OPTIMIZATION OF PROCESS VARIABLES IN BIOLUBRICANT PRODUCTION FROM PAWPAW SEED (*Carica papaya*) OIL USING RESPONSE SURFACE METHODOLOGY

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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 OF MASTER OF ENGINEERING IN THE DEPARTMENT OF CHEMICAL ENGINEERING

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ABSTRACT

Biolubricant was produced via double transesterification process of pawpaw seed oil with Ethylene Glycol (EG) as a polyol in the presence of potassium hydroxide catalyst. Pawpaw Methyl Ester (PME) was synthesized at the mole ratio of methanol-to-oil 6:1, the amount of catalyst used was 5% w/w of the oil and the reaction was conducted at a temperature of 60°C for two hours. Central composite design (CCD) in response surface methodology (RSM) was applied to this experimental layout and effects temperature, reaction time, and catalyst concentration on the synthesis of pawpaw seed oil biolubricant (PBL) were evaluated. The EG ester of pawpaw seed oil was characterized for its flash point, pour point, viscosity at 40 o C and at 100 0 C and viscosity index. Fourier Transform Infra-Red (FT-IR) and Gas Chromatography-Mass Spectrophotometer (GC-MS) analysis were carried out on the biodiesel and biolubricant to confirm the presence of ester group and the composition of the synthesized lubricant, the characterization showed favorable lubricating properties. The pawpaw seed oil methyl ester yielded 86.50 % based on the weight of the oil, while transesterification the in pawpaw seed methyl ester with EG yielded 97.00 % with desirability of 1.000 at optimum conditions of temperature at 130 ^{o}C, reaction time at 180 minutes, catalyst concentration of 0.5 % w/w KOH and a molar ratio of 3.5:1(pawpaw seed methyl to ethylene glycol) of the EG ester (Bio-lubricant). The validated bio-lubricant yield was 80.750 % obtained at a molar ratio of 3.5:1(pawpaw seed methyl to ethylene glycol), time of 128.102minutes and temperature of 97.616 ^{o}C. *The presence of ester group in the resulting biolubricant was confirmed by FT-IR analysis and the percentage of the composition of biolubricant determined by GC-MS analysis revealed a saturated fatty acid composition* is much higher than unsaturated fatty acid composition, this is promising as high saturation content in the biolubricant will leads to higher resistance towards thermal-oxidative treatment. The bio-lubricant produced is comparable to the standards commercial lubricants ISO VG- 32 and 46 for light and industrial gears applications.

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ABBREVIATIONS AND SYMBOLS

ASTM	American Society for Testing and Materials
ANOVA	Analysis of Variance
AEOE	Aqueous Enzymatic Oil Extraction
CMEs	calophyllum methyl ester
CCD	Central Composite Design
CCRD	Central Composite Rotatable Design
DF	Degree of Freedom
EG	Ethylene Glycol
FTIR	Fourier Transforms Infrared
GC–MS	Gas Chromatography Mass Spectroscopy
IEA	International Energy Agency
ISO	International Standard Organization
IV	Iodine Value
MUFAs	Monounsaturated fatty acids
NPG	Neopentylglycol
PSO	Pawpaw Seed Oil
PME	Pawpaw Methyl Ester
PPE	Pawpaw Poly Ester
PE	Pentaerythritol
%	Percentage

PV	Peroxide Value
PUFAs	Polyunsaturated fatty acids
PP	Pour Point
RSM	Response Surface Methodology
SV	Saponification Value
SAFA	Saturated Fatty Acid
TAGs	Triacylglycerols
TMP	Trimethylolpropane
VI	Viscosity Index
VIF	Variance Inflation Factor

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

The increasing global population together with industrialization and modernization has led to an increase in energy consumption. Many types of renewable energy sources, such as hydropower, geothermal, wind, solar, or biomass energy, have been proposed as potential energy sources. Biomass is renewable organic material that comes from plant and animals, this can be burned directly for heat or converted to renewable liquid and gaseous fuel through various processes. (Juan *et al.,* 2020). However, there has been growing interest in the use of vegetable oils as lubricants and hydraulic fluids due to reduction in the world's crude oil reserve together with the consumption rate, increase in petroleum prices and scarcities, issues related to management, harmfulness and environmental issues arising from conventional petroleum-based fluids have brought about renewed attention in the use of bio-based resources. Emphasis on the development of renewable, biodegradable, and environmentally friendly industrial fluids, such as diesel, lubricants and other fuels have raised the need to search for alternative renewable fuels (Bilal *et al.,* 2013 and Louis and Toyib, 2017). Nevertheless, the need for an alternative to fossil fuels has stimulated extensive research in recent years. Fossil fuels are nonrenewable sources of energy which generate pollutants and are associated to global warming, climate change. Besides, high emissions of CO_2, NOx, SO_2, particulate matter, poly aromatic hydrocarbons and hydro-carbons are generated when using fossil fuel and producing environmental problems. These facts have resulted in the search for environmentally friendly and renewable energy sources, such as biofuels.

Biodiesel has been recognized as one of the remarkable options for complementing conventional fuels. However, it's produced from renewable biological sources such as vegetable oils and fats and have been studied widely. Its advantages over petroleum-based diesel cannot be overemphasized: it is relatively safe, renewable, non-toxic, and biodegradable; it contains no sulphur; and it is a better lubricant. In addition, its use to stimulates numerous societal benefits: rural revitalization, creation of jobs, and reduced global warming (Aransiola *et al*., 2012 and Kamini and Milap 2017). Moreover, the feedstock alone represents about 75% of the overall biodiesel production cost. Therefore, minimizing the cost of biodiesel production has been the main agenda for biodiesel producers in order to be competitive with petroleum-derived diesel, it is crucial to employ inexpensive feedstock to replace expensive refined oils (Yadessa and Jorge, 2017). In spite of these benefits, bio-based lubricants are still not broadly utilized due to some key disputes and complexities concerning their production and performance. Besides feedstock dependability, reliability, and industry recognition, bio-based lubricant also has two important negative physical properties: low thermal oxidative stability and low-temperature performance. This is due to the presence of a double bond and β-hydrogen in the triacylglycerol ester responsible for this drawback. However, by using suitable chemical modification techniques including transesterification, selective hydrogenation, and epoxidation process, these two properties can be enhanced to make bio-based lubricants viable alternatives to mineral-based lubricants for diverse applications (Mohammed *et al.,* 2018).

Pawpaw (*Carica papaya* L.), belonging to the family Caricaceae, exists in almost all tropical and subtropical regions of the world, it is an invaluable plant that is prevalent throughout tropical Africa and Nigeria is the third largest producer

globally (Oseni *et al.,* 2016). Being a tree-like herbaceous plant, papaya bears fruits throughout the year. Different forms, sizes, colour of the flesh of papaya are existed depending on the variety. The flesh of the papaya fruit may vary from yellow to orange or reddish. Each fruit have a large number of seeds which are usually attached in rows to the interior part of the fruit (Noorzianna *et al*., 2014).

The pawpaw seed is presently a waste product as it is often discarded after eaten the papaya fruits owing to its very inadequate uses at the moment. There are rare information's on this quite underutilized seed despite its importance (Kamini and Milap, 2017). Besides, (Makanjuola and Makanjuola, 2018), reported that by-products of papaya, that is, seeds and skin which are often disposed, producing environmental and ecological problems related to creation of insects, rodents as well as economic problem, it contained essential nutrients that are valuable to human and animals for life sustenance. There has been a considerable interest with regard to the oil potential of papaya seeds, Vegetable oil or the fatty acids which are used in producing bio-lubricant are also cheaper than petroleum-based lubricant. Besides, bio-lubricant have a better emollient property than petroleum-based lubricant, it also has a higher viscosity index and flash point. A high viscosity index is necessary to make sure the lubricant maintains its thickness even at high temperatures.

1.1.1 Response surface methodology (RSM)

Response surface methodology (RSM) is a flexible mathematical procedure developed in optimization, modeling, and experimental design. It is an experimental modeling method that relates one or more responses to independent parameters and gives statistical indicators on individual model terms and interactions. It has been applied to the modeling of transesterification processes.

The fundamental methods for quantitative variables which involves fitting first-order (linear) or second-order (quadratic) functions of the predictors to one or more response variables and, then, examining the characteristics of the fitted surface to decide what action is appropriate (Mohammed *et al.,* 2018).

1.1 Aim and Objectives

The aim of this study is to optimized biolubricant produced from pawpaw seed oil using ethylene glycol as Polyol. This will be achieved through the realisation of the following objectives:

i. Extraction and characterization of physiochemical properties of oil from pawpaw seed

ii. Production of biodiesel and biolubricant and to study the effect of process variables (catalyst concentration, reaction temperature and reaction time) on bio-lubricant via RSM

iii Characterization biodiesel and biolubricant produced to determine desirable properties

iv Characterization of the oil, biodiesel and biolubricant produced using GC-MS and FTIR

1.2 Problem Statement

The expected depletion of fossil fuels and environmental problems associated with burning them have encouraged many researchers to investigate the possibility of using alternative fuels, the long-term energy security needed lead to the exploration for alternative of bio-based oil and those properties comparable to petroleum-based oil. The high dependence of the industrial and automobile sectors on mineral based lubricants whose feedstock are not only

toxic but subject to depletion in a human time scale has stimulate the need to search for sustainable alternatives in order to facilitate economic development and a sustainable green environment (Musa *et al*, 2016).

1.3 Justification

Production of bio-lubricant has a greater capacity to reduce environmental challenges associated with petroleum-based lubricant, biolubricant production provide more employment in the agricultural sector through cultivation of pawpaw plant and will reduce the over dependence on petroleum-based lubricant. The manufacture of bio-lubricant from papaya seed oil is geared towards the realization of the objectives of the International Energy Agency (IEA) whose long-term goal indicates that the world will need 50 % more energy in 2030.

1.4 Scope and Limitation

The scope of the study is restricted to optimization and modelling of bio-lubricant from papaya seed oil using RSM

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Pawpaw *(Carica papaya L.)* Plant

Papaya *(Carica papaya L.)* is native of tropical America but has now spread all over the tropical world. The fruit is usually cylindrical, large (weighing 0.5-2.0 kg), and fleshy. The flesh is yellow-orange, soft, and juicy. The central cavity contains large quantities of seeds that comprise about 15% of the wet weight of the fruit. The total global production of papaya is about 10.0 million metric tons, and India and Brazil are the major producers with annual production of 3.6 and 1.9 million metric tons, respectively. Papaya is grown mostly for fresh consumption and papain production; however, it can be processed into jelly, jam, candy, and pickles, and its seeds are usually discarded (Kamini and Milap, 2017). Nevertheless, few studies have been conducted on the composition of papaya seeds oil, determined the fatty acid composition and bioactive compounds of the oil extracted from seeds, papaya oil had an interesting composition (72% of monounsaturated fatty acids with 71% of oleic acid) representing a very promising new source of a special plant oil for different applications.

The global tendency with regard to the use of solid wastes and agro-industrial by products, oil extraction may add economic value to a large quantity of seeds that are generally discarded. The extraction and use of vegetable oils has for centuries played an important role in the production of a large number of industrial products and food items (Cassia *et al*., 2010). The papaya seeds contain 30% – 34% oil with nutritional and functional properties similar to that of olive oil and can be utilised as the feedstock for biodiesel synthesis (Muhammad *et al*., 2019a). However,

Soxhlet extraction of papaya seed oil using *n*-hexane to achieved yield of 34.3% was reported by Wong and Othman (2015)

2.2 Vegetable Oil

Vegetable oils are perceived to be alternatives to mineral oils for lubricant, base oils due to definite inherent technical properties and their ability to be biodegradable. Chemically, vegetable oils are esters of glycerine and long-chain fatty acids (triglycerides) which have molecular structure with three long chain fatty acids attached to the hydroxyl groups through ester linkages (Timothy *et al*., 2019). The characteristics of vegetable oils (and their derivatives, such as fatty acid methyl esters), such as viscosity or oxidative stability, depend on the percentages of these components. However, Oleic acid, with one unsaturation in its molecular structure, promotes high oxidative stabilities, whereas ricinoleic acid increases viscosity due to the hydroxyl group in its structure. As a result, many properties of these fatty acids depend on the stereochemistry of the molecular chains, the length and degree of branch or unsaturation (José *et al*., 2020). Besides, the utilization of oil in various applications is largely determined by the yield, composition, physical and chemical properties of the oil (Aladekoyi *et al*., 2016). However, different physical and chemical parameters of vegetable oil were used to monitor the compositional quality of oils. These physicochemical parameters include iodine value, saponification value, viscosity, density and peroxide value. Several researchers studied the impact of temperature on the stability, viscosity, peroxide value, and iodine value to assess the quality and functionality of the oil (Aladekoyi *et al*., 2016 and Erum *et al*., 2014). Chemically, vegetable oils are esters of glycerine and long-chain fatty acids (triglycerides) as shown in figure 2.1, which have molecular structure with three long chain fatty acids attached to the hydroxyl

groups via ester linkages (Timothy *et al*., 2019). The vegetable oils also have poor thermal stability, this is due to the β- hydrogen of hydroxyl group that presence on the glycerol, the backbone in triacylglycerol. This can also be overcome by substituting the glycerol with polyols that does not contain β-hydrogen atoms (Vanitah *et al*., 2015).

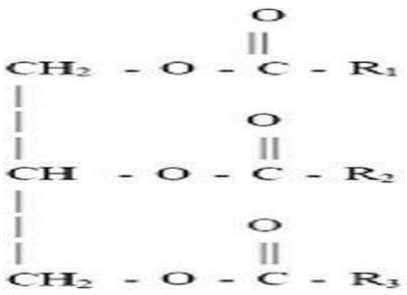

Figure 2.1: Chemical structure of triglyceride of a typical vegetable oil (Timothy *etal*.,2019).

Chemically, vegetable oils are totally different from mineral oils. They are blends of triacylglycerols (TAGs), whose properties depend on the fatty acid they have esterified to their glycerol backbone shown in Table 2.1. The TAGs that are found in oil seeds usually display the saturated fatty acids, in the sn-1,3 positions, whereas the sn-2 position of glycerol is esterified to an unsaturated or polyunsaturatedacylmoiety.This is caused by the specificity of the different enzyme s participating in their bio-synthesis mainly in palm oil and lauric fats (coconut and palm kernel fats).

Table 2.1: Fatty Acids Found in Standard Vegetable Oils

Fatty acid type	Fatty Acid	Common Name	Formula	Melting Point (°C)	Viscosity 80ºC (cST)
Saturated	Dodecanoic	Lauric	$C_{12}H_{24}O_2$	44.8	4.12
	Tetradecanoic	Myristic	$C_{14}H_4O_2$	54.4	5.49
	Hexadecanoic	Palmitic	$C_{16}H_{32}O_2$	62.9	7.41
	Octadecanoic	Stearic	$C_{18}H_{36}O_2$	70.1	8.67
	Eicosanoic	Arachidic	$C_{20}H_{40}O_2$	76.1	
	Docosanoic	Behenic	$C_{22}H_{44}O_2$	80.0	
Monounsaturated	Hexadecenoic	Palmitoleic	$C_{16}H_{30}O_2$	0.5	
	Octadecenoic	Oleic	$C_{18}H_{34}O_2$	16.2	6.55
Polyunsaturated	octadecadienoic	Linoleic	$C_{18}H_{32}O_2$	–5.0	
	Octadecatrienoic	Linolenic	$C_{18}H_{30}O_2$	–11.0	

(Rafael *et al*., 2011).

2.3 Oil Extraction System

Oil extraction is the first stage in bio-fuel production. There are three main methods that have been identified for oil extraction: mechanical extraction, enzymatic extraction and chemical or solvent extraction (Yadessa and Jorge, 2017). However, oil extraction from the original sources such as seeds, fruits, and other oil-bearing materials. A simple mechanical press can be used for extracting the oil without further processing. This process is also known as cold pressing. Not all seeds are suitable for extraction using mechanical press; some of them involve a complex process such as a combination of pressing, cooking and solvent extraction. However, solvent extraction is the process in which the oil is removed from a solid by means of a liquid solvent, the chemical extraction using *n*-hexane method

results in the highest oil yield, relatively simple and quick and solvent can be recovered and reused, reducing cost significantly which makes it the most commonly used method (Muhammed *et al*., 2019a and Yadessa and Jorge, 2017).

2.3.1 Mechanical extraction

Mechanical extraction method is often used to extract vegetable oil from oil seeds having oil content higher than 20%, this method has the advantage of low operation cost. It has a relatively low yield compared to solvent extraction and it is therefore comparatively inefficient and often with a large portion of oil left in the cake or meal after extraction, in addition, it is time consuming and labour intensive (Yusuf, 2018). The oil extracted by mechanical presses needs further treatment of filtration and degumming in order to produce a purer raw oil and another problem associated with conventional mechanical presses is that the design of mechanical extractor is suited for some seeds, and therefore, the oil yield is affected if that mechanical extractor is used for other seeds (Yadessa and Jorge, 2017).

2.3.2 Enzymatic oil extraction

Aqueous enzymatic oil extraction (AEOE) method is a promising technique for extraction of oil from plant materials. In this method, enzymes are used to extract oil from crushed seeds, aqueous enzymatic oil extraction can also be used in combination with other methods of oil extraction. However, a combination of ultra-sonication and aqueous enzymatic oil extraction (using an alkaline protease at pH = 9.0) method to extract oil from J. curcas seeds and obtained 74% of the seed oil which is very large compared to the 17–20% oil extracted by aqueous oil extraction alone. The main advantages of using enzymatic oil extraction are that it is environmental-friendly and does not produce volatile organic compounds, but the long process time is the main disadvantage associated with this technique (Yadessa and Jorge, 2017).

2.3.3 Chemical extraction

Removing one constituent from a solid by means of a liquid solvent is known as chemical extraction. It is also known as solvent extraction process. The rate of extraction of oil depends on the type of liquid chosen, particle sizes, temperature and agitation of the solvent. The most common solvent used in the chemical extraction process is hexane due to its low cost and low toxicity. Most researchers have found the chemical extraction process as convenient to extract oil from both papaya seed and stone fruit seed (Muhammed *et al*., 2019a). Bilal *et al*., (2013) Studied the extraction of oil from Jatropha curcas seed using hexane as a solvent in a 5-liter, three neck flasks. The volume of hexane needed was determined by the ratio of 6:1 and a reflux condenser were fitted and the mixture was heated at 60°C and stirred for about 8 h. The resulting oil and solvent mixture were filtered to remove the suspended solids. Then, the mixture was placed in a rotary evaporator to evaporate the solvent and thus, Jatropha oil was obtained.

Conversely, plant seeds were detached manually from papaya and rambutan fruit, the seeds were dried in an oven at 60 ºC for 24 hours. The dried seeds were pulverized into small particles and the oil were extracted using *n*-hexane for 8 hours in a Soxhlet apparatus. The extracted oil was then undergone evaporation using a rotary evaporator to remove the remaining solvent (Wong and Othman, 2015). Oil was extracted from the dried seeds (with residual moisture of around 7%) and the extraction was achieved in a Soxhlet apparatus with n-hexane organic solvent at a temperature of 68 °C for a period of 6 hours. The solvent was recovered at 45 °C in a rotary vacuum evaporator, and the oil was dried in a water bath at 90 ºC for one hour (Maria and Damião, 2016). Soxhlet extraction, which is traditionally considered as the extraction method resulting with the maximum

yield, was carried out in a classic Soxhlet extractor in the presence of ethanol, diethyl ether, petroleum ether, hexane or acetone as a solvent. 10 g of safflower seed mixed with 200 cm^3 solvents was processed until the oil in ground seeds were all played out. After the operation completed, the solvent was removed until the oil came to the constant weighing (Takadas and Doker, 2017).

Biofuels are alcohols, esters and other organic compounds manufactured from biomass such as herbaceous and woody plants, residues from agriculture and forestry, and some agro-industrial waste such as waste from the food industry. The term biomass refers to any substance which can be obtained by photosynthesis. Most plants utilize solar energy to create sugars, starting from simple substances such as water and carbon dioxide. This energy is stored in molecules of glucose, starch, oil. Biofuels could include ethanol, biodiesel, and bioethanol among others. Most developed and used are bioethanol and biodiesel

2.4 Historical Development of Biodiesel

The idea of using vegetable oils as fuel for internal combustion engines is from 1895, when Rudolf Diesel developed his engine. In presenting the diesel engine at the World Exhibition in Paris in 1900, Mr. Diesel used peanut oil as fuel. The high viscosity of the oils (about 10 times more than diesel) restricted their use, because this suggests a deprived fuel atomization and an incomplete combustion. The high flash point of vegetable oils and their tendency to oxidize thermally hindered the use of the oil, due to the formation of deposits in the injector nozzles and a decrease in lubricity (Agarwal, 2007). However, it was attempted to transform the properties of the oils and to evaluates those properties to that of diesel, through other techniques such as dilution or transesterification. The idea of using biodiesel in their engines, renewed in the late twentieth century, this time in the form of

biodiesel (which is only modified vegetable oil) mainly driven by environmental concerns related to climate change. Other motivations, in addition to the ecological, to encourage the use of biodiesel were the surplus soybean production in the United States, or the surplus of agricultural production in Europe (Boris, 2012).

Historically, the term biodiesel has been used to refer to all types of alternative fuels such as vegetable oils, vegetable oils mixed with diesel oil, vegetable oil micro emulsions, pyrolysis products of vegetable oils, methyl and ethyl esters prepared from vegetable oils or animal fat. However, with increasing production and development of methyl and ethyl esters as diesel fuel, the term biodiesel increasingly refers to those esters that are in agreement with American Society for Testing and Materials (ASTM) (Agarwal, 2007). Although the use of lubricants is as old as mankind, scientific attention on lubricants and lubrication technology is relatively new. Mankind has used lubricants from the early days of civilization to assist in minimize the energy needed to slide one object against another. It is recorded that grease, oil, or mud have been used as lubricant as early as 2400 B.C. and liquid lubricant was valuable as the original lubricant for transporting sledges in the Sumerian and Egyptian civilizations (Biniyam *et al*.,2016). Nevertheless, during the 1950s, the most vital requirements for base oils were appropriate viscosity and the nonappearance of acidic components and base oils were downgraded into solvents or carriers for additives. During the 1970s, several synthetic fluids with a uniform and basic chemical structure exhibited superior performance compared with those of mineral base oils. During the1980s, low-priced, quasi-synthetic hydro-cracked oils were introduced in Western Europe; these oils had properties that closely matched those of synthetic hydrocarbons. During the 1990s, base oil development was influenced by the demands on

lubricant performance, as well as by environmental, health, and safety criteria. This phenomenon led to more chemically pure oils, and their oleo chemical derivatives experienced a renaissance because of their rapid biodegradability. The trend toward increasing performance and improved compatibility continued during the first decade of the new millennium. The current quality trends in lubricants indicate a significant shift toward viscosity grades and product specifications (Mobarak *et al.*, 2014).

2.5 Oil Esterification

This is a method by which the free fatty acid (FFA) content of the oil is reduced, as it may lead to high saponification. The high FFA content of the oil was reduced by esterification of the oils with methanol using sulphuric acid as catalyst. However, Muhammad *et al*., (2019b) weighed 500g of the oil samples and transferred into 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 °C. Mechanical stirrer was inserted through one of the necks while the other two necks were stopped, the stirrer rotating at 700 rpm and the temperature of the bath was maintained at 60 °C for homogeneity. At this moment, timing started. After 60 min, 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.

2.6 Transesterification

Generally, transesterification is one of the methods used to produce bio-lubricant. Transesterification of oleo chemical ester is the process of breaking the raw plant oil into their methyl or ethyl esters chemically using an alcohol in the presence of alkaline catalyst such as sodium hydroxide with glycerol as a by-product. The reactions of transesterification with higher alcohols C_8 to C_{14} are used in producing lubricants while the reaction with lower alcohol such as methanol, ethanol and isopropanol are used in production of biodiesel (Loo, 2014). However, transesterification of vegetable oil is more likely to produce a lubricant of appreciable fluidity with better temperature performance (Musa *et al*., 2015). In other words, Production (synthesis) of biolubricant involves a two-stage transesterification process; 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 (Muhammad *et al*., 2019b). This technique helps to effectively replace the hydrogen atom on the β-carbon structure of the oil, leading to the establishment of polyol ester.

Various polyhydric alcohols utilized in transesterification of fatty acids methyl ester are ethylene glycol, trimethylolpropane, pentaerythritol, and neopentylglycol. Ethylene glycols are recognized to have a good branched structure and anti-freezing properties, which constitute the main properties of bio-lubricant production (Mohammad *et al*., 2018 and Musa *et al* 2016). Bilal *et al*., (2013). studied the application of ethylene glycol for the synthesis of bio-based lubricants using jatropha curcas oil as feed stock. Matthew *et al.* (2015) studied the classical experimental design that changes one factor at a time and does not illustrate the interaction between process variables due to a large volume of laboratory

experimental runs, making this approach time consuming. Hence, based on the reported compound model, the optimization of bio-lubricant production by reducing the number of experimental trials has received insignificant attention in this area of research. The biolubricant was produced through a transesterification reaction of biodiesel with ethylene glycol using calcium oxide heterogeneous catalyst. The chemical reaction is shown in 2.2 figure below

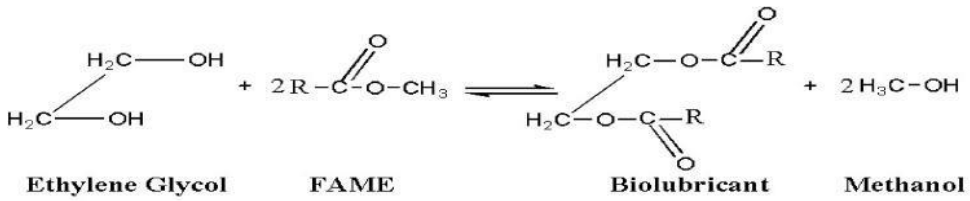

Figure 2.2. Biolubricant synthesis chemical reaction (Rade *et al*., 2021).

2.7 Advantages and Disadvantages in the Use of Biodiesel Fuel

The use of biodiesel has energetic, environmental and economic advantages. Today's diesel engines require a clean fuel to be burned, as well as it remains stable under the different conditions. Biodiesel can be used directly in any diesel engine without any necessary modifications in the engine. Their properties are similar to petroleum diesel fuel (equivalent density, viscosity only slightly higher). It can be mixed with fossil diesel in any proportion, without any problem (Alamu *et al*., 2018). In comparison to fossil diesel, biodiesel has a lower calorific value (around 10%) and a worse performance at low temperatures with a tendency to solidify at extreme cold conditions, which requires the use of specific additives. Additional advantages include a high cetane number. However, the high flash point indicates low risk of fire at high temperature. Even though bio-lubricant seems to be a better choice of lubricant, it still has some disadvantages. The presence of a double bond in the fatty acids causes the poor oxidative stability which is important for a longer projection life of the lubricant. These fatty acids contain bis-allylic hydrogen that

provides a space for free radical attack and this can be improved by some chemical modification such as epoxidation and oxirane ring opening (Juan *et al.,* 2020).

2. 8 Advantages and disadvantages of biolubricant

Vegetable oils can be used as lubricants in their natural form. They have several advantages and disadvantages when considered for industrial and machinery lubrication. On the positive side, vegetable oils have excellent lubricity, which is far superior compared with that of mineral oils. Vegetable oils also have a high viscosity index and high flash points when compare with mineral oils. More importantly, vegetable oils are biodegradable, generally less toxic, renewable, and reduce dependency on imported petroleum oils. On the negative side, vegetable oils in their natural form lack sufficient oxidative stability for lubricant application. Low oxidative stability indicates that oil will oxidize rapidly during use if unprocessed, becoming thick and polymerizing to a plastic-like consistency. Vegetable oils also have low-temperature limitations, unpleasant smell, poor compatibility with paints and sealants, flushing propensity because of low viscosity, and filter-clogging tendency (Mobarak *et al.,* 2014).

2.9 Classification of Biolubricant

Biolubricants can be classified according to their chemical fluid composition in natural, refined and synthetic oils. Natural oils are made via vegetable oils or animal fats, while synthetic oils use the natural oils as starting materials to form more advanced biolubricants. Among them, it was reported that ester synthesis, involving modification by microorganisms, alcohols, poly alcohols, poly glycols and other species, are able to graft to a natural oil, in such a way that the synthesized biolubricant exhibited thermo-oxidative stability, wear resistance, and lubricity properties even greater than those exhibited by mineral oils. However,

synthetic esters also display several restrictions, since chemical modification raises the price of the lubricant, slightly increases the volatility and toxicity, diminishes the friction tolerance, and the esters do not work well with mineral oils in comparison to unmodified vegetable oils (Juan *et al.*, 2020).

2.9.1 Natural oils

Natural oils are obtained from vegetables, fruits, or seeds, as well as fats obtained from animals, have been used as starting materials to obtain their respective oils through several extraction and distillation methods. These oils are widely available, are inexpensive, and exhibit higher biodegradability than those obtained from mineral oils. Generally, the physicochemical properties of vegetable oils depend on the composition of free fatty acids. Natural oils display variable compositions, since both environmental and biological parameters strongly influence chemical composition (Mobarak *et al.,* 2014). Nonetheless, some parameters of natural oils are generally better than those of traditional mineral oils. However, the use of these natural oils to synthesize biolubricants is inconsistent, since most interfere with the food chain, thereby causing speculation regarding the prices of consumable vegetable oils and producing increased prices and social imbalance (Juan *et al.*, 2020).

2.9.2 Refined oils

Oils derived from crude or petroleum reserves, such as paraffinic, naphthenic, and aromatic oils (Mobarak *et al.,* 2014).

2.9.3 Synthetic oils

Oils synthesized as end products of reactions that are tailored per requirement; examples are synthetic esters, silicones, and polyalpha olefines (Mobarak *et al.*, 2014).

2.10 Polyol

Transesterification of vegetable oil is more likely to produce a lubricant of appreciable fluidity with improved temperature performance. This method helps substitute the hydrogen atoms into the beta-carbon structures of the oil, leading to the formation of polyol ester. Various polyhydric alcohols utilized in transesterification of fatty acids methyl ester are ethylene glycol, trimethylolpropane (TMP), pentaerythritol (PE), and neopentylglycol (NPG). Ethylene glycols are known to have a good branched structure and anti-freezing properties, which constitute the main properties of bio-lubricant production (Mohammed *et al*., 2018). Bilal *et al*., (2013) studied the application of ethylene glycol for the synthesis of bio-based lubricants using jatropha curcas oil as feed stock. The study utilizes the classical experimental design that changes one factor at a time and does not illustrate the interaction between process variables due to a large volume of laboratory experimental runs, making the approach time consuming. Hence, based on the reported compound model, the optimization of bio-lubricant production by reducing the number of experimental trials has received insignificant attention in this area of research. Nevertheless, polyol esters have overall better physical properties, therefore it deserves more attention. As mentioned earlier, the reactants used in synthesizing polyol esters are polyhydric alcohols such as neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) and with a mono-functional fatty acid such as oleic acid. The

summary of the typical physical properties of esters lubricant is illustrated in Table 2.2

Table 2.2: Typical Physical Properties of Ester Lubricant

	Monoester	Diesters	Polyol esters	Complex esters
Viscosity index	150 to 230	0 to 90	40 to 170	130 to 230
Pour point (°C)	-35 to 25	-70 to -40	-60 to 7	-60 to -20
Flash point (°C)	180 to 220	200 to 260	250 to 320	240 to 280
Oxidative stability	Fair	Good	Excellent	Fair
Biodegradability	Excellent	Good	Excellent	Excellent

(Loo, 2014).

2.11 Methyl Ester Synthesis

Methyl ester is produced from wide range of feedstock, for both economics and food security reasons there is more emphasis on non-edible oils. Nevertheless, irrespective of the source, biodiesel preparation is influenced by a number of factors including reaction temperature, reaction time, methanol/oil ratio and concentration of the catalyst. The optimal levels of these factors are function of the nature of oil being esterified (Kyari *et al*., 2017). Samuel *et al*., (2017) Report the optimum conditions for obtaining biodiesel with improved properties were found to be close for both oils. For the palm kernel oil, the maximum conversion of the triglyceride to methyl ester was 98 % at an optimum temperature of 56 oC for catalyst concentration of 0.6, 6:1 methanol-oil ratio and lube oil yield of 92 %, while for soybean oil, the conditions for maximum conversion (95%) of the triglyceride in the soybean oil occurred at 60 oC, for 0.5 catalyst concentration and 6:1 methanol-oil ratio with lube oil yield of 88 %. 400 g of the oil was trans

esterified with methanol using sodium hydroxide as catalyst with the weight ratio of oil-to-methanol was 3:1; the amount of catalyst used was 0.5% w/w of the oil and the reaction was conducted at a temperature of 60 °C for one hour to produce biodiesel and glycerin. The biodiesel was separated by gravity from the glycerin using separating funnel after leaving it to settle for 20 h (Muhammad *et al*., 2019b). Refaat *et al*, (2008) studied optimization and quality assessment of biodiesel from waste vegetable oil and obtained the best yield percentage (96.15 %) using a methanol/oil molar ratio of 6:1, potassium hydroxide as catalyst (1%) and 65 °C temperature for one hour. Nevertheless, irrespective of the source, biodiesel preparation is influenced by a number of factors including reaction temperature, reaction time, methanol/oil ratio and concentration of the catalyst used and the optimal levels of these factors are also a function of the nature of oil being esterified (Kyari *et al.*,2017). The reaction for biodiesel formation is shown in Figure 2.3

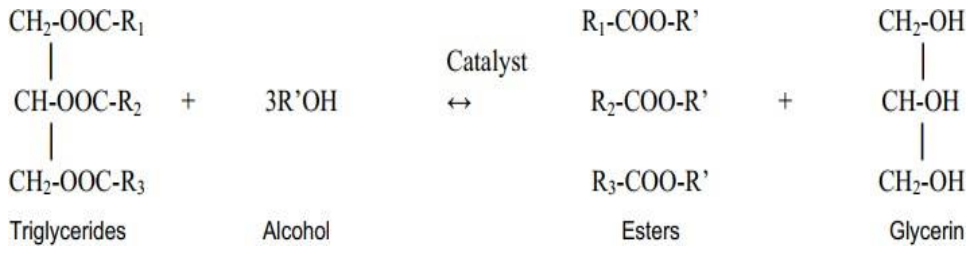

Figure 2.3. Transesterification reaction for biodiesel production (Yadessa et al.,2017).

2.12 Polyol ester (Biolubricant) Synthesis

Bilal *et al.*, (2013) produced biolubricant from the Nigeria jatropha oil through a two-step transesterification process using ethylene glycol. The physicochemical, temperature and rheological properties of the produced biolubricant were studied and compared to that of the raw jatropha oil and results obtained indicated that the

biolubricant had a better pour point (-7°C) and lower rheological properties compared to the jatropha oil (with pour point of (5°C). It was concluded that the synthesized biolubricant conformed to the ISO VG46 standard lubricant and would be a favorable substitute for petroleum-based lubricants for light gear applications. The study did not measure the iodine value, peroxide value, cloud point and flash point of the jatropha oil. The corrosion inhibition properties as well as the biodegradability of the jatropha oil were not determined. These properties are of importance in the application of any oil for lubrication purposes Muhammad *et al*., (2019) studied transesterification of the methyl ester with ethylene glycol using potassium hydroxide as catalyst. The weight ratio of vegetable oil methyl ester-to-ethylene glycol was 4:1, potassium hydroxide catalyst was measured base on the percentage of each experimental run into the reactor, temperature of the reaction was raised to that of each experimental run and the reaction time was maintained base on each experimental run. Constant vacuum condition was applied at each experimental run in other to reduce excessive foam formation as a result of methanol loss. Matthew *et al*., (2015) studied the properties Fluted pumpkin seed oil (FPSO) and Fluted pumpkin biolubricant (FPBL) for its suitability for use as a biolubricant base fluid. The results are presented in Table 2.3 in comparison with the properties of raw FPSO, other biolubricants and the ISO (International Organization for Standardization) viscosity grades requirement. The kinematic viscosity, viscosity index, pour point and flash point of the samples were determined using American Society for Testing and Material (ASTM) standard methods D445, D2270, D97 and D92, respectively (ASTM2003).

Table 2.3: Properties of FPB in Comparison with other Plant Based Biolubricants and ISO Grades

Properties	FPBL	FPSO	Calophyllum oil biolube	Palm oil biolube	ISO VG32	ISO VG46	ISO VG68
Viscosity@ 40 ^{0}C (cSt)	60.78	55.75	56.40	52.40	>28.80	>41.40	>61.40
Viscosity@ 100^{0}C (cSt)	11.03	10.30	8.80	10.20	>4.10	>4,10	>4.10
Viscosity Index (VI)	176	176	193	186	>90	>90	>198
Pour Point ^{0}C	< -14	< -5	< -3	< -5	< -10	< -10	< -10
Flash Point ^{0}C	220	152	218	-	200	220	230
Density g/Cm^3	-	-	-	-	0.857	0.861	0.865

(Matthew *et al*.,2015)

2.13 Factors Affecting Traseterification

2.13.1 Temperature

Temperature is the one of the major parameter that affect the rate of reaction. In transesterification the higher the temperature, the more energy is delivered to overcome activation energy required in the reaction and produced more yield. Matthew *et al*., (2015) studied process optimization and kinetics of biolubricant synthesis from fluted pumpkin seed between temperature of 140 ^{0}C and 160 ^{0}C using trimethylolpropane (TMP) with calcium hydroxide, $Ca(OH)_2$ as catalyst and achieved optimal yield (82.75 %) of biolubricant product at 160 ^{0}C. In another related studies, Bilal *et al*., (2013) studied the synthesis of biolubricant from Jatropha curcas seed oil and obtained the optimum yield at temperature of 120 ^{0}C for 2.5 hours. Yeti *et al.,* (2014) reported optimal yield (79 %) at 130 ^{0}C when

studied the effect of temperature on transesterification of calophyllum methyl ester (CMEs*)* and trimethylolpropane between 110 ^{0}C to 150 ^{0}C using calcium oxide as catalyst. Besides, Said *et al.,* (2015) studied the temperature variation (90 ^{0}C to 130

^{0}C) on biolubricant production from jatropha methyl ester (JME) and TMP using paphiaundulata shell waste as a catalyst and reported the highest percentage of tri-ester (78. 67%) at temperature of 110 ^{0}C. Increase in temperature gave rise to the increase in tri-ester composition, until at about 140°C when the increase in tri-ester composition became negligible. This was attributed to the fact that at higher temperature the quantity of FAME in the reactor was low due to vaporization, favoring the reverse reaction (Samuel *et al.*, 2021).

2.13.2 Catalyst type and concentration

Generally, catalyst plays vital role in the transesterification process, it reduces time of reaction. Homogenous catalysts such as inorganic acids and alkali have been being applied widely in the transesterification process either in biodiesel and biolubricant production (Said *et al*.,2015). Reda *et al.*, (2021) investigate the effect of different levels of catalyst dosage on reaction conversion biolubricant while keeping other three parameters constant (temperature, time and molar ratio) and the catalyst percent 0.8% (w/w) is completely insufficient for dragging the reaction to high conversion. The catalyst percent 1% (w/w) gives a relatively good conversion value. While the two other levels 1.2% and 1.5% (w/w) give very close results. Therefore, the catalyst percent 1.2% (w/w) is taken to be the optimum. The amount and type of catalyst used for transesterification reaction process, for the purified feedstock, any kind of catalyst might be used. Conversely, feedstock with much moisture and free fatty acids content heterogeneous catalyst are suitable Yeti *et al.*, (2014).

2.13.3 Time of reaction

The transesterification increases with the reaction time. The transesterification of peanut, cottonseed, sunflower and soybean oils with methanol in a ratio methanol/oil of 6:1 at 60° C and NaOH as catalyst, and yield of 80% biodiesel was obtained after 1 min for soybean and sunflower oils. After 1 h the conversion was 93-98% for all four oils. The formation of methyl esters is high in the first minutes. Then the rate diminished and finally reaches equilibrium after 1 h. (Boris, 2012). Reda *et al.*, (2021) Studied the effect of different levels of reaction time between 60 and 180 minutes and the optimum operating reaction conditions for the biolubricant production was achieved at temperature 130 ◦C, FAMEs: EG molar ratio of 3.5: 1, 1.2% (w/w) CaO catalyst (based on reaction mixture) and reaction time of 90 min. Nevertheless, Muhammad et al., (2019) studied double transesterification of jatropha and ethylene glycol be 1 to 3 hours and reported maximum yield of 95.30 % at optimum conditions 2.63 hours, 149.70 ◦C and 0.95% catalyst concentration.

2.13.4 Molar ratio

One of the methods to promote forward reaction is by using excess amount of one of the reactants, since one reactant is relatively cheaper compared to the other. However, in order to obtain better and more product yield, the reactants molar ratios were kept above the stoichiometric values, this is because the reaction was driven more toward completion. The increased in the molar ratio beyond 4:1 gave negligible improvement in tri-ester yield for palm kernel biolubricant. This phenomenon can be attributed to the low rate of conversion of di-ester to tri-ester, as well as occurrence of reverse reaction that caused the breaking of di-ester to tri-ester (Samuel *et al.*, 2021). Yeti *et al.*, (2014) investigated the effect of CMEs:

TMP molar ratio to conversion to TMP esters at 130 0C in 5 hours and catalyst was maintained at 3 % w/w in all experiment. The show that there is no significant effect of increasing molar ratio on the conversion of TMP ester. Slightly higher percentage of TMP esters was obtained at molar ratio of 1: 3.7 and 1: 3.9. However, the difference was so small (70.40 %and 71.80 %) that no conclusion could be withdrawn from the study.

2.13.5 Stirring speed

The speed of agitation plays a vital role in the improvement of the desired product, the mixing of oil and catalyst promote the reaction (Alemayehu and Abile, 2014). Nevertheless, low stirring speed shows low product development and higher stirring speed favors soap formation and this as a result of the reversible reaction of transesterification reaction (Bilal *et al.*, 2013)

2.14 Properties of biolubricant

Biolubricant properties that are commonly considered for assessing the suitability of a biolubricant for a particular application include the fluidity range, viscosity index, low temperature fluidity, oxidation stability (inhibited), hydrolytic stability, thermal stability, mineral oil compatibility, additive solvency, volatility, rust control (inhibited), boundary lubrication, fire resistance, elastomer compatibility. Current research efforts are directed towards improving the low-temperature stability of vegetable oils by chemical modification, blending with functional fluids, and by the use of additives. The main properties to take into account are as follows (Jumat *et a*l., 2014)

2.14.1 Pour point

The pour point (PP) is the temperature below which the liquid loses its flow characteristics, in biolubricant, the pour point is directly related to the viscosity

index. Presence of ternary alcohols, such as trimethylolpropane (TMP), diminishes the pour point of the biolubricant, although it also causes a decay in the thermo-oxidative stability of the alcohol. The use of bigger branched alcohols, such as neopentyl polyols, has emerged as a potential alternative to obtain biolubricant with low pour points and higher oxidative stability levels. Besides, the temperature is known as the pour point and is defined as the lowest temperature at which movement of the specimen is observed. Pour Point values have traditionally been measured when the sample no longer moves on tilting the tube containing the sample (pour point). Pour points lower than 0°C are considered to be low (Jumat *et al*., 2014). It was reported the presence of –C=C– bonds decrease the pour point; however, these lubricants are more vulnerable to oxidation processes. The optimum pour point is obtained for saturated fatty acids with short hydrocarbon chains, since an increase in the length of the carbon chain causes a higher pour point. In plants, chains generally contain between 16 and 18 carbon atoms, indicating that the saturation of these acids causes them to become solid at temperatures of 65–75 ◦C. The position of the –C=C– unsaturated bond does not seem to affect the pour point temperature. However, its conformation slightly influences the pour point temperature, with cis-configuration chains, where the hydrogen atoms are located on the same side, being observed to have a lower pour point than hydrocarbon chains with trans-configuration (Juan *et al.*, 2020).

2.14.2 Flash point

The flash point is defined as the minimum temperature at which a liquid produces a sufficient concentration of vapor above it to form an ignitable mixture with air. Oils with a lower flash point are a greater fire hazard. The flash point should be high enough to allow safe operation and minimum volatilization at the maximum

operating temperature. For the most demanding applications, such as aviation jet engine biolubricants, an effective liquid range over 300°C may be required (Jumat *et al*., 2014). Flash point is an important property that must be considered in evaluating the overall flammability hazard of a biolubricant and other similar materials (Samuel *et al*., 2021)

2.14.3 Viscosity

Viscosity is the resistance to flow. These properties are related to temperature, pressure and layer formation. Beside, oil with higher viscosity of offer higher opposition to flow and if the viscosity opposition to flow would be minimum (Mobarak *et al*., 2014). However, the viscosity of oil usually increases as the temperature decreases and vice versa. The kinematic viscosity of palm lubricant was determined according to ASTMD 455 (ASTMD standard 15). The viscosity of fatty acids and vegetable oils is a quantitative measure of its resistance to flow. It is the key property of base stocks since it is a major factor in determining their application; for example, low viscosity stocks can be used for automotive transmission oils, while higher viscosity stocks are employed in diesel engine oils. Base stocks are usually named according to their viscosity. Viscosity measurements on base stocks assume that the liquids are Newtonian in which shear stress and shear rate are linearly related. Viscosity is critical to determining the quality of a biolubricant film. In metal forming applications, the biolubricant viscosity determines the effectiveness of the film in separating the tool from the work-piece, thereby controlling friction and wear. Metal removal operations, on the other hand, have diverse lubrication needs, and, hence, the optimum biolubricant viscosity must be estimated for each operation. This is accomplished by considering the ability of the biolubricant to enter and remain in the contact zone,

the durability of the biolubricant film, the desired rate of spreading, and its cooling capability (Jumat *et al*., 2014).

2.14.4 Viscosity index

The Viscosity Index, commonly designated VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature, high Viscosity Index indicates small oil viscosity changes with temperature. A low viscosity index indicates high viscosity change 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 (Nuran, 2014).

2.14.5 Oxidative stability

Oxidation is the most important reaction of oils resulting in increased acidity, corrosion, viscosity, and volatility when biolubricant-based oils are used as engine oils. The triacylglycerol structure forms the backbone of most available vegetable oils that comprise different fatty acid chains. Therefore, a complex association of different fatty acid molecules attached to a single triacylglycerol structure constitutes a vegetable oil matrix. The presence of unsaturation in the triacylglycerol molecule, owing to the presence of oleic, linoleic, and linolenic acid moieties, functions as the active site for various oxidation reactions. Saturated fatty acids have relatively high oxidation stability, which decreases with increasing unsaturation in the molecule. Several oxidation tests are available primarily as screening tools for oxidative stability of fatty acids and vegetable oils. The evaluation of oxidation is extremely complex, and a fully acceptable protocol is yet to emerge. The direct use of vegetable oils as biolubricant has disadvantages

because of a variety of factors. Vegetable oils have poor oxidative and thermal stability due to the presence of the glycerol backbone in oil, which gives rise to a tertiary β-hydrogen, which is thermally unstable. Fortunately, there are different ways and methods to overcome it. For example, the chemical modification of vegetable oils by reactions such as epoxidation, esterification, and acetylation across the double bonds constitutes a promising method for obtaining valuable commercial products from renewable raw materials (Jumat *et al.*, 2014).

2.15 Application of Biolubricant

Lubricants can be employed in both closed and open systems. In open systems, lubricants are constantly released into the environment, while in closed systems, lubricants should be kept protected so uncontrolled releases cannot take place; however, human error can cause unwanted disposal of lubricants into the environment. Considering these factors, lubricants used as potential alternatives to traditional mineral oils must have high levels of biodegradability. Besides, the physicochemical properties of a biolubricant depend on its intended application. The applications of the biolubricants are indicated in Table 2.4

Table 2.4 Significant Properties of Biolubricant for Several Applications.

Application	Properties	Advantages
Engine oil	Low volatile organic compound emission.	Reduce engine emissions. Improves engine
	Good lubricity	performance
Hydraulic oil	Low compressibility Fast air release rate	Better pressure transmission
		Less vibration and noise
Compressor oil	High thermal stability	Tolerates high
		temperature and pressure
Metal working oil	Low volatility Good antirust capacity.	Less harmful mist generation. Longer tool life
	Good emulsifiability	
	Good lubricity	Stable emulsions at high temperature
Transmission oil	Good lubricity Higher weld load	Suitable additives can be added
Chainsaw oil	Low volatility	Less harmful mist generation
Insulating oil	Higher water solubility level High dielectric constant	Decreases the effect of moisture on insulation strength
		Better Insulation properties

(Juan *et al.*, 2020).

2.15.1 Engine oils

Engine oil plays a key role in motors by reducing friction and wear of moving parts, preventing corrosion of the engine system, improving sealing, and cooling the motor. In engine systems, lubricants must operate under severe pressure and/or temperature conditions and must be stable to prolonged exposure of contaminating acids, which can cause progressive deterioration of the biolubricant. Juan *et al*, (2020) reported that biolubricants with low sulfur and phosphorus contents exhibited less volatility with better properties than lubricants obtained from mineral

oils. Nowadays, several biolubricants used as engine oils are marketed by several companies, such as Green Earth Techologies (USA), Biosynthethic Technologies (USA), and Renewable Lubricants Inc. (USA). The physicochemical properties,

mainly the viscosity, of these oils are adapted to diesel and gasoline engines following the International Lubricant Standards Association (ILSAC GF-5) and American Petroleum Institute (API) standards. Biolubricant can be used in various industrial and maintenance applications. Some of their important applications are as follows: industrial oils such as machine oils, compressor oils, metalworking fluids, and hydraulic oils; automotive oils such as engine oils, transmission fluids, gear box oils, as well as brake and hydraulic fluids; and special oils such as process oils, white oils, and instrumental oils (Mobarak *et al.*, 2014).

2.15.2 Hydraulic fluids

Hydraulic fluids must be formulated to transfer energy/power in a hydraulic system as well as to lubricate the system. A key parameter of hydraulic fluids is their compressibility, since the design of a hydraulic fluid with lower compressibility improves the pressure transmission velocity, which is directly related to a faster response and a better use of energy. However, Vegetable oils display low isothermal compressibility and appropriate viscosity for use as hydraulic fluids. It was reported that soybean oil displayed better power transmitting properties than mineral oils. Several vegetable oils, such as rapeseed oil, palm oil, moringa oil, passionfruit oil, and rubber seed oil, have shown excellent properties when used as hydraulic oil. (Junan *et al.*, 2020). Nowadays, important companies, such as Shell, Mobil, or Chevron Texaco, are marketing hydraulic fluids and hydraulic systems using environmentally friendly vegetable oils with approved several pump test standard (Mobarak *et al*., 2014).

2.15.3 Compressor oils

Compressor oils must maintain stability under severe conditions of pressure and temperature. Among the parameters that compressor oils must satisfy, these

lubricants should avoid corrosion of the component, seal the compression cylinder, and regulate temperature during the compression process. The main challenge of compressor oils is related to their thermal stability at elevated temperatures, since some CO_2 or propane systems can reach about 215 ^{0}C; therefore, compressor oils must tolerate a temperature of 250 ^{0}C. The market for bio-based compressor oils is very scarce; they are intended for use in compressors such as vacuum pumps, reciprocating compressors, centrifugal compressors, and stationary rotary compressor (Juan *et al.*,2020).

2.15.4 Transmission oils

Transmission oils must display high viscosity, high thermal stability, and high friction resistance, since these processes involve great amounts of friction. The temperature at which a transmission engine is regulated is another very important parameter to consider improved thermo-oxidative stability, allowing oils to have longer service lives, and improved process. Nowadays, the use of bio-based lubricants as starting materials for transmission oils is limited. It was reported that the addition of tetraoleate ester was possible, although this bio-based lubricant exhibited a higher weld load and lower wear scar diameter than commercial transmission oils Currently, the few commercialized bio-based gear and transmission oils that are employed mainly in gear in roller machinery are based on rapeseed oil (Juan *et al.*,2020).

2.15.5 Chainsaw Oils

Chainsaw lubricants must be renewable and biodegradable since they are often thrown to the ground or into water during their handling this biodegradability has led to high commercialization of these products from several companies, mainly soybean oil and rapeseed oil. these bio-based lubricants must display high flash

point temperatures and low vapor pressures to minimize the inhalation of volatile compounds in order to improve chainsaw oil formulations (Junan *et al.*,2020).

2.15.6 Grease

Generally, grease can be classified based on the thickener, which is between 10 wt.% and 15 wt.% of the total grease. The thickener used most often on the industrial scale is a lithium compound and this compound presents low biodegradability, the challenge in this field, therefore, involves the synthesis of bio-based thickeners as environmentally benign alternatives. Juan *et al.* (2020) reported that 12 hydroxystearic acid and its respective alkyl-ester derivatives could become a natural alternative due to the presence of intermolecular and intramolecular interactions, which favor its use as a thickener (Mobarak et al., 2014).

2.15.7 Insulating oils

Insulating fluids are commonly used to avoid electrical discharge, disintegrate heat, and lubricate and insulate surfaces. These fluids must display high electrical resistivity to avoid electrical arcing. Currently, traditional mineral oils are engaged as insulating fluids in capacitors, bushings, or transformers, even though strict environmental regulations have led to continuous modifications of their formulations (Juan *et al.*,2020).

2.16 Benefit of Biolubricant Applications

2.16.1 Economic benefit

The energy security of the country can be improved with the large-scale production of non-edible seed plantations, it also provides means of foreign exchanges and hence non- edible seeds plantations provides employments the rural masses. It also generates infrastructure facilities for oil extraction, bio-mass exploitation and commercialization from the exiting trees. Plantation of these trees will be

maintaining ecological stability and reduce over dependency on mineral oil (Prerna and Chhibber, 2013)

2.16.2 Environmental benefit

The environmental problems associated with the use of petroleum products and the geopolitical policies regarding crude oil management are the driving forces behind the introduction of alternative fuels and lubricants from renewable raw materials that can contribute to the vertical organization of the national economies. The search for bio-based material as industrial and automotive lubricants has been accelerated recent years (Ebtisam *et al.*, 2016). However, accelerating research and development in this area has also been driven by public demand, industrial concern, and government agencies and better ways to protect the ecosystem or reduce the negative impact of spills or leakage of lubricants must be outlined. (Jumat *et al.*, 2010).

2.16.3 Sustainability benefits

Globally, there are more than 350 oil-bearing crops identified as potential sources for biofuel production, the availability of wide range of biofuel feed stocks is one of the most significant factors that enables the sustainable production of biolubricant. However, satisfactory replacement of petroleum lubricant with biolubricant depends on two basic requirements which includes easy availability and environmentally acceptability, and being economically reasonable. Availability of feedstock for producing biofuel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country (Yadessa *et al*.,2017). The sustainability for lubricants involves factors beyond just functionality and eco-friendliness, as attentions must be made in regard to future applications and problems. Even those advocating lubricants manufactured from

renewable resources, like biolubricants, must consider the option of using non-edible plant feed stocks in anticipation of controversies such as the food-versus-fuel debate. The other option for renewable resources represents biomasses, such as lignocellulose, straw, used frying oils, sugar. Notably research and development regarding to third and fourth-generation biomass is predominantly centered on biofuel production, use of these renewable feed stocks is applicable to manufacturing biolubricants as well. Most previous studies were carried out with vegetable oils that could interfere with the food chain, such as soybean, sunflower, rapeseed, or palm oil, since the use of these oils could cause price speculation and social imbalances. Due to this, the cultivation of non-edible oils, such as jojoba oil, karanja oil, jatropha oil, and castor oil, has grown over the last few years as sustainable alternative and in recent years, microalgae has also emerged due to its high oil content, even over 70% in some cases (Juan *et al.*,2020).

2.16.4 Performance benefit

Biolubricant designed for one application may be suitable for another application with a loss in performance. Biolubricant properties that could be considered for assessing the suitability of a bio based for the particular application such as fluidity range, reduced expansion of metal due to frictional, heat and destruction of material. It acts as coolant of metal due to heat transfer media and avoid unsmooth relative motion, reduces maintenance cost and power loss in internal combustion engine (Mobarak et al., 2014). Conversely, improved process yields under mild conditions Over the last few years, the use of enzymatic processes has emerged as an alternative to obtain biolubricants at low reaction temperatures. The use of nanoparticles was shown to improve biolubricant physio chemistry by minimizing asperity contact and wear (Juan *et al.*,2020).

2.17 Experimental Design

One of the most important stages in the development of an efficient and economic production of high value products is the optimization of process parameters. Response Surface Methodology (RSM) is a statistical tool for optimization in which several factors and their interactive effect can be analyzed in a few experimental runs. RSM has been widely applied in several areas some of which include processing of food products, development and improvement of new products, biotechnology and bioprocessing such as in fermentation studies and enzymatic hydrolysis (Nuran,2014). The use of RSM gives the optimum condition with minimum cost of analysis and their related numerical noise. The interaction can be can be represented using graphical method, either in the 3-dimensional shapes or contours plot that assist in visualizing the shapes of the response surface (Mohammed *et al*., 2012). However, RSM is a collection of mathematical and statistical techniques for designing experiments, building models, evaluating the effects of factors, and searching optimum condition of factors for desired responses. The optimization process of this methodology involves studying the response of statistically designed combinations, estimating the coefficients by fitting it in mathematical model that fits best the experimental conditions, predicting the response of the fitted model, and checking the adequacy. Central composite design (CCD) and Box-Behnken design (BBD) are amongst the most commonly used in various experiments due to their less experimental runs (Muhammad *et al*., 2019).

2.18 Central Composite Design (CCD)

Central Composite Design (CCD) has received a lot of interest in the current time as the most suitable second order design for complete evaluation of feedstock based upon second order models. Box and Wilson first introduced CCD in 1951 to optimized surface response. The CCD provides complete factorial design with levels (2k) or limited factorial designs (2k-f) fabricate with many design points. CCD comprises of three types of design points. CCD comprises of three types of design points such as; Factorial point, Axial point and central points (Muhammad *et al*., 2019).

2.19 Factorial Design

To build an estimated model that can arrest the interactions among N design variable, a complete factorial technique would be essential to examine all the likely combinations. A factorial experimental design, is the investigational approach in which design variables are varied collectively, as a replacement of after the other. The lower and higher boundaries of the number for the design s variables in the optimization problems need to be identified (Andre and Siuli, 2014). The acceptable choice is subsequently discredited at different levels. If each one of the variables is known at only the lower and higher bounds (two levels), the experimental design is called 2N complete factorial design. However, if the mid-point is incorporated, the design is called 3N complete factorial design. Factorial designs are used to developed second-order models and can considerably enhanced the process of optimization when a first-order model suffered lack of fit as a result of interaction among variables and surface curve. A universal second-order model is used to developed as estimated model that can captured interaction among N design variables (Venu and Vaibhav, 2015).

2.20 Statistical Analysis

Analysis of results is done statistically with the aid of design expert software. The analysis of variance (ANOVA) is similar to regression. It is used to investigate and model the relationship between a response variable and one or more independent variables (Andre and Siuli 2014). Nevertheless, ANOVA differs from regression method because the independent variables are qualitative and no assumption is made about the nature of the relationship. In effect, ANOVA extend the two sample T-test for testing the quality of the populations mean to a more than two means, versus them not all being equal. P-test and t-test was done in order to get the optimum equation for the transesterification of methyl ester (Mohammed *et al*., 2012)

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

Most of the chemicals used in this investigation were of analytical grade. They were obtained from Pamlac in Minna, Department of Chemical Engineering (CHE), Agricultural and Bioresources Engineering (ABE) all of Federal University of Technology in Minna, Niger State, Nigeria. The equipment was obtained from Department of Chemical Engineering and Agricultural and Bio-recourses Engineering, Federal University of Technology Minna, Niger State, Nigeria. Table 3.1 and 3.2 shows the chemicals and equipment used for this research respectively. While Table 3.3 show the flow diagram of the steps used in this study.

Table 3.1: List of Equipment Used

Equipment	Manufacture	Source
Digital weighing balance	Ohus corp. china.	ABE Dept. FUT Minna
Magnetic stirrer	Stanhope-seta Ltd. UK	ABE Dept. FUT Minna
Measuring cylinder	Pyrex, England	CHE Dept. FUT Minna
Two neck round bottom flask	Pyrex, England	CHE Dept. FUT Minna
Beaker	Pyrex, England	CHE Dept. FUT Minna
Conical flask	Pyrex, England	CHE Dept. FUT Minna
Retort stand and clamp		ABE Dept. FUT Minna
Digital rotary Viscometer	NDJ- 5S (4541)	ABE Dept. FUT Minna
Heating mantle	Dibby	ABE Dept. FUT Minna
Oven	Gallen kamp, England	ABE Dept. FUT Minna
Refrigerator	Revo	ABE Dept. FUT Minna
Thermometer		CHE Dept. FUT Minna
Separation funnel	Pyrex, England	ABE Dept. FUT Minna

Table 3.2: List of Chemical Used

Chemicals	Manufactures	Percentage (%) purity
Methanol	BDH Chemical Ltd. Poole England	99.9
Potassium hydroxide		
Sodium hydroxide	Lab. Burgoyne Reagent. India	99.0
Ethylene glycol	BDH Chemical Ltd. Poole England	99.5
Hydrochloric Acid	Analar BHD	99.9
Orthophosphoric Acid	May and Baker Ltd, Dagenham Eng.	99.9
n- Haxane	BDH Chemical Ltd. Poole England	
Distilled Water	CHE Dept FUT Minna	

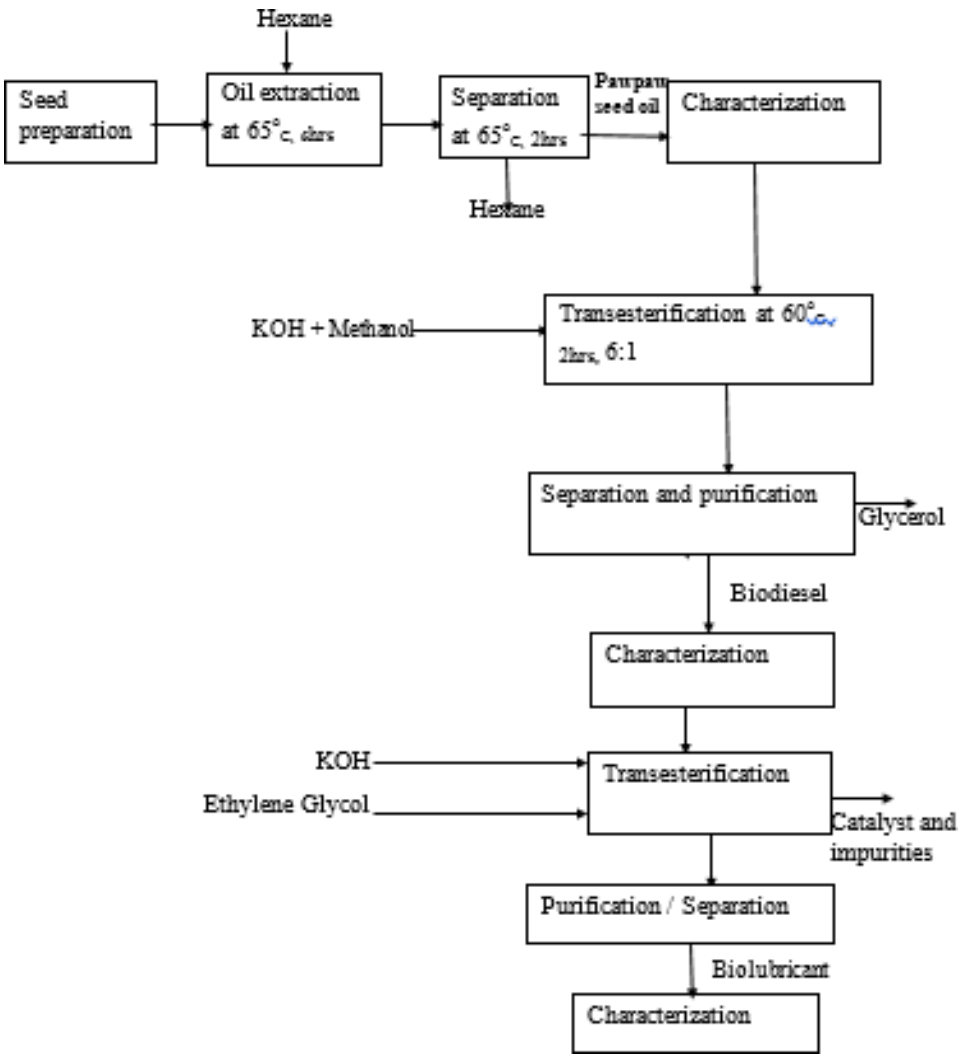

Figure 3.1: Flow Diagram of steps for Producing Pawpaw Based Biolubricant

3.2 Methods

Fresh Pawpaw seeds were harvested randomly from different locations in Bida Local Government Area of Niger state, Nigeria to have a good representation of the samples.

3.2.1 Preparation of the pawpaw seed

Matured seeds from ripe Pawpaw fruit were removed freshly and the seeds separated manually. The seeds were washed with water 3 times to remove the gelatinous and 3 to 5 days of sun drying were required to completely dry 1 kg of fresh feed. The seeds were milled mechanically by small milling machine in the Agricultural and Bio-recourses Engineering and then stored in a clean bottle for extraction process (Aladekoyi *et al*., 2016; Elvianto and Erni 2017). Plat I show pawpaw plant, fruit and seed.

Plate I: The Pawpaw Plant, Fruit and Seed

3.2.2 Extraction oil

A pre oven dried thimble was weighed with analytical weighing balance (w_1). 10g of the powdered sample was added to it (w_2), and put inside the Soxhlet apparatus. 500 cm^3 boiling flask was filled to 2/3 with solvent (Hexane) and fitted to the Soxhlet carrying the condenser to cool the solvent. It was heated gently and allowed to siphon after soaking the sample for 6 hours. After the extraction, the thimble with the extracted sample were removed and allow to dry at low temperature in an oven for few minutes, cool and weighed (w_3). Percentage crude oil was determined from each stage. The process was done until the required quantity of the oil has been collected. The extracted oil and solvent ware transferred from the round bottom flask on to evaporating dish placed on electric cooker inside the fume cupboard, the sample was then heated at 65 ^oC for 30 minutes to remove solvent. The oil was stored at room temperature until it is required for analysis (Aladekoyi *et al.*, 2016). The total quantity of crude pawpaw seed oil obtained from extraction was around 2 liters from 6.5 kg of pawpaw seed. The set-up for continuous Soxhlet apparatus for oil extraction is shown in plate II.

Plate II: The: Set-up of Continuous Soxhlet Apparatus for Extraction Process.

3.3 Chemical properties pawpaw oil

Determination of peroxide, iodine and saponification values, un-saponifiable matter and free fatty acid (FFA) contents was carried out using the methods of Palm Oil Research Institute of Malaysia (PORIM 1995).

3.3.1 Saponification value

Accurately weigh out 2 g of oil into a 250 cm^3 of conical flask, add 25 cm^3 of alcoholic KOH and dissolve the oil completely. Connect air condenser to the flask and boil for about 30 mins on a boiling water bath. Cool to room temperature; add 2 drops of phenolphthalein indicator and mix. Titrate against standard 0.5 N HCl until the pink colour disappears. Treat blank similarly in absence of oil. The saponification value was calculated using equation 3.1

$$\text{Saponification value} = \frac{(Blank + Titre)x(100)}{Weight\ of\ oil} \qquad (3.1)$$

3.3.2 Iodine value

Weight out 0.2g of oil into 500 cm^3 conical flask. Add 20 cm^3 of chloroform and dissolve the oil completely. Keep in dark for 30 minutes. Add 20 cm^3 of KI solution and mix well. Titrate against 0.1 N $Na_2S_2O_3$ solution using starch as an indicator with vigorous shaking to extract iodine from the chloroform layer. Conduct blank similarly in absence of oil. The iodine value was calculated using equation 3.2

$$\text{Iodine number} = \frac{A \times N \times 0.1269 \times 100}{Weight\ of\ oil} \quad (3.2)$$

Where, A = ml of $Na_2S_2O_3$

N = Normality of $Na_2S_2O_3$

3.3.3 Free fatty acid content

The free fatty acid in oil was estimated by titrating it against KOH in presence of phenolphthalein indicator. The acid number is defined in 1 g of sample. However, the free fatty acid is expressed as oleic equivalents. 1 ml N/10 KOH= 0.028g Oleic acid.

3.3.4 Density

An empty density bottle was weighed and the weight of the bottle was recorded, the bottle was then filled with water and the weight of density bottles with water was recorded. The sample was poured in to the density bottle and the weight of both bottle and sample was taken and then recorded. The density was calculated by taking the ratio of the weight of the water to that of the sample gives specific gravity. The specific gravity is then multiplied by 1000 Kg/Cm^3 to give density (Bilal *et al*.,2013**).** The equation 3.3 was used to calculate specific gravity of the oil

$$\text{Specific gravity} = \frac{(weight\ of\ water)(g)}{(Weight\ of\ sample)(g)} \quad (3.3)$$

3.3.5 Peroxide value

One gram of the oil was weighed into dry test tube, followed by addition of 1.0 g of powered potassium iodide and 20 cm^3 of a solvent mixture of glacial acetic acid and chloroform (2:1). This was placed in a boiling water bath so that the contents are boiled for 30 seconds. The contents were quickly poured into a flask containing 20 cm^3 of 5 % potassium iodide. The tube was washed twice with 25 cm^3 of distilled water and poured into the flask. It was titrated with 0.002 M sodium thiosulphate using starch indicator. The blank titration was done also.

3.4 Biodiesel Production

Ninety-four grams (100 ml) of crude pawpaw oil was fed on to two-neck round bottom flask laboratory reactor (2 liters in size) placed on magnetic stirrer. The oil was then pre-heated to 60 ^oC, this temperature was maintained throughout the reaction by the thermostat. The mole ratio of methanol to oil used were 6:1, the amount of catalyst (potassium hydroxide) was 5 % w/w of oil were dissolved in methanol (MeOH) and was added to the pre-heated oil, the reaction continues for 2 hours (Biniyam *et al.*, 2016 and Sarianto *et al*., 2019) with modification. The figure 3.2 shows the reaction between pawpaw seed oil (triglyceride) and alcohol (methanol) with potassium hydroxide as catalyst to produce mixture of alkyl ester and glycerol.

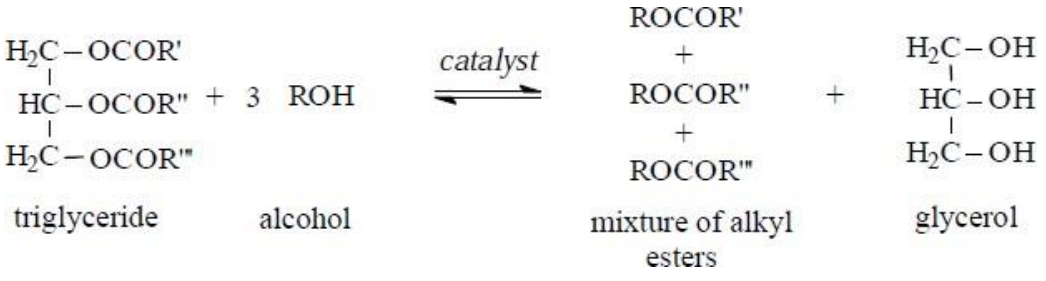

Figure 3.2: Reaction for biodiesel production

3.4.1 Separation of glycerol from methyl ester

At the end of transesterification, the mixture formed was allowed to settled for 24 h and then separated based on density variation by means of the separating funnel. Catalyst and glycerol part were withdrawn from lower part of the funnel. The fraction of the pawpaw seed methyl ester was washed with warm distilled water (70 ^{0}C) three times to eliminate the residuals that include catalyst, glycerol, soap, and methanol and oven dried at 105 ^{0}C for 30 minutes (Mohammed *et al.,* 2019). Equation 3.4 show percentage yield of biodiesel produced.

$$Biodiesel\ yield = (\frac{wt\ of\ biodiesel\ obtained}{wt\ of\ the\ oil\ used}) * 100 \quad (3.4)$$

3.5 Experimental Designs

For optimization of the reaction condition to produced higher yield of biolubricant with excellent purity. A three-factor test to study the effect of reaction temperature (A), reaction time (B) and catalyst concentration (C) on biolubricant yields was investigated using central composite rotatable design (CCRD). The CCRD used for this work contains twenty (20) experimental runs using 2^k+2k+n, where k is the number of factors and n is the number of center point. Besides, there are eight (8) factorial point (2^k), six (6) axial point (2k) and six (6) replicated point (n=6). Here k is the independent variable and k=3 (Muhammad *et al*., 2019). The limitation of apparatus and reactant condition used in biolubricant production were carefully used in determining the factors level for factorial design. The catalyst concentration 0.5 and 1.0 % by weight of methyl ester for low and high level for low and high level, this is in agreement with Noor and Jumat, (2011). A high and low level of 130 ^{0}C and 90 ^{0}C was reported by Said, (2015). However, Bilal et al., (2013) Studied the synthesis of biolubricant from jatropha curcas seed oil and reported 120

^{0}C for 2.5 h. Besides, Muhammad et al., (2019) studied double transesterification of jatropha and ethylene glycol be 1 to 3 h. The Table 3.3 and Table 3.4 show range level of process parameter in design and composite experimental design for biolubricant production.

Table 3.3 Range of Level of Process Parameter in Design

Independent Factors	**Symbol**	**Low level (-)**	**Medium level (0)**	**High level (+)**
Temperature (^{o}C)	A	90	110	130
Time (mins)	B	60	120	180
Catalyst Concentration (w/w %)	C	0.5	0.75	1.00

Table 3.4 Composite Experimental Design for Biolubricant Production

Std	**Run**	**A (^{0}C)**	**B (Min)**	**C (w/w)**
10	1	143.64	120	0.75
3	2	90	180	0.5
8	3	130	180	1
6	4	130	60	1
9	5	76.36	120	0.75
11	6	110	19.09	0.75
7	7	90	180	1
19	8	110	120	0.75
5	9	90	60	1
15	10	110	120	0.75
20	11	110	120	0.75
14	12	110	120	1.17
12	13	110	220.91	0.75

18	14	110	120	0.75
1	15	90	60	0.5
16	16	110	120	0.75
2	17	130	60	0.5
17	18	110	120	0.75
13	19	110	120	0.33
4	20	130	180	0.5

3.6 Production of Biolubricant from Pawpaw Methyl ester

Twenty-seven and half (27.5) grams of pawpaw methyl ester (PME) was weighed and pre-heated to 60 ^{0}C after which amount of ethylene glycol needed was determined molar ratio of PME to ethylene glycol 3.5:1 (Bilal et al., 2013). Processing time, temperatre condition and percentage by weight catalyst based on total weight of PME and ethylene glycol are mentioned in an experimental design matrix (Table 3.4). The equation for the reaction and set-up for the production of biolubricant is shown in Figure 3.2 and plate III respectively.

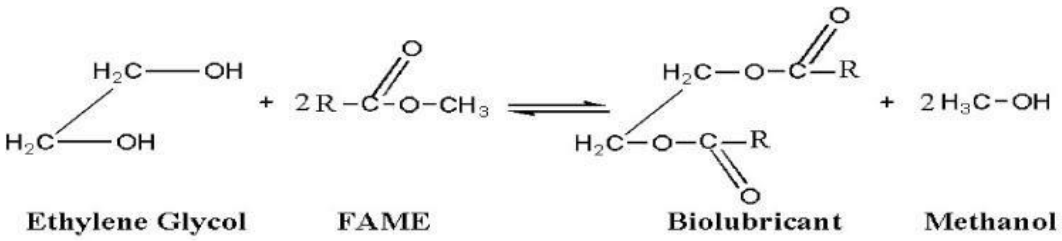

Figure 3.2; Reaction for biolubricant production

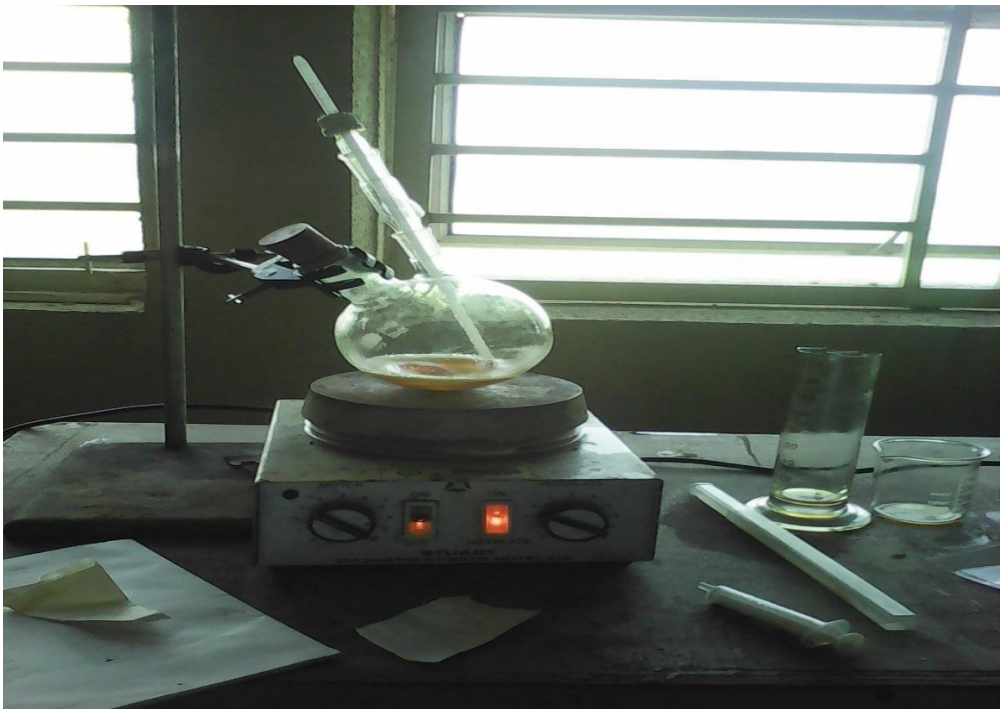

Plate III: Setup for Biolubricant Production

3.6.1 Washing of biolubricant

When the reaction is completed, the product was cooled for 5minutes before the mixture was poured into a separating funnel and allowed to settled for 24 h which result in to 2 phases based on the density difference, the upper phase was biolubricant and lower phase that was drained contains methanol, catalyst and impurities. The biolubricant was then washed with acidified water (10 percent ortho-phosphoric acid solution at 40 ^{0}C), make it neutral and then with distilled water repeatedly until distilled water is cleared. The sample was then oven dried at temperature of 105 ^{0}C for 30 minutes to dried off the water, after which the sample was weighed (Musa *eal*., 2016). The set up for the washing of biolubricant is shown in plate IV and the percentage yield of biolubricant was determined according to equation 3.5.

Percentage yield of biolubricant= $\frac{mass\ of\ dried\ biolubricant}{mass\ of\ methyl\ ester\ charged\ in}$ (3.5)

Plate IV: The Set up for the Washing of Biolubricant

3.7 Characterization of Biolubricant

3.7.1 Pour point

The oil Sample was poured into a medium sized test tube and (the test tube with its content) placed in a test tube holder. The set up was placed in a refrigerator and allowed to solidify. After it solidifies, the test tube was removed and a thermometer was used to read the temperature at which the solidified sample begins to melt and flow. This temperature was noted and recorded as the pour point of the oil sample (Bilal *et al*., 2013).

3.7.2 Flash point

Thirty ml of biolubricant sample was poured in to evaporating dish and the thermometer was suspended at the center of the dish using retort stand and clamp, the sample was then heated slowly with electric cooker to the minimum temperature at which the sample give enough concentration of vapor above it to form a combustible mixture with air oils and temperature at this point is noted and recorded as flash point of the sample (Mohammed *et al*., 2018) with modification. The set up for flash point of biolubricant is shown in plate V

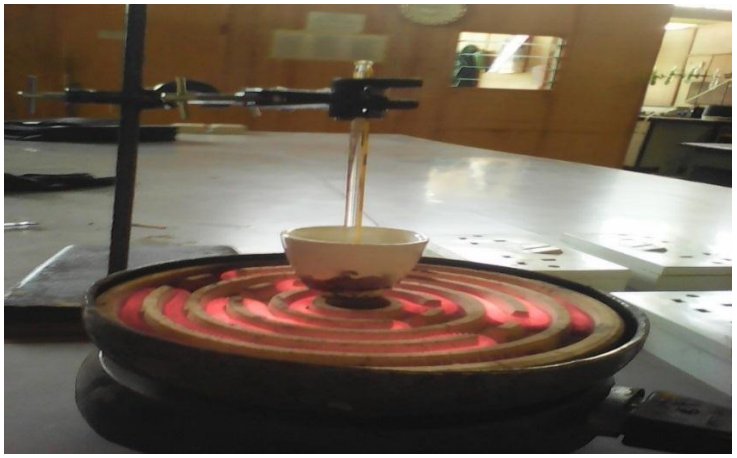

Plate V; Setup for Flash point of Biolubricant

3.7.3 Determination of kinematic viscosity

The digital rotary Viscometer was adjusted through the lifting screw until the level bubble is located on the center point, the sample was poured in to 250 ml beaker and the spindle three (3) was selected for the sample. The sample temperature raised to 40 and 100 ^{0}C for each case, the spindle was deep in to the sample, the viscometer was turned on and begins to rotate until the stable values was achieved and recorded (Bilal *et al.,* 2013) with modification**.**

3.7.4 Viscosity index (VI)

The value of viscosity at 40 ^{0}C and 100 ^{0}C values were used to calculate the viscosity index, when the value of viscosity at 100 ^{0}C is less than 70 cP. The value of H and L was obtained from the viscosity table, see appendix 1, ASTM D 2270 method and equation 3.3 was used to calculate the V

$$VI = \frac{U-L}{H-L} * 100 \qquad (3.6)$$

Where; VI is the viscosity index

U is the viscosity at 40 ^{0}C of the biolubricant,

L and H where are the kinematic viscosity of the reference oils (Mohammed *et al*., 2018)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physicochemical Characteristics and Oxidative Stability of Pawpaw Seed Oil

The results of the physicochemical characterization and the oxidative stability of the oil extracted from papaya seeds are presented in Table 4.1. The iodine value displays the level of unsaturation of the oil and also effects the oxidation and deposition formed in internal combustion engines. It is used in determining the drying property of the oil low iodine value (53.8 g/100 g) which confirmed it as non-drying oil. Other oils classified as non-drying are macadamia, olive, and peanut oils. Low iodine values for Carica papaya L. seed oil (79.95 g/100 g) was also obtained by (Cassia *et al*., 2010). However, the iodine value of Jatropha oil reported by Timothy *et al.,* (2019) was 88.9 gI_2/100g which is high and high value of Iodine implies high degree of unsaturation of the oil.

The saponification value of oil is a degree of the tendency of the oil to form soap during the transesterification reaction. However, high saponification value indicates that the oil will be more suitable for soap and cosmetic making than using the oil for biolubricant production, thus it may be necessary to modify the oil before it can be used as a lubricant. The saponification value 158 mg KOH/g of oil was achieved and it is in close agreement with 155 mg KOH/.g of oil reported by Syed *et al.,* (2011) which are lower when compare with the value of 190.00 mg of KOH/g of oil reported by Eriola *et al*..(2012) who studie Statistical Approach to the Optimization of oil from Beniseed oil seeds and 220.46mgKOH/g of oil reported by Timothy *et al.,* (2019) However, the Acid value is a measure of the free fatty acids in oil. The higher the acid value found, the higher the level of free

fatty acids which translates into decreased oil quality. The free fatty acids and the peroxide values are valuable measures of oil quality. The papaya seed oil showed 1.08% of free fatty acids and 6.70 m mol.kg^{-1} of peroxide value. These values are not considered high since crude vegetable oil maximum contents of 5% of free fatty acids and 10 m mol.kg^{-1} of peroxide value may be verified (Cassia *et al*., 2010). Fatty acids compositions of the extracted Papaya seed oil are presented in Table 4.3 which shows high level of oleic acid. Besides, the lower the acid number the better the oil as a lubricant as the high acid number oil is likely to corrode and wear machine parts that are lubricated. The oil will need modification to bring down its acid value to be a better industrial lubricant.

Table 4.1: Physicochemical characteristics of pawpaw seed oil in comparison with other plant-based oil and SAE

Parameters	**This Study**	**Paw paw Oil [a]**	**Paw paw Oil [b]**	**Paw paw Oil [c]**	**Jatro pha Oil [d]**	**SAE 20W 50 [d]**
Iodine value (g I_2/100g)	53.8	79.95	65.50	76.90	88.90	-
Peroxide value (M mol/kg)	6.70	5.370	-	-	-	-
Calorific value (Mj/kg)	44.37	-	-	-	-	-
Specific gravity	0.940	-	-	-	0.913	0.878
FFA (%)	1.08	1.27	0.32	0.90	15.0	
Viscosity at 40 ^oC	49.20				83.20	236.9
Saponification value (mg KOH/g)	158.60	96.40	155.50	193.5	220,46	-
Oil yield (%)	31.60	29.16	30.10	29.20	-	-

[a]Cassia *et al*. (2010), [b]Syed *et al*. (2011), [c]Noorzianna *et al*. (2014) and [d]Timothy *et al*. (2019**)**

4.2 Fourier Transform Infrared Spectroscopy (FTIR) Spectrum Analysis of Pawpaw Seed Oil, Biodiesel and Biolubricant

The extracted pawpaw seed oil sample and the synthesized biodiesel and biolubricant samples were analyzed using FTIR spectroscopy in order to determine the functional groups present in them. The Figure 4.1 show the analyzed samples and are compared with known signature of identified materials in the FTIR library. For all the samples, the main peaks of importance are discussed. However, the individual FTIR of pawpaw seed oil, biodiesel and biolubricant are shown in Appendices A, B and C respectively.

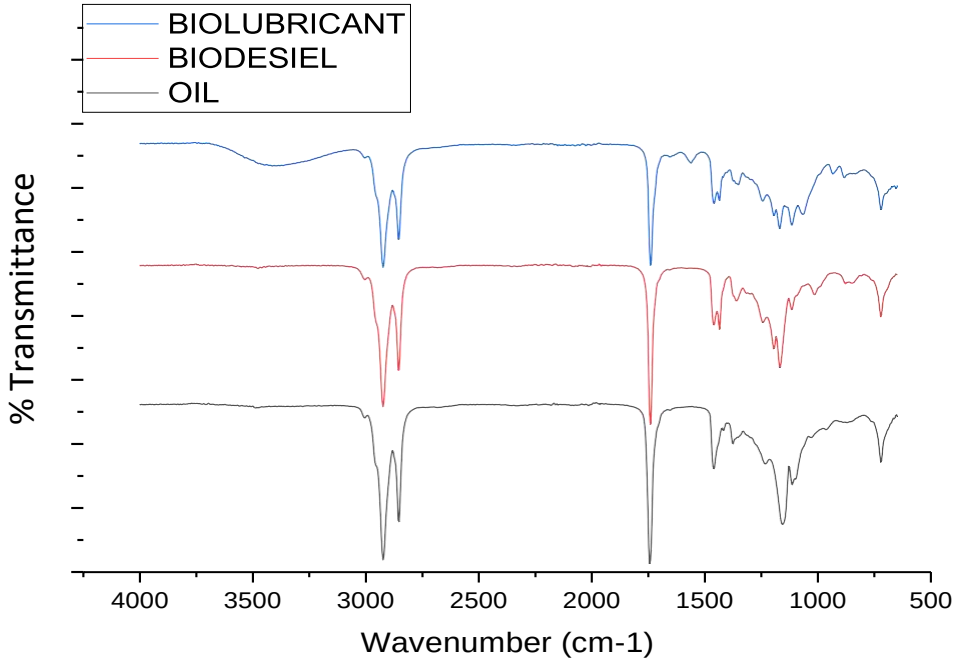

Figure 4.1; FTIR spectrum of Pawpaw Seed Oil, Biodiesel and Biolubricant

4.3 Functional groups of Pawpaw Seed Oil, Biodiesel and Biolubricant

For the pawpaw oil sample, the peak at 1114.5 cm^{-1} ;74.535 is a characteristic of C–O stretching, indicating the presence of alcohol and phenol which are oxygen-containing compounds. Likewise, the peaks at 3488.8 cm^{-1}; 98.535 are

characteristic of O–H stretching, indicating the presence of carboxylic acids, which are oxygen-containing compounds and water; which results in the easy biodegradability of the oil sample. Similarly, the FTIR spectrum of synthesized biolubricant confirming that the transesterification reaction between methyl esters and ethylene glycol actually occurred. From the spectrum, the peak at 1740.7 cm^{-1}; 61.994, which falls in the range of carbonyl (C=O) group, indicates the absorption for esters. However, the absorption peaks at 2922.2 cm-1; 61.318 and 2855.1cm^{-1}; 70.1 are within the absorption range for C–H stretching in the hydrocarbon component of the biolubricant. Finally, the broad peak at 3391.9cm^{-1}; 92.943 indicates the presence of O–H groups, indicating the presence of oxygen-containing compounds and water molecules which appear as impurities in the ethylene glycol. Nevertheless, the appearance of the band peaks of 1118.2 cm^{-1}; 74.572 and 1056 cm^{-1}; 77.43, which were not present in the pawpaw oil and methyl ester samples, is characteristics of the of double transesterification. This is because the functional group of Aliphatic C–O stretching of esters, indicate the presence of oxygen-containing compounds. Thus, the FTIR spectra is similar to that of (Reda *et al.,* 2021 and Samuel *et al.,* 2021). Table 4.2 shows the wave number, group attribution, function group, vibration type and absorption intensity of the biolubricant produced.

Table 4.2: Functional Group of Pawpaw Seed Oil Biolubricant Detected in the FTIR Spectrum

Wavember Cm^{-1}	Group Attribution	Functional Group	Vibration Type	Absorption Intensity
3391.9	-OH	Alkyl	Stretch intermolecular bonding	Weak
2922.2	$-CH_2$	Aromatic	Asymmetric stretching	Strong
2855.1	CH_3	Methyl	Aliphatic symmetric	Strong
1740.7	$-CH_3$	Alkanes	Bending Vibration	Strong
1461.1	C=O	Carboxylic acid	Scissor vibration	Middling
1353.0	CH3	Aliphatic deformation	Bending Vibration	Weak
1244.9	C-O-C	stretching of ethers oxirane ring	Asymmetric stretching	Middling
1170.4	C-O	Stretch aliphatic ether	Rocking vibration	Middling
1118.2	C-O	Stretch aliphatic ether	Rocking vibration	Middling
1056	C-O	Stretch aliphatic ether	Rocking vibration	Middling
723.1	$-CH_2$	Straight chains with more than four CH_2 group	Skeletal vibration	Middling

4.4 Gas Chromatography Mass Spectroscopy (GC–MS) Analysis of Pawpaw Seed Oil, Biodiesel and Biolubricant

The extracted pawpaw seed oil sample and the synthesized biodiesel and biolubricant samples were analyzed using GC mass spectroscopy in order to determine the fatty acid present in them. Figure4.2 and Table 4.3, compared the analyzed sample and the main peaks of importance were discussed

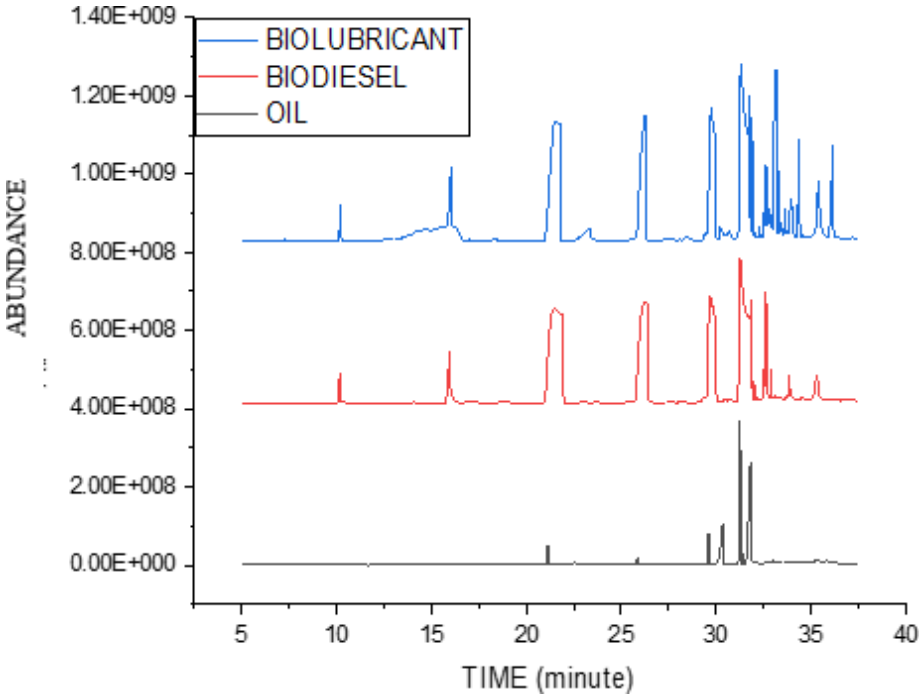

Figure 4.2; GC-MS of Pawpaw Seed Oil, Biodiesel and Biolubricant

The fatty acid composition of pawpaw seed oil, biodiesel and biolubricant is shown in table 4.3, the major monounsaturated fatty acid obtained in the pawpaw were oleic (59.98 %) and palmitic (16.36 %) which is in agreement with that reported by Syed *et al*., (2012) (oleic 59.98 % and palmitic 16.36 %). However, results disclose that the biodiesel produced from the transesterification pawpaw seed oil consists predominantly of methyl ester of lauric (27.49 %), myristic (16.24 %), palmitic (15.37 %) and oleic (25.88 %), this also shows that modification has occurred because of percentage reduction free fatty acid of oil (oleic). In general, all the fatty acids methyl ester is either saturated or monounsaturated with no detectable di-, triand polyunsaturated fatty acids. This is a desirable property with respect to the stability of the biodiesel, high degree of unsaturation has been linked to low stability index. However, such low levels of unsaturation and relatively high proportion of long chain compounds could also have a negative effect on cold finger plugging point and might therefore be responsible for the high levels of

cloud and pour points of the biodiesel. Thus, this is similar to that of Kyari *et al.*, (2017). The transesterification of pawpaw methyl ester to poly ester produced high saturated fatty acid compared to unsaturated fatty acid composition; this is promising as high saturation content in the biolubricant will leads to higher resistance towards thermal- oxidative treatment. However, a high degree of saturated fatty acid could develop a lubricant with high biodegradability and good low-temperature performance which is in closed agreement with Nurazreen *et al.*, (2020). In general, the level of saturation and unsaturation of fatty acid reduces from biodiesel to biolubricant and appearance of ethylene glycol and glycol ether in biolubricant sample confirmed that biodiesel has been modified to biolubricant. However, the individual fatty acid composition of pawpaw seed oil, biodiesel and biolubricant are shown in Appendices D, E and F respectively.

Table 4.3: Relevant fatty acid composition (%) pawpaw seed oil, biodiesel and biolubricant

Fatty Acid Type	Systematic Name	Common Name	Percentage		
			Pawpaw Oil	Biodiesel	Biolubricant
Saturated	Dodecanoic	Lauric	5.15	27.49	19.75
	Tetradecanoic	Myristic	0.94	16.24	I0.02
	Hexadecanoic	Palmitic	4.55	15.37	16.13
	Octadecanoic	Stearic	3.2	_	_
	Eicosanoic	Arachidic	0.28	4.00	3.40
	Docosanoic	Behenic	_	_	
	Triethylene glycol	Ethylene glycol	_	_	3.50
	Butoxytriglycol	Glycol ether	_	_	6.94
	Decanoic	Caprinic	5.75	2.67	7.06
	Heptanoic	Heptoic		0.01	_
	Nonanoic	Pelargonic		0.05	_
	Eugenol	Eugenic		0.37	_
Monounsaturated	Hexadecenoic	Palmitic	16.36	0.30	-
	Octadece	Oleic	59.9	25.88	22.54

	noic		8		
Polyunsaturated	Octadecadienoic	Linoleic			_
	Octadecatrienoic	Linolenic		0.04	0.04

4.5 Optimization of Process Variables for the Yield of Pawpaw Seed Tri-ester

The optimization process result for tri-ester yield is shown in table 4.4, the design expert was used to analyze the result. Temperature, Te and Catalyst concentration of reactant were all fixed between 90 -130 ^{0}C, 60-180 min and 0.5-1.0 mol w/w, respectively. It was found that within the given rang, the highest triester yield of 97.0 was achieved at a temperature of 130 ^{0}C, reaction time 180 min and 0.5 mol w/w of catalyst concentration. However, 0.24 total error was achieved between actual yield (experimental yield) and predicted yield

Table 4.4: Experimental Yield of Biolubricant for CCDR Arrangement

Run	Std	Temp (oC)	Time (min)	Catalyst (%wt)	Actual Yield (%wt)	Predicted Yield (%wt)	Error (€)
10	1	143.64	120	0.75	93.50	90.66	2.84
3	2	90	180	0.5	75.00	72.48	2.52
8	3	130	180	1	90.00	89.64	0.36
6	4	130	60	1	79.50	82.92	-3.42
9	5	76.36	120	0.75	64.00	65.51	-1.51
11	6	110	19.09	0.75	95.50	94.69	0.81
7	7	90	180	1	70.00	71.44	-1.44
19	8	110	120	0.75	88.00	88.69	-0.69
5	9	90	60	1	82.50	80.47	2.04
15	10	110	120	0.75	92.50	88.69	3.81
20	11	110	120	0.75	84.50	88.69	-4.19
14	12	110	120	1.17	75.00	73.93	1.07
12	13	110	220.91	0.75	95.50	94.97	0.53
18	14	110	120	0.75	88.50	88.69	-0.19
1	15	90	60	0.5	80.00	81.25	-1.25
16	16	110	120	0.75	89.50	88.69	0.81
2	17	130	60	0.5	93.50	92.96	0.54
17	18	110	120	0.75	89.00	88.69	0.31
13	19	110	120	0.33	83.50	83.24	0.26
4	20	130	180	0.5	97.00	99.93	-2.93

Total Error	0.24

4.6 The Analysis of Variance (ANOVA) for Tri-ester Yield

The summary of P-values and model statistics are shown in table 4.5 and 4.6. A quadratic model was suggested from the CCD module with a high adjusted and predicted R^2 values of 0.9054 and 0.7230 respectively. However, the ANOVA carried out confirmed the adequacy of the quadratic model.

Table 4.5: ANOVA for Response Surface Quadratic

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	
Model	1539.48	9	171.05	21.21	< 0.0001	Significant
A-Temp	763.52	1	763.52	94.66	< 0.0001	
B-Time	3.45	1	3.45	0.4277	0.5279	
C-Catalyst	104.61	1	104.61	12.97	0.0048	
AB	124.03	1	124.03	15.38	0.0029	
AC	42.78	1	42.78	5.30	0.0440	
BC	0.0313	1	0.0313	0.0039	0.9516	
A^2	202.67	1	202.67	25.13	0.0005	
B^2	91.92	1	91.92	11.40	0.0071	`
C^2	184.23	1	184.23	22.84	0.0007	
Residual	80.66	10	8.07			
Lack of Fit	47.32	5	9.46	1.42	0.3550	not significant
Pure Error	33.33	5	6.67			
Cor Total	1620.14	19				

The ANOVA result in Table 4.5 show that the Model F-value of 21.21 is high with lowest P-value ($P<0.0001$), this implies that the model is significant. However, the larger the magnitude of F-value and smaller the magnitude of P-value, the higher will be the significance of the corresponding coefficient (Matthew *et al*., 2015). The values of "Prob > F" less than 0.0500 indicate model terms are significant (Table 4.2). In this case A, C, AB, AC, $A^{2,}$ B^2 C^2 are significant model terms while B and BC are the insignificant model terms. Values greater than 0.1000 indicate

the model terms are not significant, however model reduction may be applied to insignificant model terms in order to improve the model. The value of regression

coefficient R^2 for the model is 0.9502, this indicate that the model adequately represents the experimental results. This is in agreement with Musa *et al*., (2016). A quadratic model was suggested from the CCD module with a high adjusted and predicted R-squared values of 0.9504 and 0.7230 respectively shown in Table 4.6.

Table 4.6: Regression Analysis

Parameter	Value
Std. Dev.	2.84
Mean	85.42
C.V. %	3.32
R^2	0.9502
Adjusted R^2	0.9054
Predicted R^2	0.7230
Adeq Precision	17.1460

Adequate Precision measures the signal to noise ratio and it compadre the range of the predict value at design point to the average prediction error. The adequate precision value greater than 4 is desirable for sufficient model efficiency. Therefore, the obtained adequate precision value of 17.146 indicates an adequate signal. The fitness of the model equation was validated using the coefficient of regression, R^2. The high R^2 value of 0.9502 implies that 95.02% of the variability in the response can be explained by the model, this also confirmed that the model can be used to steer the design space. However, the higher the value0 of the adjusted coefficient of determination, the more the significant the fitted model. In this work, the coefficient determination is higher which shows that the fitted model is significant. The final equation in term of coded factors was obtained and shown as equation 4.1 and 4.2 respectively.

4.7 Final Equation in Terms of Coded Factors

$$Yield = 88.70 + 7.48*A - 0.5026*B - 2.77*C + 3.94*AB - 2.31*AC - 0.0625*BC - 3.75*A^2 + 2.53*B^2 - 3.58*C^2 \quad (4.1)$$

4.8 Final Equation in Terms of Actual Factors

$$\text{Yield} = -73.86986 + 2.38901*A - 0.534542*B + 126.25595*C + 0.003281*A*B - 0.462500*A*C - 0.004167*B*C - 0.009373*A^2 + 0.000701*B^2 - 57.30415*C^2 \quad (4.2)$$

Equation 4.2 above shows the coefficient of the full regression, numerical significant and the exact impact on each model expression on the yield. The above positive and negative sign before each term shows synergistic or antagonistic effect respectively. The temperature, catalyst concentration and interaction between temperature and time and square of time has synergistic effect on the biolubricant yield while time, the interaction between temperature and catalyst concentration, time and catalyst concentration, square of temperature and square of catalyst has antagonistic effect on yield. The model was found more significant at 95 percent confident level for computed F values (21.21) with very low probability value ($p < 0.0001$). However, all terms in the model was found to be significant at 95 percent confident level as the computed F values for the particular terms were higher. Nevertheless, the smaller the p-value for a parameter the more important the parameter and therefore it shows the relative significance of the term related with the parameter (Matthew *et al*., 2015). The Table 4.7 shows the coefficients of regression and response of significance of quadratic model.

Table 4.7: Coefficient of regression and response of significance of Quadratic model

Factor	Coefficient Estimate	Df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	88.70	1	1.16	86.12	91.29	
A-Temp	7.48	1	0.7685	5.76	9.19	1.0000
B-Time	-0.5026	1	0.7685	-2.21	1.21	1.0000
C-Catalyst	-2.77	1	0.7688	-4.48	-1.06	1.0000
AB	3.94	1	1.00	1.70	6.17	1.0000
AC	-2.31	1	1.00	-4.55	-0.0752	1.0000
BC	-0.0625	1	1.00	-2.30	2.17	1.0000
A^2	-3.75	1	0.7479	-5.42	-2.08	1.02
B^2	2.53	1	0.7481	0.8585	4.19	1.02
C^2	-3.58	1	0.7494	-5.25	-1.91	1.02

4.9 Process Variable Optimization and Validation

Table 4.8 shows the optimization and validation results for papaya biolubricant synthesis. Predicted responses were generated using point prediction node (under optimization node in the CCD module). Temperature, time and catalyst concentration were all fixed in the range of 90–130 ^{0}C, 60 – 180 minutes and 0.5–1.0 wt/wt % respectively. TE yield was maximized within the experimental range of 80.750 –82.643%. Using these criteria, the software suggested (see Table 4.8) the following optimum conditions: temperature of 97.61 ^{0}C, time of 128.10 min catalyst concentration 0.873 wt/wt % and yield of 80.750 % at a desirability value of 1000.The histogram of biolubricant yield and validated biolubricant yield are shown Appendix G and Appendix H respectively.

Table 4.8: Process Validation

Parameter	Optimum operating condi
Temperature (^{0}C)	97.616
Time (min)	128.102
catalyst concentration wt%	0.873
Yield (optimum)	97.00
Yield (validated) %	80.750
Yield (predicted) %	99.93
Desirability value	1.000

The normal plot of residuals in Figure 4.2 and the predicted vs actual plots in figure 4.3 were used to check the distribution of residuals. The close distributions of the points along the straight lines indicate the excellent relationship between the experimental and predicted values of the response. These plots also validate that the chosen model was sufficient for prediction of the response variables in the experimental values.

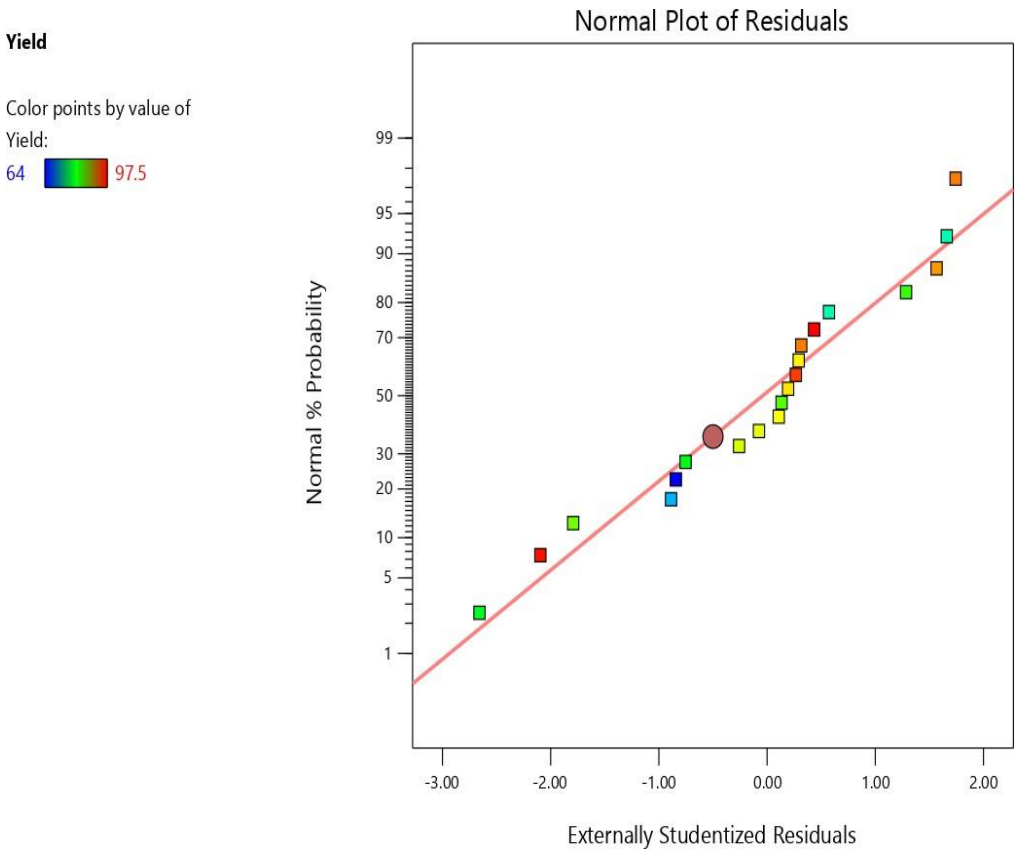

Figure 4.3: Normal plot of residuals Pawpaw Biolubricant

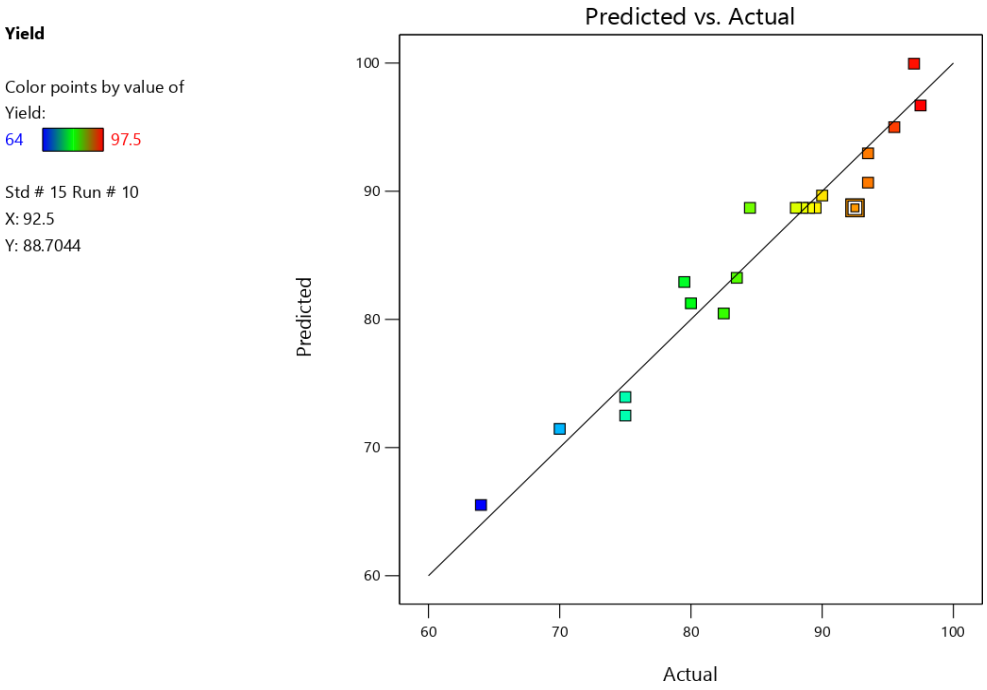

Figure 4.4: A Graph of Predicted Yield against Actual Yield

4.10 Response Surface Measurements

The 3-dimensional (3D) surface plot of the second order model shown in Figure 4.5, 4.6 and 4.7 helps to understand better the interactive effect of the variables on the yield of biolubricant and how tri-ester yield varied as a function of any two factors selected for display. The nature of the response surface curves reveals the communication between the variables. An elliptical shape in a curve shows worthy interaction between the variables. The elliptical nature of the contour in the graphs also indicates that there was a relative significant interaction between every two variables.

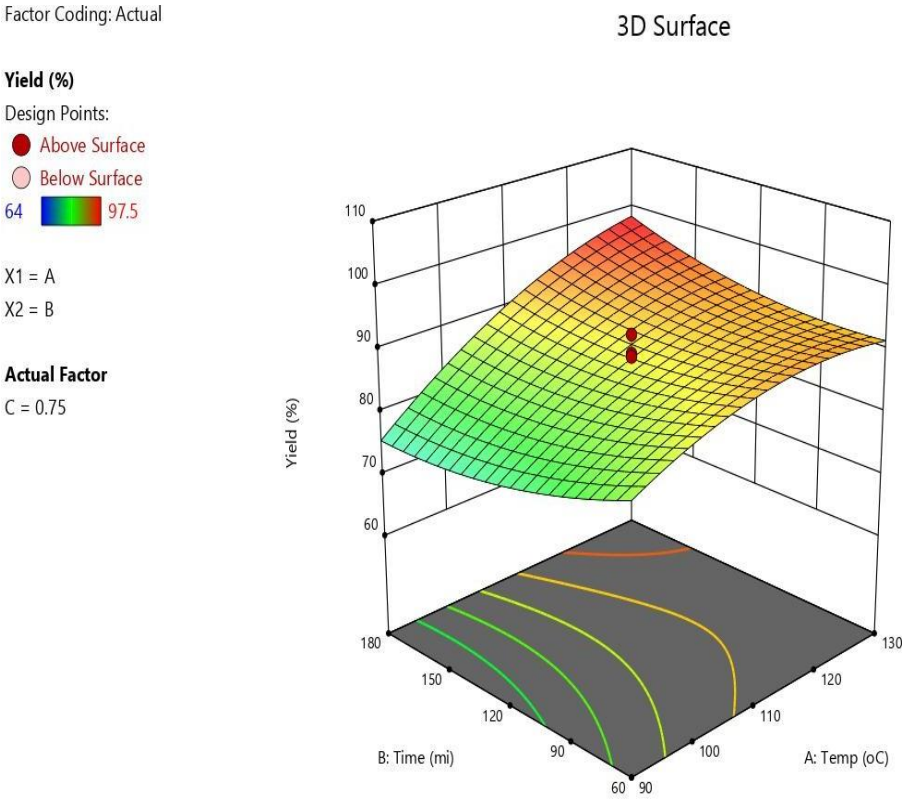

Figure 4.5: 3D Surface Plot Showing Combined Effect of Time and Temperature

Figure 4.5 shows the interactive effect of temperature and time on biolubricant yield. It can be seen that the biolubricant yield increases as temperature increases which might be due to increase in the reaction speed resulting to higher conversion of the ester. The increasing effect of temperature shows that 64.00 % yield was recorded at temperature of 76.36 ^{0}C, reaction time of 120 mins and 0.755 % catalyst concentration while 92.50 % yield was recorded at temperature of 110 ^{0}C, reaction time of 120 mins and catalyst concentration of 0.75 %w/w. It is also clearly shown that the biolubricant yield increases with increase in the reaction time. The increasing effect of time shows that 92.50 % yield was recorded at temperature of 110 ^{0}C, reaction time of 120 mins and 0.75 % catalyst concentration. While 95.50% yield was recorded at 110 ^{0}C, 220.91 mins reaction time and 0.75 catalyst concentration. Figure 4.4 shows a clearer view of the interaction of time and temperature on biolubricant yield. However, excessive increase in temperature of the reaction over a period of time cause the most volatile component of methyl ester to vaporized leading to a reduction in mole of methyl ester to ethylene glycol for a complete reaction.

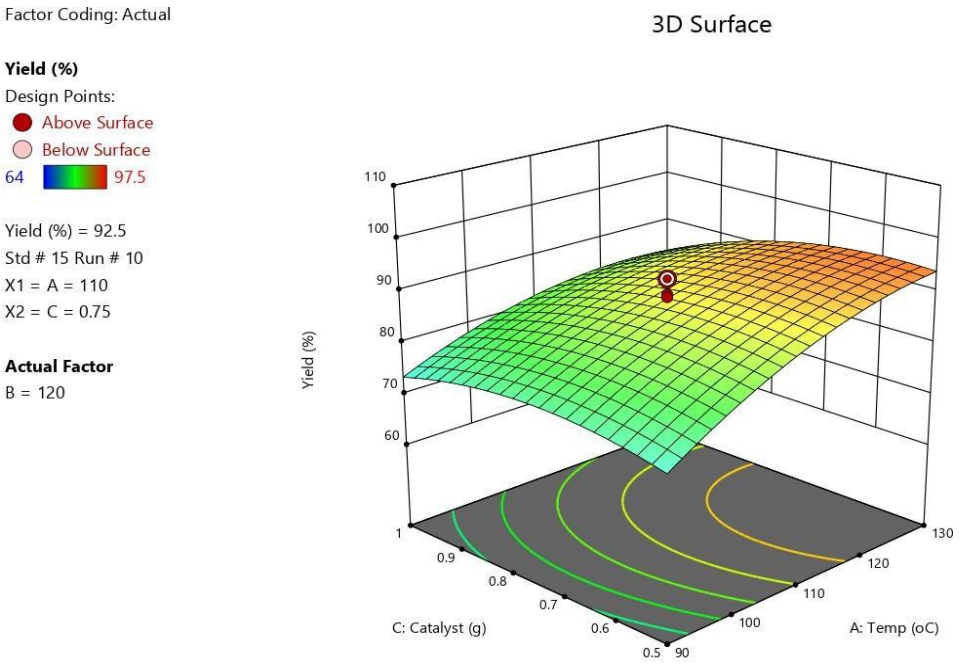

Figure 4.6: 3D Surface Plot Showing Combined Effect of Temperature and Catalyst

Figure 4.6. presents the interactive effect of catalyst concentration and temperature on the yield of biolubricant yield. The biolubricant yield decreases with increase catalyst concentration; this is due to saponification reaction leading to soap formation and therefore result into less conversion of the ester into biolubricant. The decreasing catalyst's effect shows that yield of 73.93 % was recorded at the reaction condition; temperature of 110 ^{0}C, catalyst concentration of 1.17% w/w and reaction time of 120 minutes while the yield was 92.50 % at the reaction condition; temperature of 110 ^{0}C, reaction time of 120 mins and catalyst concentration of 0.75 % w/w. Increase in temperature leads to increase yield of the biolubricant, when temperatures increase, the reaction rates are obviously higher because molecules consume more energy, but the saponification reaction rate speeds up, therefore the transesterification reaction yield decreases (Musa *et al.,* 2016). The increasing effect of temperature indicated that 64.00 % yield was recorded at temperature of

76.36 ^{0}C, reaction time of 120 mins and catalyst concentration of 0.75 %w/w while 92.50 % yield was recorded at temperature of 110 ^{0}C, catalyst concentration of 0.75 %w/w and reaction time of 120 mins. At lower temperature, the reaction is slow irrespective of increase in catalyst concentration because the mixing of pawpaw methyl ester with ethylene glycol over the catalyst affect the yield of biolubricant. Thus, a moderately high temperature and low catalyst concentration favors the conversion of methyl ester to biolubricant.

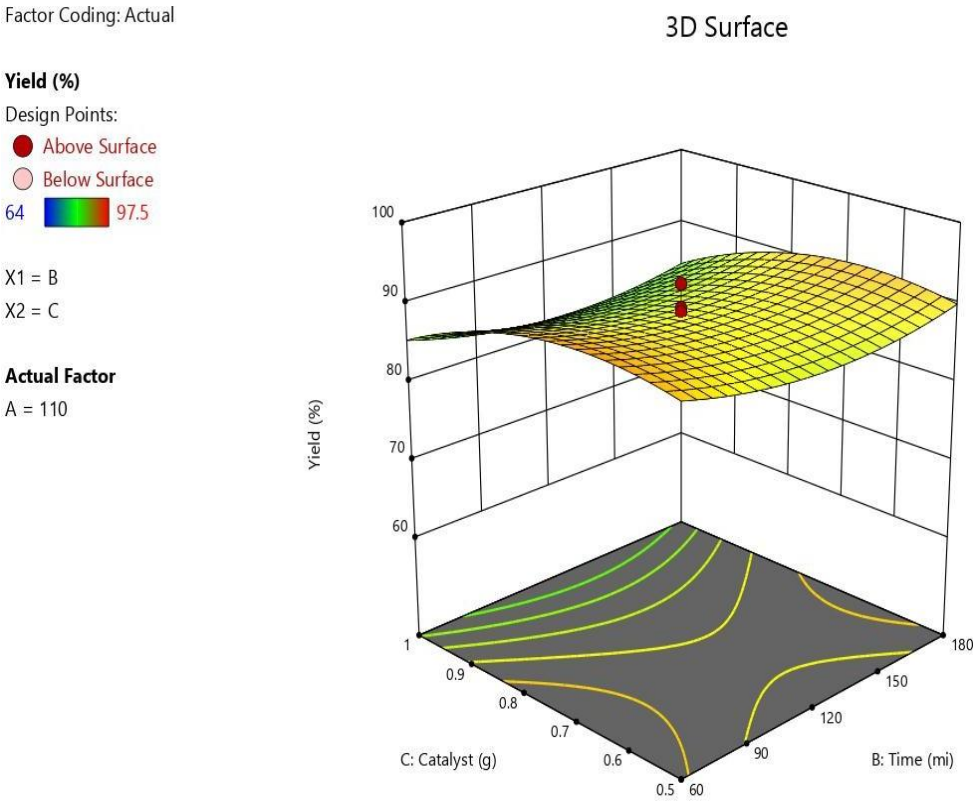

Figure 4.7: 3D Surface Plot Showing Combined Effect of Time and Catalyst Concentration

Figure 4.7 shows the interactive effect of catalyst concentration and time on the yield of biolubricant. There was no significant effect of the increase in catalyst concentration on the yield, this is due to the saponification reaction leading to high

soap formation. 92.50 % yield was recorded at temperature of 110 ^{0}C, catalyst concentration of 0.75 % w/w and reaction time of 120 mins while 90.50 % yield was recorded at reaction time of 220.19 mins, catalyst concentration of 0.75 %w/w and temperature of 110 ^{o}C. The biolubricant yield has a linear relationship with the reaction time, the yield increases from 75.00 % to 95.50 % the reaction time increases from 120 to 220.91 mins Increase in reaction time influence the conversion of pawpaw ester to biolubricant at low catalyst concentration.

4.11 Analysis of Lubricant Properties

The lubricant properties of the produced pawpaw seed tri-ester were examined to decide its suitability for use as a biolubricant based fluid. The values are shown in table 4.9 in comparison with pawpaw methyl ester and tri-ester, other biolubricant and the ISO (International Standard Organization) viscosity grade requirement. The kinematic viscosity, viscosity index, pour point, flash point and density were determined using American society for testing and material (ASTM)

Table 4.9: Properties of PME and PPE in comparison with other plant based biolubricant and ISO grades

Properties	***Methyl Ester this study***	***Poly Ester this study***	***FPBL[a]***	***JPE[b]***	***TMPE[c]***	***ISO VG 32[d]***	***ISO VG 46[d]***	***ISO VG 68[d]***
Viscosity@ 40 {cP}	*45.2.0*	*58.5*	*60.78*	*35.8*	*56.40*	*>28.80*	*>41.40*	*>61.40*
Viscosity@ 100^0C{cP}	*9.70*	*17.80*	*11.03*	*9.30*	*8.80*	*>4.10*	*>4.10.*	*>4.10*
Viscosity Index [VI]	*156*	*165*	*176*	*169*	*193*	*>90*	*>90*	*>190*
Pour point ^0C	*-4*	*-8*	*-5*	*7*	*-3*	*<10*	*<10*	*<10*
Flash point ^0C	*156*	*198*	*152*	*_*	*212*	*>200*	*>220*	*>230*
Density g/cm^3	*0.925*	*0.905*	*_*	*_*	*_*	*0.857*	*0.861*	*0.865*

[a]Mathew *et al.,* (2015), [b] Muhammad *et al.,* (2019) [c]Yeti *et al.,* (2014) and Take from [d]Mathew *et al*., (2015)

4.11.1 Viscosity

The viscosity property is indirectly related to temperature and directly proportional to pressure and film development. Oil with greater viscosity offer greater resistance to flow and if the viscosity of oil is low, it gives low resistance to flow. However, kinematic viscosity is one of the deciding parameters to assess the effectiveness of a lubricant. A rise in kinematic viscosity means increase in the lubricating property of the fluid (Timothy *et al*., 2019). The transesterification has increased the kinematic viscosity of pawpaw seed methyl ester at 40 ^{0}C from 45.20 to 58.5 cSt, this shows

upgrading in biolubricant properties. Conversely, the viscosities of the biolubricant at 40 and 100 ^{0}C are very essential lubricant properties, it determines fluidity of the lubricant at a low and temperature and also show thermal constancy of the lubricant. The viscosity index of pawpaw seed biolubricant were established to be some extent lower than that of Mathew *et al.,* (2015), Muhammad *et al.,* (2019), Yeti *et al.,* (2014), but the viscosities at 40 and 100 ^{0}C and viscosity index pawpaw tri-ester is in agreement with ISO VG 32 and 46 and could meet the requirement since its viscosities is within the range. When the viscosity index of lubricant is high, it indicates that the change in viscosities at higher temperature will be minimal and the viscosity index of pawpaw seed tri-ester is not considered to be low. In general, viscosity index is an important lubricity property for high value viscosity index, the better the lubricant. Nevertheless, the pawpaw biolubricant meets the ISO viscosity grade specifications and therefore can be use as light gear oil, crankcase and hydraulic fluid.

4.11.2 Pour point

This is lowest temperature at which a liquid is capable of flow. Low pour point value is essential for efficient performance of lubricants in cold environments. The pour point pawpaw methyl ester was improved from -4 to -8 ^{0}C, this as a result of a chemical modification on pawpaw seed biodiesel. The pour point obtained was lower when compared with -5, 7 and -3 ^{0}C reported by Mathew *et al.,* (2015), Muhammad *et al.,* (2019) and Yeti *et al.,* (2014) respectively and in agreement with ISO VG 32, 46 and 68 can be use as light gear oil, crankcase and hydraulic fluid.

4.11.3 Flash point

Flash point is the lowest temperature at which a liquid gives adequate concentration of vapor, above it, the mixture form combustible Substances. Flash point is therefore inversely proportional to the fuel volatility (Mohammed *et al*., 2019). The flash point of pawpaw methyl ester was improved from 156 to 198 ^{0}C due to chemical modification on pawpaw methyl ester. Conversely, the flash point obtained for the synthesized pawpaw biolubricant (198 ^{0}C) was found to be better, when compared with 152 ^{0}C reported by Mathew *et al.*, (2015) and low compared to 212 ^{0}C reported by Yeti *et al.*, (2014). Nevertheless, at high flash point the lubricants are safe from fire hazard.

4.11.4 Density

The density of pawpaw bio-based also decrease from 0.925 to 0.905 g/cm^3 when compared with pawpaw methyl ester. This is attributed to modification, hence it improved the lubricity of the biolubricant (Bilal *et al*., 2013The study of papaya seeds oil showed high oil content (31.6), the seed has sufficient oil content and the oil has suitable properties which are similar with other oils that have been applied for bio-fuel production. However, the physicochemical properties of papaya seed oil are in close agreement with that of Syed *et al*. (2011) The high percentage of unsaturated fatty acids would make the oil an acceptable substitute for other highly unsaturated oils. Information provided by present study is of great importance and revealed industrial utilization of the papaya seeds oil as feedstock for bio-fuel production.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

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

I. Pawpaw seeds oil showed high oil content (31.6 %), the seed has sufficient oil content and the oil has suitable properties which are similar with other oils that have been applied for bio-fuel production. However, the physicochemical properties of papaya seed oil are in close agreement with that of Syed *et al*. (2011) The high percentage of unsaturated fatty acids would make the oil an acceptable substitute for other highly unsaturated oils. Information provided by present study is of great importance and revealed industrial utilization of the papaya seeds oil as feedstock for bio-fuel production.

II. The transesterification of pawpaw seed oil with methanol in the presence of potassium hydroxide to produce pawpaw methyl ester (86.50 %). Biolubricant from pawpaw seed oil methyl ester was successfully synthesized by chemical modification through transesterification. The optimization of transesterification via. vital process variable on the yield of pawpaw seed biolubricant. was made possible by three-factorial central composite design using response surface methodology in 20 experimental runs. A second-order quadratic model capable of predicting the pawpaw biolubricant yield based on the process variables was developed. 97.00 % optimum yield was achieved with desirability of 1.000 at optimum conditions of temperature at 130 ^{o}C, reaction time at 180 minutes and catalyst concentration of 0.5 % w/w KOH. Statistical analysis of variance (ANOVA) of results show that temperature has a positive effect on the biolubricant yield, reaction time effect is less significant and catalyst concentration has a negative influence on the

biolubricant yield, though temperature has higher effect than the catalyst concentration.

III. The desirable Properties of biolubricant (viscosity, viscosity index, pour point and flash point) produced were compared with other plant based biolubricant and ISO grades and are in closed agreement with Yeti *et al.* (2014) and ISO 32 and 46 viscosity grade requirement which established its potential usage as light gear oil.

IV. FTIR analysis result shows the appearance of the band peaks of 1118.2 cm^{-1}; 74.572 and 1056 cm^{-1}; 77.43, which were not present in the pawpaw oil and methyl ester samples, is characteristics of the of double transesterification. Complimentary GC-MS analysis result shows that all the fatty acids methyl ester is either saturated or monounsaturated with no detectable di-, tri- and polyunsaturated fatty acids. This is a desirable property with respect to the stability of the biolubricant, high degree of unsaturation has been linked to low stability index. However, such low levels of unsaturation and relatively high proportion of long chain compounds could also have a negative effect on cold finger plugging point and might therefore be responsible for the high levels of cloud and pour points of the biolubricant

5.2 Recommendations

From investigational results and studies, the following recommendations were suggested;

1. The effect of mole ratio, stirring speed and different catalyst on biolubricant production from pawpaw oil methyl ester should be study.

2. The statistical optimization of pawpaw seed oil transesterification should be study using other RSM such as tauguchi, orthogonal and Box bekhen and measure up to the predicted result of this technique with central composite design method used in this study.
3. The kinetics of biolubricant synthesis from pawpaw seed oil should be study to determine the rate constant
4. Other polyols such as trimethylolpropane (TMP), pentraerythriol (PT) and neopenty glycol (NPG) should be used to produce biolubricant from pawpaw seed oil and the result should be compare with that of ethylene glycol.

5.3 Contribution to Knowledge

1. The papaya seed oil was successfully synthesized in to biolubricant through transesterification with validated yield of 80.75 % under the following conditions; temperature of 97.616 0C, 128.102 min and catalyst concentration of 0.873 wt/wt % at a desirability value of 1.000
2. The ethylene glycol was used in this research work and the results were compared with that of trimethylolpropane and ISO grades, which is in agreement with ISO VG 32 and 46.
3. The total error of 0.24 was achieved between actual yield and predicted yield which indicates the fitness of the model equation.

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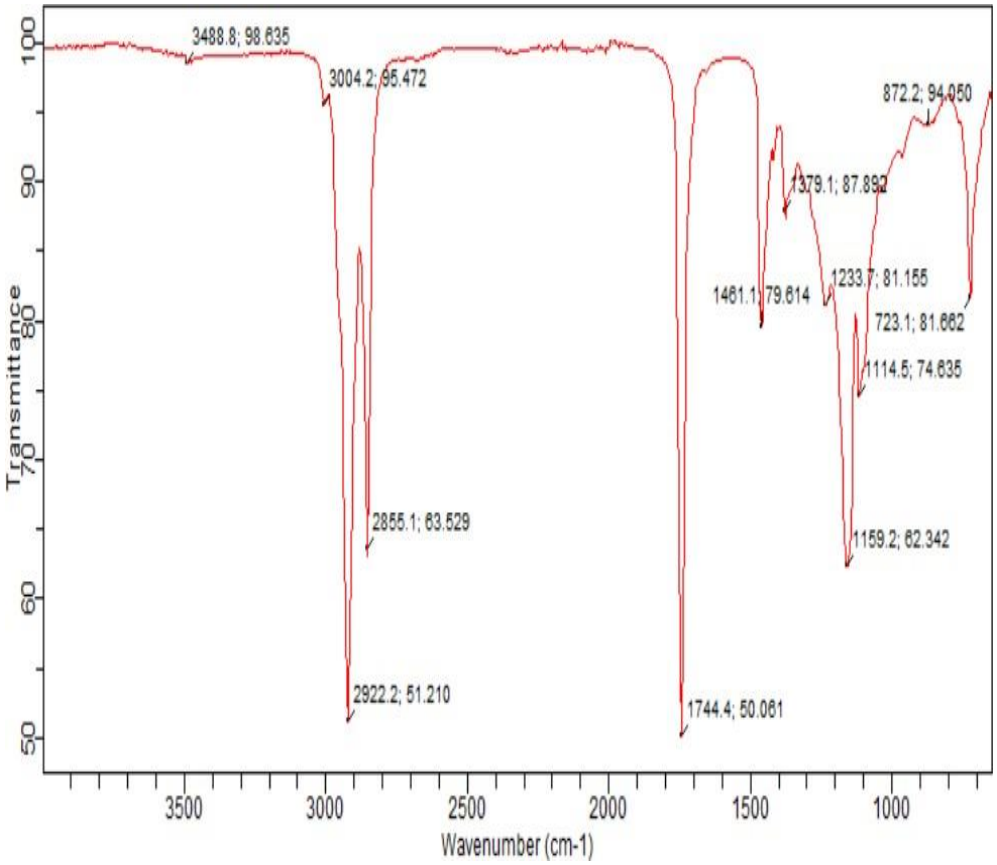
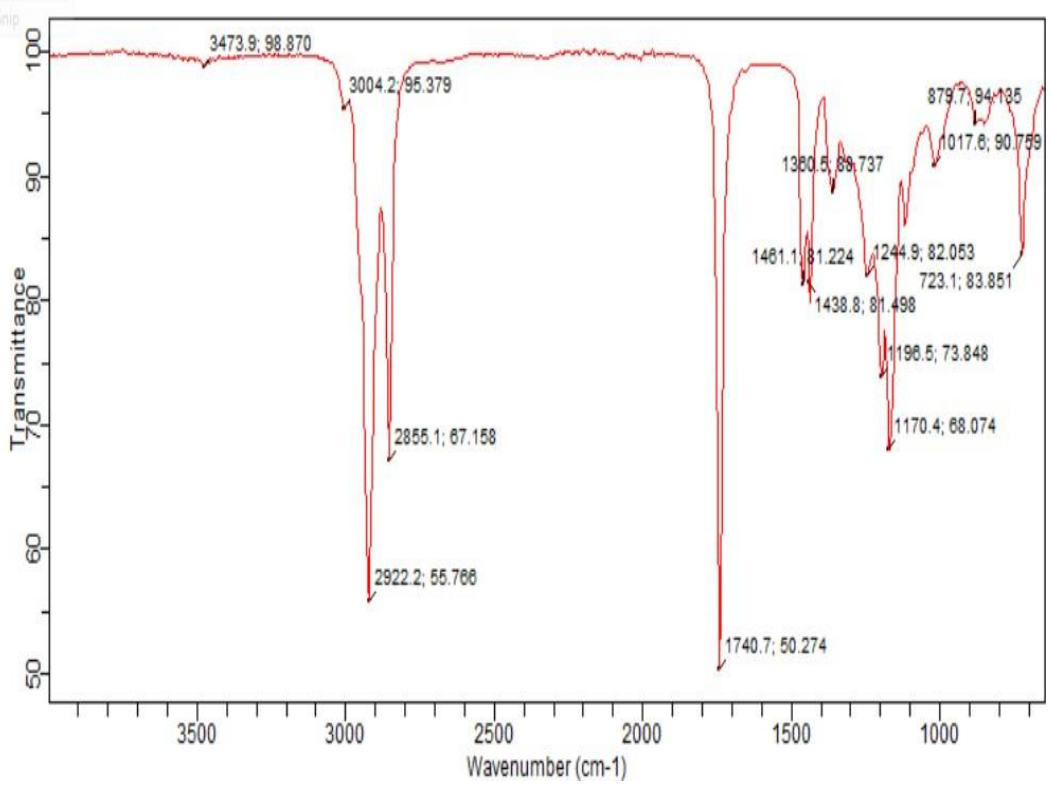
APPENDIX A



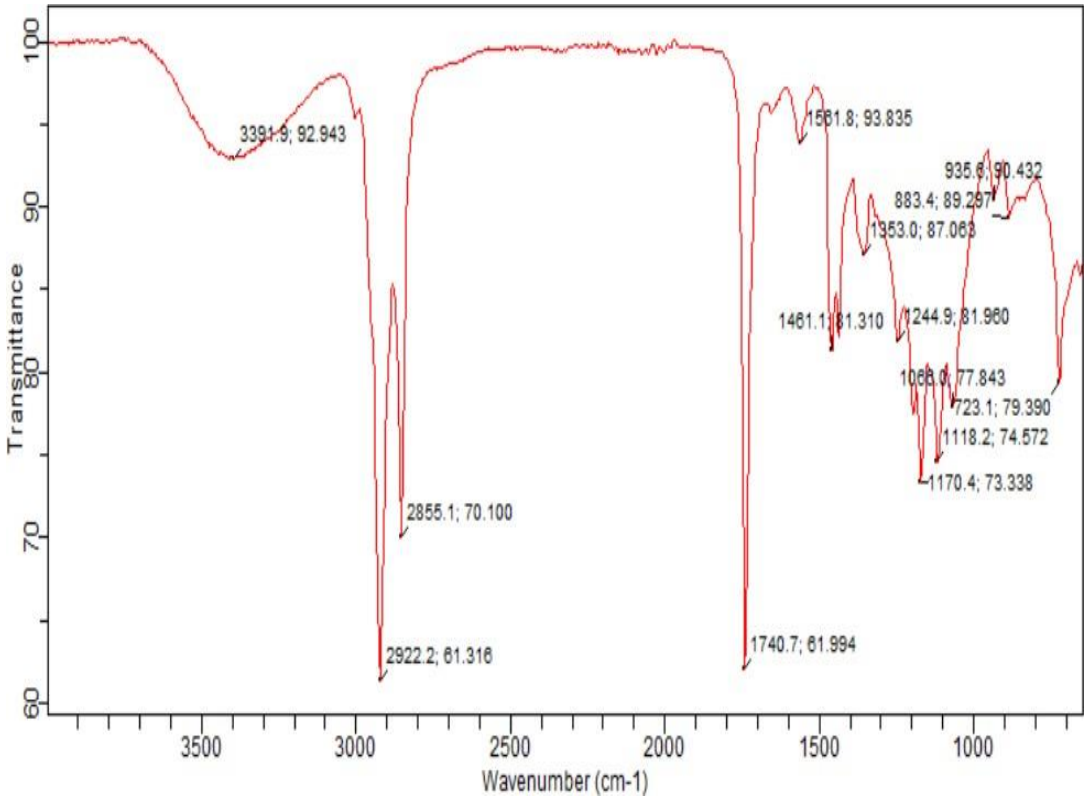
Appendix A1: FTIR Spectrum of Pawpaw Seed Oil

APPENDIX B



Appendix B1: FTIR Spectrum of pawpaw seed oil methyl ester

APPENDIX C



Appendix C1: FTIR Spectrum of Pawpaw Seed Oil Poly Ester

APPENDIX D

Appendix D1: Fatty Acid Composition of Pawpaw Seed Oil

Peak	Time/(min)	Relative content (%)	Component
1	6.357	0.0737	Benzene, 1,2,3-trimethyl-
2	10.642	0.1524	Benzyl nitrile
3	14.1295	0.3885	2-Decenal, (E)-
4	15.8738	0.176	Decanoic acid, methyl ester
5	17.0511	0.4267	Benzene, (isothiocyanatomethyl)-
6	21.1412	4.4173	Dodecanoic acid, methyl ester
7	22.5909	1.1534	Dodecanoic acid
8	25.8491	1.5587	Methyl tetradecanoate
9	27.0254	0.9385	Tetradecanoic acid
10	27.2805	0.1346	1-Octadecene
11	29.599	4.5436	Pentadecanoic acid, 14-methyl-, methyl ester
12	29.9854	0.3557	Palmitoleic acid
13	30.3394	15.3558	n-Hexadecanoic acid
14	30.5901	0.1139	n-Hexadecanoic acid
15	31.2646	20.9668	6-Octadecenoic acid, methyl ester, (Z)-
16	`	1.1295	Methyl stearate
17	31.8088	35.7172	6-Octadecenoic acid
18	31.8797	3.2126	Octadecanoic acid
19	32.5182	0.1925	cis-11-Eicosenoic acid, methyl ester
20	32.653	0.09	eicosanoic acid, 2-methyl-
21	32.8819	0.1307	Dodecanoic acid, 1,2,3-propanetriyl ester
22	32.9966	0.4778	Hexadecane-1,2-diol
23	33.0952	0.085	Dodecanoic acid, 1,2,3-propanetriyl ester
24	33.8669	0.3054	Dodecanoic acid, 1,2,3-propanetriyl ester
25	34.0522	0.1221	Dodecanoic acid, 1,2,3-propanetriyl ester
26	34.2589	0.1714	Dodecanoic acid, 1,2,3-propanetriyl ester
27	34.6873	0.6744	Dodecanoic acid, 1,2,3-propanetriyl ester
28	35.0078	1.012	Dodecanoic acid, 1,2,3-propanetriyl ester
29	35.257	3.1563	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester
30	35.6614	1.0243	Dodecanoic acid, 1,2,3-propanetriyl ester
31	35.838	1.1493	ttDodecanoic acid, 1,2,3-propanetriyl ester
32	36.36	0.3878	Supraene
33	36.9018	0.2059	N-Benzylpalmitamide

APPENDIX E

Appendix E1: Fatty Acid Composition of Biodiesel

Peak	Time (min)	Relative content (%)	Componet
1	7.235	0.0107	Heptanoic acid, methyl ester
2	9.5106	0.0144	Nonanal
3	10.1617	0.7474	Octanoic acid, methyl ester
4	14.0768	0.0381	2-Decenal, (E)-
5	15.9576	2.6733	Decanoic acid, methyl ester
6	16.9193	0.3735	Phenol, 2-methoxy-3-(2-propenyl)-
7	18.5402	0.0373	Undecanoic acid, methyl ester
8	18.8506	0.0539	Nonanoic acid, 9-oxo-, methyl ester
9	21.5075	26.5748	Dodecanoic acid, methyl ester
10	22.8167	0.0067	Cetene
11	22.9486	0.0685	Methyl 10-oxo-8-decenoate
12	23.5852	0.0812	Tridecanoic acid, methyl ester
13	25.5266	0.0733	Methyl Z-11-tetradecenoate
14	26.2601	16.2404	Methyl tetradecanoate
15	27.4533	0.0351	1-Octadecene
16	28.0554	0.0706	Pentadecanoic acid, methyl ester
17	29.3236	0.3	Methyl hexadec-9-enoate
18	29.6921	15.3703	Hexadecanoic acid, methyl ester
19	30.4455	0.1768	cis-10-Heptadecenoic acid, methyl ester
20	30.6424	0.3153	Heptadecanoic acid, methyl ester
21	31.2674	21.0182	trans-13-Octadecenoic acid, methyl ester
22	31.8415	4.7476	9-Octadecenoic acid, methyl ester, (E)-
23	32.1617	0.1143	Nonadecanoic acid, methyl ester
24	32.4618	0.673	Oxiraneoctanoic acid, 3-octyl-, methyl ester, trans-
25	32.5753	2.3515	cis-Methyl 11-eicosenoate
26	32.6936	1.6098	Eicosanoic acid, methyl ester
27	32.8782	0.6889	2-Isopropylidene-5-methylhex-4-enal
28	33.1081	0.63836	Dodecanoic acid, 1,2,3-propanetriyl ester

31	33.6982	0.322	Methyl 11-docosenoate
32	33.8477	1.2334	Methyl 20-methyl-heneicosanoate
33	34.3132	0.1735	Dodecanoic acid, 1,2,3-propanetriyl ester
34	34.5327	0.3372	Methyl 20-methyl-docosanoate
35	35.3019	2.3709	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester
36	35.8199	0.1188	Dodecanoic acid, 1,2,3-propanetriyl ester
37	36.3435	0.1215	4-Cyclopropylcarbonyloxytridecane
38	36.6515	0.0456	Dodecanoic acid, 1,2,3-propanetriyl ester

APPENDIX F

Appendix F1: Fatty Acid Composition of Biolubricant

Peak	Time (min)	Relative content (%)	Component
1	6.66	0.0209	Octanal
2	7.2706	0.0304	Heptanoic acid, methyl ester
3	9.5661	0.0158	Nonanal
4	10.2098	0.7176	Octanoic acid, methyl ester
5	12.9199	0.2794	Octanoic acid
6	13.0569	0.0803	12-Crown-4
7	14.1818	1.5437	Triethylene glycol
8	14.7323	1.8832	Triethylene glycol
9	16.0246	7.0627	Decanoic acid, methyl ester
10	17.0345	0.0742	(E)-Hexadec-2-enal
11	18.4175	0.1721	n-Decanoic acid
12	18.6114	0.0402	Undecanoic acid, methyl ester
13	19.0147	0.0731	Nonanoic acid, 9-oxo-, methyl ester
14	21.5896	17.7469	Dodecanoic acid, methyl ester
15	23.3662	1.6021	Dodecanoic acid
16	23.6137	0.1259	Tridecanoic acid, methyl ester
17	25.5467	0.1585	Octanoic acid, 2-propenyl ester
18	26.2296	9.6423	Methyl tetradecanoate
19	27.4791	0.2832	Tetradecanoic acid
20	28.0932	0.0411	Pentadecanoic acid, methyl ester
21	28.444	0.3017	Dodecanoic acid, 2,3-dihydroxypropyl ester
22	29.3797	0.1691	9-Hexadecenoic acid, methyl ester, (Z)-
23	29.7519	10.8703	Hexadecanoic acid, methyl ester
24	30.2251	0.8239	1,4,7,10,13,16-Hexaoxacyclooctadecane
25	30.6959	0.5226	n-Hexadecanoic acid
26	31.3061	17.3698	8-Octadecenoic acid, methyl ester, (E)-
27	31.7425	3.0826	Dodecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester
28	31.9491	1.0238	Isobutyric acid, tetradecyl ester
29	32.2717	0.3198	Palmitoyl chloride

30	32.5863	1.8049	cis-13-Eicosenoic acid, methyl ester
31	32.7102	1.6246	Eicosanoic acid, methyl ester
32	32.9039	0.4878	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester, trans-
33	33.1436	6.9361	Silane, [(methylsilyl)methyl](silylmethyl)-
34	33.3308	1.0706	9-Octadecenoic acid (Z)-, 2-hydroxyethyl ester
35	33.4667	0.2939	Methyl 2-octylcyclopropene-1-octanoate
36	33.629	0.6066	Glycidyl oleate
37	33.749	0.2089	(E)-13-Docosenoic acid
38	33.9679	1.7918	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester
39	34.3674	2.4023	Propionic acid, 3-(sec-butylthio)-

Peak	Time (mins)	Relative Content (%)	‘Component
40	34.5801	0.1211	Tricosanoic acid, methyl ester
41	35.3996	3.4643	Oleic acid, 3-hydroxypropyl ester
42	36.1351	2.9461	Propionic acid, 3-(sec-butylthio)-
43	36.4019	0.0817	Cyclohexanone, 2-(1-mercapto-1-methylethyl)-5-methyl-, trans-
44	36.9652	0.0296	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester
45	37.2091	0.0521	Quinolin-4-ol, 7-trifluoromethyl-2-methyl-

APPENDIX G

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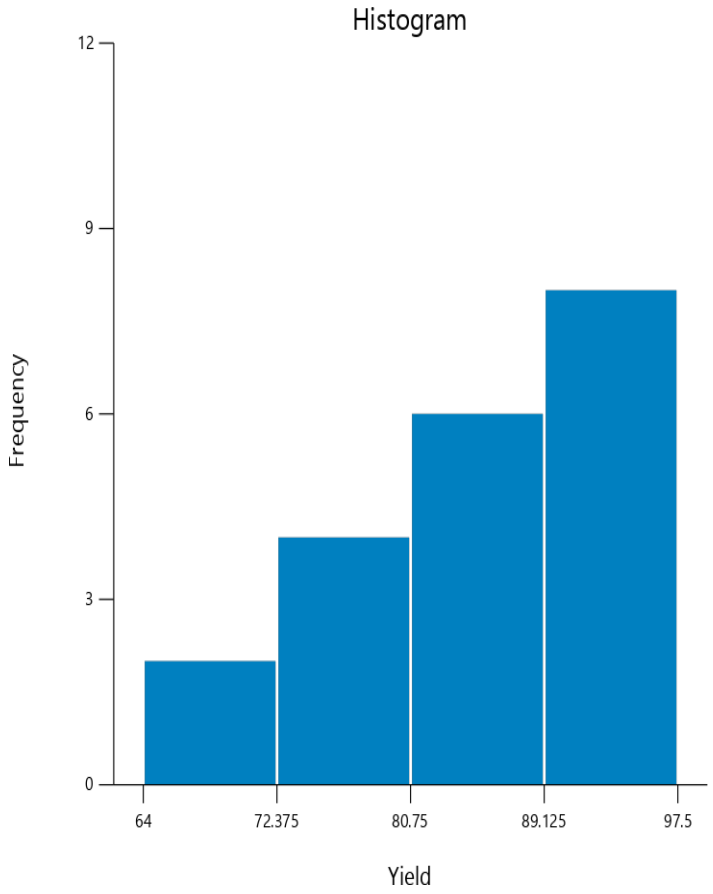

Appendix G1: Histogram on Biolubricant Yield

APPENDIX H

Appendix H1: Validated Biolubricant Yield

Number	Temp. (^{0}C)	Time (Mins)	Catalyst (%)	Yield (%)	Desirability
1	**97.616**	**128.102**	**0.873**	**80.750**	**1.000**
2	95.688	123.865	0.811	80.750	1.000
3	93.967	112.882	0.755	80.750	1.000
4	90.583	61.828	0.989	80.750	1.000
5	90.387	67.525	0.514	80.750	1.000
6	93.629	102.201	0.831	80.750	1.000
7	98.211	176.291	0.514	80.750	1.000
8	97.984	151.707	0.542	80.750	1.000
9	101.032	171.251	0.951	80.750	1.000
10	94.670	121.570	0.715	80.750	1.000
11	100.742	156.277	0.934	80.750	1.000
12	101.821	118.062	0.969	80.750	1.000
13	91.214	77.261	0.548	80.750	1.000
14	96.353	118.398	0.558	80.750	1.000
15	95.972	87.022	0.959	80.750	1.000
16	96.223	169.988	0.647	80.750	1.000
17	95.756	134.271	0.765	80.750	1.000
18	96.372	131.657	0.598	80.750	1.000
19	100.343	137.333	0.927	80.750	1.000
20	96.105	170.951	0.661	80.750	1.000
21	93.315	89.234	0.547	80.750	1.000
22	94.594	118.626	0.670	80.750	1.000
23	100.47	156.324	0.928	80.750	1.000

	6				
24	103.528	160.541	0.985	80.750	1.000
25	91.931	79.650	0.539	80.750	1.000
26	91.337	72.497	0.516	80.750	1.000
27	97.684	142.051	0.550	80.750	1.000
28	91.619	79.916	0.551	80.750	1.000
29	93.950	103.186	0.838	80.750	1.000
30	93.014	98.746	0.618	80.750	1.000
31	101.752	157.079	0.954	80.750	1.000
32	96.162	132.385	0.613	80.750	1.000
33	92.668	85.368	0.902	80.750	1.000
34	95.824	102.102	0.901	80.750	1.000

Number	Temp	Time (mins)	Catalyst	Yield	Desirability

	(^{0}C)		(%)	(%)	
35	95.923	175.227	0.741	80.750	1.000
36	92.611	102.647	0.733	80.750	1.000
37	91.582	92.171	0.648	80.750	1.000
38	96.025	149.815	0.701	80.750	1.000
39	95.926	144.814	0.722	80.750	1.000
40	95.184	81.936	0.966	80.750	1.000
41	94.968	125.401	0.718	80.750	1.000
42	103.056	106.718	0.998	80.750	1.000
43	97.085	147.872	0.585	80.750	1.000
44	105.008	138.404	0.996	80.750	1.000
45	91.350	92.486	0.672	80.750	1.000
46	96.542	141.503	0.803	80.750	1.000
47	100.613	96.866	0.990	80.750	1.000
48	95.975	141.331	0.663	80.750	1.000
49	97.488	140.557	0.557	80.750	1.000
p50	98.622	92.437	0.978	80.750	1.000
51	104.908	154.512	0.999	80.750	1.000
52	95.888	129.428	0.799	80.750	1.000
53	97.583	131.961	0.541	80.750	1.000
54	98.325	129.567	0.510	80.750	1.000
55	105.075	131.080	0.998	80.750	1.000
56	98.147	177.083	0.883	80.750	1.000
57	94.528	85.348	0.941	80.750	1.000
58	101.643	107.522	0.982	80.750	1.000
59	94.953	124.731	0.734	80.750	1.000

60	98.410	117.541	0.914	80.750	1.000
61	95.665	130.261	0.779	80.750	1.000
62	93.279	105.311	0.782	80.750	1.000
63	94.354	117.159	0.746	80.750	1.000
64	96.545	120.994	0.558	80.750	1.000
65	95.845	121.352	0.592	80.750	1.000
66	97.483	133.147	0.547	80.750	1.000
67	94.851	120.163	0.655	80.750	1.000
68	96.975	148.445	0.592	80.750	1.000
69	98.261	134.835	0.519	80.750	1.000
70	96.999	158.502	0.594	80.750	1.000
71	94.088	114.817	0.739	80.750	1.000
72	104.050	135.077	0.985	80.750	1.000
73	95.522	123.017	0.805	80.750	1.000
74	94.385	77.243	0.973	80.750	1.000

Number	Temp (^{0}C)	Time (mins)	Catalyst (%)	Yield (%)	Desirability
75	97.689	102.590	0.937	80.750	1.000
76	97.194	120.561	0.532	80.750	1.000
77		124.030	0.963	80.750	1.000
78	97.230	153.734	0.580	80.750	1.000
79	96.875	113.936	0.525	80.750	1.000
80	95.466	120.102	0.816	80.750	1.000
81	92.687	94.014	0.600	80.750	1.000
82	96.028	146.534	0.678	80.750	1.000
83	97.695	150.318	0.555	80.750	1.000
84	91.756	63.220	0.999	80.750	1.000
85	102.334	102.240	0.997	80.750	1.000
86	95.344	94.834	0.918	80.750	1.000
87	103.834	130.170	0.984	80.750	1.000
88	95.126	100.493	0.538	80.750	1.000
89	102.420	116.835	0.978	80.750	1.000
90	95.655	111.687	0.860	80.750	1.000
91	95.674	108.605	0.551	80.750	1.000
92	95.361	107.133	0.557	80.750	1.000
93	98.864	119.159	0.920	80.750	1.000
94	93.979	113.620	0.743	80.750	1.000
95	96.487	138.096	0.807	80.750	1.000
96	95.863	125.765	0.608	80.750	1.000
97	94.499	119.438	0.705	80.750	1.000

98	94.214	107.273	0.825	80.750	1.000
99	103.284	175.320	0.996	80.750	1.000
100	130.000	79.908	1.000	82.643	0.887