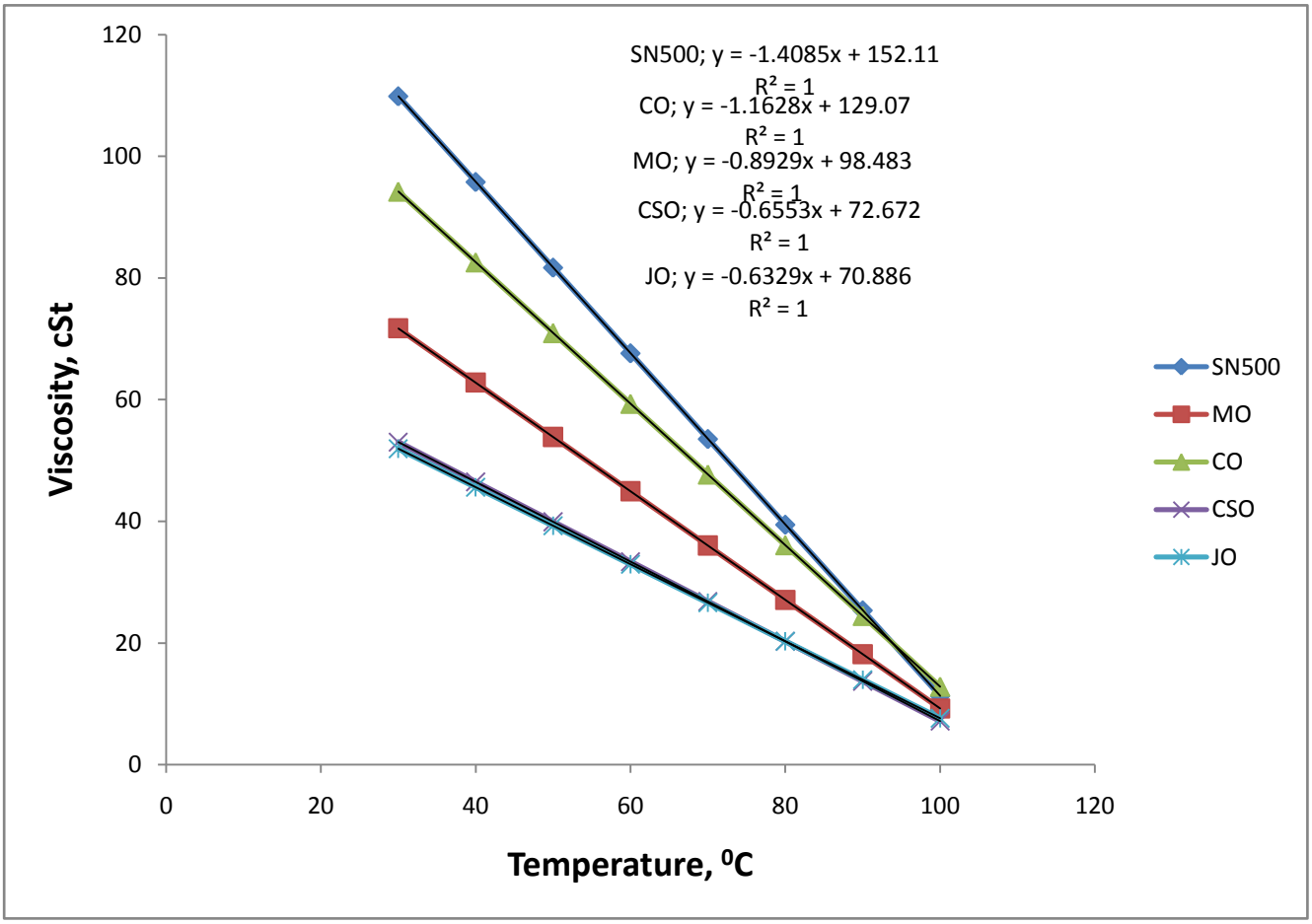


Figure 4.1: Effect of temperature change on viscosity for synthesized biolubricant blend base oil in comparison with mineral base oil

As the temperature increased from 30^0C to 100 the viscosity reduces by 37.97, 53.46, 69.58 and 39.32 cSt, which correspond to the slope of 0.633, 0.89, 1.16, 0.66 for Jatropha, Moringa, Castor and Cotton seed biolubricant respectively. Jatropha and Casotton seed biolubricant showed the least viscosity changes with temperature increase of 37.97 and 39.32cSt as shown in Figure 4.1. They have the least slope compared to Moringa, Castor and SN500. The least slope value was responsible for their less viscosity change with temperature. This is so because the temperatures increase weaken or breaks the cohesion force of attraction between the molecules of the lubricant

thereby reducing its viscosity (John, 2008). This little decrease in viscosity with increase in temperature can also be attributed to the relative high viscosity index of the lubricant. A high viscosity index means a low viscosity decrease with increase in the temperature. This variation also indicates the suitability of the use of the synthesized biolubricant as engine oil because of its high stability over such wide temperature range (John, 2008).

The Moringa, Castor biolubricant blend and mineral oil (SN500) has an advantage of high viscosity at low temperature but their resultant drop in viscosity is high due to change in temperature, this can cause engine noise while working.

4.4 FTIR ANALYSIS

Since the infrared radiation spectrum is a plot of transmittance against wave number, the bond vibration energies vary horizontally on the graph. In Figure 4.2, the peaks show that there is low transmittance, and hence large absorption. The horizontal axis represents wave number, and it increases as we move to the left. Areas that do not have peaks show that photons are not being absorbed at that frequency, indicating that the specific bond at that frequency does not exist in the molecule.

From Figure 4.2 the IR spectrum are broken into five zones. Zone 1 extends from about 3700 – 3200 cm^{-1} and is used to locate alcohol O-H, terminal alkyne C-H, and amine or amide N-H bonds. The alcohol peak is usually broad and wide and can be distinguished easily. The more concentrated the solution is with O-H molecules, the more likely it is to form hydrogen bonds.

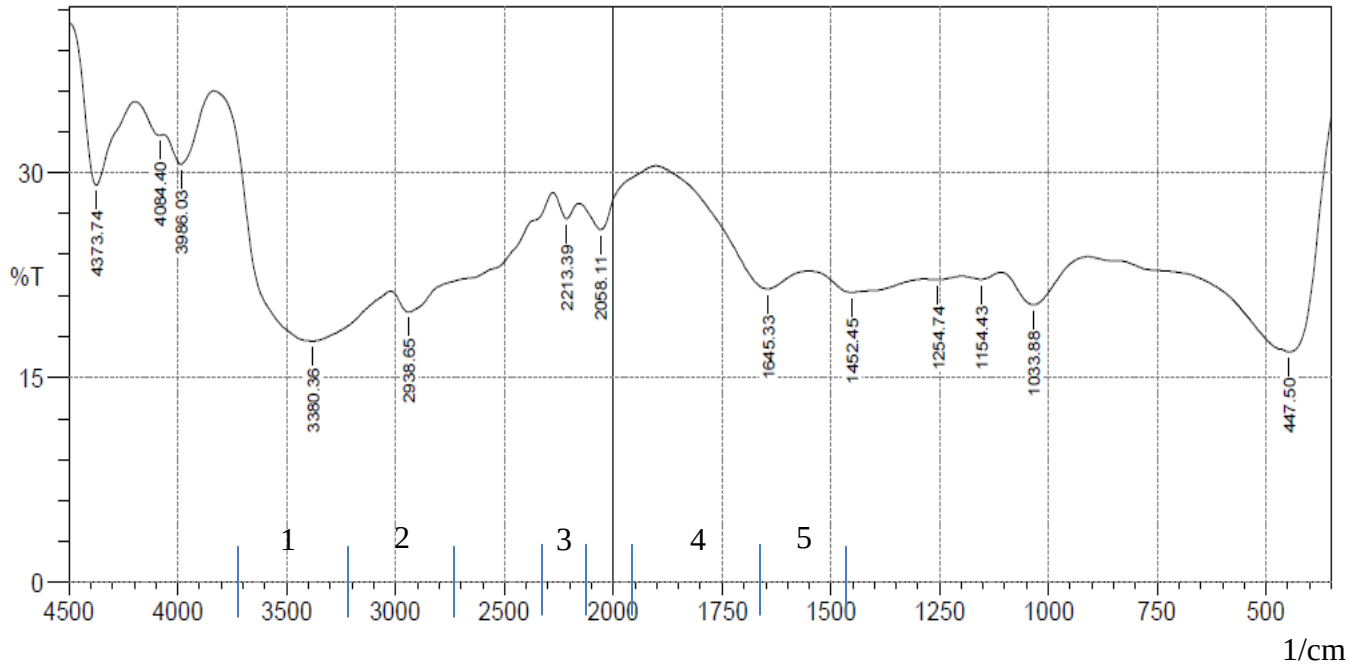


Figure 4.2: FTIR spectrum for Trimethylolpropane

Since it is easier to stretch hydrogen bonds (because the oxygen pulls away the electrons), less energy is required and the peaks appear broader. Alkyne C-H bonds have strong peaks around 3300 cm^{-1} mark. The peak band at 3380.36cm^{-1} mark in zone 1 appears to be O-H bonds of alcohol due to the broadness of the peak with percentage peak area of 24.38%. This was in conformity with trimethylolpropane with two functional groups (alkanes and alcohol functional groups).

In zone 2, absorption by alkane C-H bonds, aryl and vinyl C-H bonds, aldehyde C-H bonds, and carboxylic acid C-H bonds can be found. The sp^3 C-H bond peak can usually be found slightly to right of 3000cm^{-1} mark. The sp^2 C-H bonds can be distinguished because they are located slightly to the left of 3000cm^{-1} mark. Both of these C-H bonds have many peaks. Evidence of the presence of an aldehyde can be found around 2700cm^{-1} and 2900cm^{-1} mark. Lastly, the carboxylic acid O-H bond appears as a wide, broad peak in the spectrum. The peak band at 2938.65cm^{-1} mark in zone 2 appears to be C-H bonds of sp^3 (alkanes) since it was located to the

right of 3000cm^{-1} mark with percentage peak area of 21.47%. However, absence of peak band at 2700- 2900cm^{-1} mark and broadness peak in the zone proves the non-existence of sp^2 C-H and carboxylic acid O-H bands. This was in conformity with the presence of alkane group in trimethylolpropane.

Zone 3 reaches from 2300- 2100cm^{-1}. Here, we can find the absorptions of alkyne triple bonds and nitrile triple bonds. These peaks are variable in intensity. The peak band at 2213.33cm^{-1} mark in zone 3 appears to be C-H bonds of alkyne triple bond, although percentage peak area was very small (3.08%).

Zone 4 shows absorption peaks by carbonyl double bonds. These peaks are usually very strong and intense. They allow us to identify the existence of ester, aldehyde, ketone, carboxylic acids, or amide functional group. The last zone, zone 5 has absorption peaks caused by alkene double bonds and aromatic carbon-carbon bonds. Benzene has two peaks around 1600cm^{-1} and one around 1500cm^{-1} mark. It can be seen from Figure 4.2 that there is no existence of peak bands at zone 4 and zone 5. The only functional groups present are alkane and alcohols as can be seen from the compound Trimethylolpropane.

4.5 GCMS ANALYSIS

Jatropha and Castor oils were selected for GCMS analysis based on their high lubricant properties observed after synthesized biolubricant characterization. To identify the fatty acid composition of quantify oils of jatropha and castor the gas chromatography coupled with mass spectrometry (GC-MS) analysis was used.

Table 4.6 – 4.7 present the fatty acid composition of the raw castor and Jatropha oil. These results were extracted from the GC-MS result in appendix B.

Table 4.6: Fatty acid composition of crude castor oil

Fatty Acid	**Mol. Weight, g/mol.**	**Area (wt. %)**
Caproicacid	150	24.45
Ethylene oxide cyclic tetramer	176	6.26
Capricacid	220	2.82
Palmiticacid	256	13.39
Stearic acid	284	5.32
Ricinoleicacid	296	45.86
Linoleic acid	264	1.90
	Avg. =235 g/mol	Total =100%

The GC-MS result indicates that the oil contained more unsaturated fatty acid 47.76% (ricinoleic, and linoleic acid) than the saturated acids 45.98% (caproic, capric, palmitic and stearic acid). This account for the higher iodine value of the oil (27.49g of Iodine/100g) of sample, because the unsaturated glycerides have the ability to absorb a definite amount of iodine. The presence of high amount of unsaturates also further confirms why most vegetable oils do not congeal at room temperature making it good oil for biolubricant synthesis (Abitogun *et al.*, 2009).

Table 4.7: Fatty acid composition of crude jatropha oil

Fatty Acids	**Mol. Weight, g/mol.**	**Area (wt. %)**
Lauricacid	200	0.58
Palmiticacid	256	27.68
Stearic acid	284	10.60
Linoleic acid	298	42.56
Oleicacid	264	18.58
	Avg. =260 g/mol.	Total = 100 %

Table 4.7 indicates that the oil contained more unsaturated fatty acid 61.14wt.% (linoleic, and oleic acid) than the saturated acids 38.86wt.% (lauric, palmitic and stearic acid). This account for the higher iodine value of Jatropha oil 27.06g of Iodine/100g of sample, which was due to the

fact the unsaturated glycerides have the ability to absorb a definite amount of iodine. The presence of high amount of unsaturates also further confirms why most vegetable oils do not congeal at room temperature making it good oil for biolubricant synthesis (Abitogun*et al.*, 2009). The result is in comparable to those reported by Makkar*et al.*, (1997) and Mohammed-Dabo *et al.*, (2012), 74.37 and 25.62wt.%.

Table 4.8 and 4.9 presents the composition of the synthesized biolubricant produced from the castor and Jatropha curcas oil as extracted from the obtained various peaks of the GC-MS (Appendix B) used. The Table shows that the produced biolubricant consisted principally of the fatty acid methyl esters of palmitic, linoleic, ricinoleic, oleic and stearic acids, hence confirming a high quality product. Also from Table 4.8 - 4.9 ricinoleic and linoleic triesters have the highest percentage area of 36.42 and 33.01wt.% respectively which is comparable with the work of Mohammed-Dabo *et al.*, (2012), 44.95wt.%. It can equally be observed that traces of other methyl esters were also observed in the composition of the produced biolubricant. These traces could not affect the quality properties of the fuel as indicated in Table 4.3.

Table 4.8: Fatty acid composition of synthesized castor oil biolubricant

Fatty Acid	**Mol. Weight, g/mol.**	**Area (wt. %)**
Phenyl methane	92	26.40
Tridecanioc acid methyl ester	228	6.76
Palmiticacid	256	2.13
Palmitoleicacid	254	13.35
Linoleic acid	264	2.84
Ricinoleic acid methyl ester	296	36.42
Oleic acid	298	8.35
Sandaraco	332	3.75
Total	Avg. =252 g/mol.	Total =100%

Monoesters (ME) = 26.66%, Diesters (DE) = 30.16%, Triesters (TE) = 43.18%

Table 4.9: Fatty acid composition of synthesized jatropha oil biolubricant

Fatty Acid	Mol. Weight, g/mol.	Area (wt. %)
Ethylene Glycol Ether	239	0.45
4-methyl-3-heptanone	128	29.09
Palmitic acid	256	4.85
2,4-dipyridine	156	1.91
Linoleic acid methyl ester	296	33.01
Palmitic acid methyl ester	270	10.26
Eicosanoic methyl ester	326	0.57
2-decenoic acid methyl ester	184	0.32
Oleic acid	296	4.49
Stearic acid	298	2.61
Octadecanamine	297	5.65
Monoglyceride	330	1.82
13-docosenoic acid	338	2.35
Lauryl vinyl ether	212	2.58
	Avg. =259 g/mol.	Total = 100%

Monoesters (ME) = 11.95%, Diesters (DE) = 43.89%, Triesters (TE) = 44.16%

CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The following conclusions were drawn from the investigation carried out.

1. Jatropha and Cotton seed oil lubricant blend have the least change on viscosities when the temperature was increase from 30 to 100^0C.
2. The synthesized biolubricant of Jatropha, Moringa and Cotton seed have higher viscosity index compared to the mineral oil used.
3. The synthesized biolubricant blend conform with ISO viscosity grade 32 and 46 for gear oil and other low temperature application.
4. Increases in pour points were also observed when the synthesized biolubricant were blend with mineral oil (SN500).
5. Jatropha and Castor vegetable oils consist mainly of palmitic, linoleic, ricinoleic, oleic and stearic acids while their synthesized biolubricant produced consisted principally of ricinoleic and linoleic triesters with a percentage area of 36.42 and 33.01% respectively. The two oils were analyzed for GC-MS due to their high lubricant properties observed after characterization.

5.2 RECOMMENDATIONS

The following recommendations are suggested for further research:

1. Additives especially pour point depressants and viscosity improvers should be incorporated in the synthesized biolubricant blend in other to improve the low temperature properties and high temperature application.
2. Further research should be done by blending two or more vegetable oils together with mineral oil. This may enhance some of these lubricating properties.

5.3 CONTRIBUTION TO KNOWLEDGE

1. This research developed a novel method for the synthesis of biolubricant from vegetable oils that involved the use of heterogeneous catalyst (CaO) with about 95-100% conversion of raw oil to methyl esters compared to the previous works that uses homogeneous catalyst (NaOH) with about 45-60% conversions.
2. An improved pour point was observed when the synthesized biolubricant produced were blended with mineral oil (SN500).

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APPENDIX A

A1. Evaluation of Free Fatty Acid

$$\% \text{ Free Fatty Acid} = \frac{(\text{mL of titrant})(\text{N of titrant}) * 28.2}{(\text{sample wt.})} \times 100$$

	Castor oil	Cotton seed oil	Jatropha oil	Moringa oil
V_1,ml	4.4	4.9	3.5	2.5
V_2,ml	2	2.5	2.5	2
V_3,ml	1	1.5	1	0.8
V_4,ml	0.6	0.6	0.6	0.4
V_5,ml	0.23	0.26	0.2	0.18
Titra vol.				
FFA_1, %	12.408	13.818	9.87	7.05
FFA_2, %	5.64	7.05	7.05	5.64
FFA_3, %	2.82	4.23	2.82	2.256
FFA_4, %	1.692	1.692	1.692	1.128
FFA_5, %	0.6486	0.7332	0.564	0.5076

Where, V_i=mL of titrant, N of titrant = 0.1ml, sample weight = 1g

The Free Fatty Acid ($FFA_1 - FFA_2$) was determined by substituting the titrant volumes ($V_1 - V_5$) into the above equation

A2. Determination of Free Fatty Acid

$$\% \text{ Free Fatty Acid} = \frac{(\text{mL of titrant})(\text{N of titrant}) * 28.2}{(\text{sample wt.})} \times 100$$

$$\text{Density} = \frac{\text{SampleWeight } (W_2)}{\text{SampleVolume (V)}}$$

$$W_2 = W_1 - W_0$$

Where,

W_0 = weight of an empty beaker, g

W_1 = weight of beaker plus sample, g

W_2 = sample weight, g (1g)

V = sample volume, cm^3 (25ml)

Raw oil

Parameters	Jatropha oil	Moringa oil	Castor oil	Cotton seed oil
W_1	23.1	23.1	23.1	23.1
W_2	46.11	45.795	45.6	46.25
Density	0.9204	0.9078	0.9	0.926

Biolubricant oil

Parameters	Jatropha oil	Moringa oil	Castor oil	Cotton seed oil
W_1	23.1	23.1	23.1	23.1
W_2	46.045	45.5075	43.75	46.025
Density	0.9178	0.8963	0.826	0.917

Lubricant blend

Parameters	Jatropha oil	Moringa oil	Castor oil	Cotton seed oil
W_1	23.1	23.1	23.1	23.1
W_2	45.2325	45.4325	46.0525	45.375
Density	0.8853	0.8933	0.9181	0.891

The density was determined by substituting the sample weight (W_2) and sample volume (V) into the above equation

A3. Determination of Saponification Value

$$\text{Saponification value} = \frac{(\text{Sample titra value}) \times \text{Normality of HCl} \times 56.1\text{mg}}{weight\ of\ oil\ sample}$$

Where, B - S =Sample titra value, Normality of HCl = 0.5ml, sample weight = 2g

Raw oil				
Parameters	Jatropha oil	Moringa oil	Castor oil	Cotton seed oil
B,ml	48.1	48.1	48.1	48.1
S,ml	33.93	34.336	34.1	34.214
SV,mg/KOH	198.73425	193.0401	196.35	194.75115
Biolubricant oil				
B,ml	48.1	48.1	48.1	48.1
S,ml	34.328	34.83	35.07	34.467
SV,mg/KOH	193.1523	186.11175	182.74575	191.202825

The Saponification Value (SV) was determined by substituting the titrant volumes (B – S), acid normality and weight of oil into the above equation

A4. Determination of Iodine Value

$$\text{Iodine value (IV)} = \frac{(\text{Sample titral value}) \times \text{Normality} \times 12.69}{weight\ of\ oil\ sample}$$

Where, B - S =Sample titra value, Normality = 0.1ml, sample weight = 1g

Raw oil				
Parameter Value	Jatropha oil	Moringa oil	Castor oil	Cotton seed oil
B,ml	37.5	37.5	37.5	37.5
S,ml	14.6	18.35	22.45	15.9
IV	29.0601	24.30135	19.09845	27.4104
Biolubricant oil				
B,ml	37.5	37.5	37.5	37.5
S,ml	23.72	22.87	29.45	28.22
Iodine Value (IV)	17.48682	18.56547	10.21545	11.77632

The Iodine Value (IV) was determined by substituting the titrant volume (B – S), acid normality and weight of oil into the above equation.

APPENDIX B