Production of Bio-Lubricant from Citrullus Colocynthis (Bitter Apple) Seed Oil by Two Step Process

Ababu Girma Teshome

Thesis Paper Submitted to Chemical Engineering

School of Mechanical, Chemical, and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

November 2022

Adama, Ethiopia

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Advisors: Zelalem Tumsa (Ph.D.)

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DECLARATION

I hereby declare that this Master Thesis entitled "Production of Bio-Lubricant from Citrullus Colocynthis (Bitter Apple) Seed Oil by Two Step Process" is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Ababu Girma _____ _____

Name of the student Signature Date

RECOMMENDATION

We, the advisor(s) of this thesis, hereby certify that we have read the revised version of the thesis entitled "Production of bio-lubricant from citrullus colocynthis (bitter apple) seed oil by two step process" prepared under my/our guidance by Ababu Girma Teshome submitted in partial fulfillment of the requirements for the degree of Mater's of Science in Chemical Engineering (Specialization Process Engineering). Therefore, I/we recommend the submission of the revised version of the thesis to the department following the applicable procedures.

Zelalem Tumsa (PhD)	_____	_____
Major Advisor	Signature	Date
Melaku Tesfaye (PhD)	_____	_____
Co-Advisor	Signature	Date

Approval Page

We, the advisors of the thesis entitled "Production of bio-lubricant from citrullus colocynthis (bitter apple) seed oil by two step process" and developed by Ababu Girma Teshome hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Zelalem Tumsa (PhD)	_____	_____
Major Advisor	Signature	Date
Melaku Tesfaye (PhD)	_____	_____
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Ababu Girma have read and evaluated the thesis entitled "Production of bio-lubricant from citrullus colocynthis (bitter apple) seed oil by two step process" and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering (Specialization in process engineering).

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LIST OF ACRONYMS, and ABBREVIATIONS

AOCS	American Oil Chemists' Society
ASTM	American Society for Testing and Materials
CCO	Citrullus colocynthis seed oil
CCOME	Citrullus colocynthis oil methyl ester
CP	Cloud point
DAG	Diglyceride
DE	Diesters
EG	Ethylene glycol
EP	Ester phase
FA	Fatty acids
FAME	Fatty acid methyl esters
FFA	Free fatty acids
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography Mass spectroscopy
GP	Glycerol phase
ISO-VG	International Standards Organization Viscosity Grade
MAG	Monoglyceride
ME	Methyl esters
NMR	Nuclear magnetic resonance
NPG	Neopentyl glycol
PE	Pentaerythritol
PP	Pour point
PUFA	Polyunsaturated fatty acids
TAG	Triglyceride
TGA	Thermal gravimetric analysis
TE	Triesters
TMP	Trimethylolpropane
VI	Viscosity index
LD_{50}	Lethal Dose

ABSTRACT

Bio-lubricants are functional fluids made from seed oils and animal oils. Bio-lubricants could be applying to all lubricants that are both rapidly biodegradable and non-toxic to humans and aquatic environments. Environmental problems caused by petroleum based lubricants and the depletion of oil reserves that have led to the need for renewable and biodegradable lubricants that derived from alternative sources. Bio-lubricants have several advantages over mineral oil lubricants such as high biodegradability, low toxicity, excellent lubricating performance, and minimal impact on the environment and human health. This aimed to develop and evaluate a biodegradable lubricant-grade ester using a Citrullus colocynthis (Bitter apple) seed oil as primary feedstock. To synthesis bio-lubricant, first crude oil was extracted. Response surface methodology was applied to extract Citrullus colocynthis seed oil from this plant seed to optimize the extraction parameters such as extraction temperature (78-90 ^{o}C), extraction time (3-6 hr.), and ethanol-to-solid ratio (10:1-30:1 ml/g). The fatty acid methyl ester was synthesized from extracted crude oil at a temperature of 60 ^{o}C, a reaction time of 1 hour, a molar ratio of oil to methanol 1:6, and 1% w/w NaOH as a catalyst via first transesterification. The bio-lubricant was synthesized by double transesterification of FAME with ethylene glycol, using sodium hydroxide as a catalyst. The effect of reaction temperature (160,170, &180 ^{o}C), ethylene glycol to FAME ratio (1:1,2:1&3;1), and catalyst loading (0.5%,1% &2% w/w) was analyzed. The extracted seed oil, synthesized FAME, and bio-lubricant were confirmed by FTIR, and TGA, analysis. In addition, the extracted oil was analyzed by GC-MS, whereas the synthesized FAME was analyzed by NMR. The optimum extraction conditions, obtained by the RSM were extraction temperature of 84 ^{o}C, extraction time of 4.5 hrs., and ethanol to solid ratio of 20:1 resulted in oil yield (Y1) of 52.1%. The maximum yield of bio-lubricant obtained was also 92.15% at a reaction temperature of 170 ^{o}C, ethylene glycol/FAME molar ratio 3:1, and catalyst concentration 1%w/w, reaction time of 120 minutes. The viscosity of synthesized bio-lubricant at 40 and 100 ^{o}C was 408.45 cSt and 66.62 cSt respectively. Similarly, a viscosity index of 239 was obtained. Based on this, it can be categorized under gear lubricant oil. It also had some properties better than petroleum lubricant: - (Flash point 272 ^{o}C, and the density of 0.947 g/cm^{3}, which was good as ASTM D 6751 standard. The synthesized bio-lubricant had a good surface roughness of 1.49 µm, during the machining process compared to water, mineral oil, and dry cutting processes. Therefore, as mainly proposed, this study showed that bio-lubricant from Citrullus colocynthis seed oil has a great potential to obtain lubricants with high surface finish, and better physicochemical properties.

***Keywords**: Bio-lubricant; Citrullus colocynthis seed oil; Double transesterification; Ethylene glycol; Fatty acid methyl ester; Machining.*

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Lubricants are organic compounds capable of reducing friction between two surfaces in motion, in addition to reducing heating and wear of mechanical parts by forming a protective film by interposing a lubricating substance. It is widely used in the automobile and equipment industries (Jain & Suhane, 2013, Nagendramma & Kaul, 2012, Ceró n et al., 2018). The usage of wooden axles and wheels, or perhaps a combination of metallic axles and wheels, could produce a significant amount of wear and friction. For those mechanical machines, lubrication becomes a fundamental requirement (Panchal et al., 2017). When moving surfaces move against each other, friction will result. To reduce this friction, a lubricant is used. The main purposes of lubrication are (i) to reduce wear and prevent heat loss that results due to contact of surfaces in motion, (ii) to protect it from corrosion and reduce oxidation; (iii) to act as an insulator in transformer applications; and (iv) to act as a sealing agent against dirt, dust, and water. While wear and heat cannot be eliminated, they can be reduced to negligible or acceptable levels by the use of lubricants. As heat and wear are associated with friction, both effects can be minimized by reducing the coefficient of friction between the contacting surfaces. Any material used to reduce friction in this way is a lubricant. Lubricants are to be had in liquid, solid, and gaseous forms, amongst which liquid and strong or semisolid are used widely in day-to-day lifestyles (Panchal et al., 2017), insulating transformers, and preventing rust and oxidation (Samidin et al., 2021). Nearly 10,000 different oil, grease, and other functional fluid formulas are available in the lubrication industry to satisfy more than 90% of all lubricant applications (Panchal et al., 2017). An estimated 30 to 40 million tons of lubricant are used each year, 20 million tons of which enter the environment, representing a loss of lubricant of approximately 55%. More than 95% of these lubricants that are released into the environment are petroleum-based and damaging to the environment (Heikal et al., 2017). Petroleum-based lubricants can be synthesized from mineral oil or natural gases. Petroleum-based lubricants and functional fluids (hydraulic fluids) pose a serious hazard to the environment due to their high toxicity and low biodegradability. Traditionally, over 85% of base oils are refined from crude petroleum. However, with the decreasing stocks of petroleum and high costs of synthetic lubricant, plant oils are considered to be potential to supply high-quality lubricant base oil

for lubricant production. More remarkably, some claim that bio-lubricants might replace almost 90% of all petroleum-based lubricants. The term bio-lubricants applies to all lubricants that are both rapidly biodegradable and non-toxic to humans and aquatic environments. A bio-lubricant may be seed oil-based (e.g., rapeseed oil) or derived from synthetic esters manufactured from modified renewable oils. A much less environmentally-dangerous alternative to petroleum-derived lubricants is presented as bio-lubricants, derived from seed oil and other renewable assets (Yazdi & Kabir, 2017, Nor et al., 2019, Alfieri et al., 2018). Although seed oils possess many desirable characteristics, currently they are not widely used as lubricant base oils. Largely this is due to undesirable physical properties of most plant oils, which include both a high melting point and insufficient thermal oxidative stability (Nie, 2012). Natural triglycerides (TAGs), the major component of vegetable oils, consist of a glycerol backbone with three esterified long-chain fatty acids. The base oil is usually a kind of plant oil extracted from olives, palm, soybean, canola, rapeseed, castor beans, tallow, jojoba, coconut, *Citrullus colocynthis*, and jatropha (Salih & Salimon, 2021). The physical properties of plant oils are strongly influenced by the glycerol structure and the fatty acid profile. On one hand, glycerol is not desirable in lubricants as the β hydrogen in glycerol triesters (TE) is unstable and susceptible to elimination reactions, which lead to degradation of the molecule. On the other hand, the geometry of TAG includes three ester groups arranged such that steric hindrance between the fatty acid groups is minimized. This arrangement may lead to organized packing of the molecules and the formation of crystals during cooling. The instability and high melting point of seed oils maybe significantly improved by converting natural fatty acyl esters into synthetic esters (Nor et al., 2019, Alfieri et al., 2018).

Increasing oxidative stability and pour point temperature is the main challenges to improve the quality of bio-lubricants (Nor et al., 2019). The most promising processes focus on the modification of unsaturated oils through chemical processes, since double bonds are prone to reactions with atmospheric oxygen. The bio-lubricant can be synthesized by several methods such as epoxidation, selective hydrogenation, transesterification, and estolide production (Syahir et al., 2017). Transesterification is the most widely used method and is recommended because it can produce a yield higher than 90% (Panchal et al., 2017). Furthermore, the advantage of transesterification is increased oxidative stability so that the bio-lubricant is not easily damaged by oxidation (Alfieri et al., 2018). When plant oil is utilized as the source of fatty acids for the production of synthetic esters, a more resistant

polyol may be chosen to replace the glycerol backbone (Panchal et al., 2017). This replacement reaction requires at least two reactions, one to remove the glycerol and the second to esterify the polyol (Alfieri et al., 2018). Ethylene glycol (EG), Neopentyl glycol (NPG), and trimethylolpropane (TMP) are the common polyols that have been used to produce synthetic esters lubricating oils (Syahir et al., 2017).

Depending on the catalysts used, transesterification reactions can be categorized. For example, acid catalysts, base catalysts, and enzymes have all been used for transesterification. Transesterification that is catalyzed by enzymes is a somewhat expensive reaction that is rarely used in industrial manufacturing. Acid-catalyzed transesterification is a one-step process that can produce polyol esters from polyol and fatty acids. However, acid-catalyzed reactions require a longer reaction time and may produce a lower yield of polyol esters than possible using a base catalyst (Hafizah & Salmon, 2010). Base catalyzed production of polyol fatty acid esters typically requires two stages of transesterification when the initial feedstock is vegetable oil (Alfieri et al., 2018). From 1998 to 2011, there have been several reports of polyol esters synthesis using different TAG sources via two-step base-catalyzed transesterification (Nie, 2012). Methanolysis of TAG with alkali catalyst is a preferred first reaction that achieves a high reaction rate. This reaction proceeds to near completion due to the low solubility of glycerol in the methyl ester and the effective removal of this production from the reaction (Syahir et al., 2017). The second transesterification of fatty acid methyl esters (FAME) with EG is, comparatively, a slower reaction. Driving this reaction near completion requires a high vacuum to remove the by-product methanol and excess of FAME to shift the equilibrium to the formation of a polyol ester (Syahir et al., 2017). In general, lubrication is the process, or method used to reduce the wear of one or more neighboring surfaces as they move with one another by introducing a lubricant between the surfaces to support or help deliver the load (pressure generated) among the opposing surfaces (Alfieri et al., 2018).

This study focus on the synthesis and characterization of bio-lubricant from Citrullus colocynthis seed oil using double transesterification reaction. The effect of reaction condition on bio-lubricant yield also examined. Additionally, this work focuses on determining the quality of bio-lubricant (determining the surface roughness of material using bio-lubricant as cutting fluid and comparing it with other cutting fluids (water, and mineral oil) and dry cutting.

1.2. Statement of the Problems

Nowadays, the increasing prices of crude oil, the depletion of crude oil reserves, and protecting environmental pollution have renewed interest in developing and using environment-friendly lubricants derived from alternative sources. Bio-based materials are manufactured using feedstock's originating from plants and animals (Alang et al., 2018, Mobarak et al., 2014). They differ from petroleum-based materials in that they have an unlimited and renewable raw material base. Due to their low toxicity, high lubricant viscosity index, high ignition temperature, increased equipment service life, high load-carrying capacity, excellent coefficient of friction, natural multi-grade properties, low evaporation rates, and low emissions into the atmosphere, bio-lubricants are potential alternative lubricants (Mobarak et al., 2014, Hassan et al., 2019). The non-biodegradability of mineral lubricants, their non-renewability, and contamination of soil, water, and air, poses threatening conditions for danger and damage to human health and well-being, the welfare of plants and animals as well as the environment as a whole. Especially petroleum-based lubricants can cause cancer and dermatitis (Hassan et al., 2019). Besides, the release of petroleum oil into the environment can affect animals and plants in two ways: direct from the oil and the response. Petroleum oil penetrates the structure of the plumage of birds and can impair a bird's ability to fly and the fur of mammals, reducing their insulating ability, and making them more vulnerable to temperature fluctuations and much less buoyant in the water. In addition, the release of petroleum oil into the environment affects human health and well-being, the welfare of plants and animals' digestive tract, altering liver function, and causing kidney damage (Hassan et al., 2019). Together with their diminished foraging capacity, this can rapidly result in dehydration and metabolic imbalance. Some plants and animals exposed to petroleum also experience changes in their hormonal balance, including changes in their luteinizing protein. The majority of mammals and plants affected by petroleum oil spills die from complications without human intervention (Wolfaardt et al., 2009). Finally, the release of petroleum oil can also harm air quality and can also contaminate drinking water supplies (Middlebrook et al., 2012). The chemicals in crude oil are mostly hydrocarbons that contain toxic chemicals such as benzenes, toluene, poly-aromatic hydrocarbon, and oxygenated polycyclic aromatic hydrocarbons. These chemicals can introduce adverse health effects when being inhaled into the human body (Ehrenhauser et al., 2014). Lubricants consumed worldwide are commonly originated from petroleum, coal, or natural gases. However, these sources are infinite and keep depleting due to high

fuel consumption over the world (Alang et al., 2018). Motivated researchers and scientists are now more interested than ever in finding sustainable, renewable materials to replace the fossil fuels used in lubricants. Due to their quick biodegradability and minimal environmental toxicity, bio-lubricants are preferred over conventional lubricants (Alang et al., 2018, Hassan et al., 2019). Herein, the objective of this research is to use the plant seed as a starting point to synthesize and analyze a potential environmentally friendly bio-based lubricant (bio-lubricant) from *Citrullus colocynthis* seed oil.

1.3. Research Question

The present research work aims to answer the following major research questions.

- Can it be possible to produce bio-lubricant base oil grade from *Citrullus colocynthis* seed which have high flash point in comparison with petroleum lubricant?
- Can it be possible to synthesize better quality bio-lubricant as compared to mineral oil?

1.4. Objectives

1.4.1. General Objective

The general objective of this thesis is:

- To produce bio-lubricant from *citrullus colocynthis* (bitter apple) seed oil by two step process and investigate reaction condition on the bio-lubricant yield

1.4.2. Specific Objectives

The specific objectives of this thesis are:

- To extract and characterize crude oil from *Citrullus colocynthis* seed,
- To synthesize and characterize fatty acid methyl ester from *Citrullus colocynthis* seed oil,
- To synthesize and characterize a bio-lubricant from *Citrullus colocynthis* oil methyl ester,
- To investigate the effect of reaction temperature, alcohol to FAME molar ratio, and catalyst loading on bio-lubricant yield,
- To evaluate the quality (lubricity) of bio-lubricant (the surface roughness of material being cut using a bio-lubricant in comparison to water, mineral oil, and dry cutting).

1.5. Significance of the Research

This study presents the potential of a bio-lubricant based on *citrullus colocynthis* seed oil as an alternative lubricant, this will include: the source, properties, as well as advantages and

disadvantages of the bio-lubricant the potential of *citrullus colocynthis* seed oil-based bio lubricants as alternative lubricants for any applications. This type of project will minimize importing petroleum-based lubricants by replacing them with biodegradable and renewable lubricant which has better characteristics than the recent one and will in turn decrease the cost of importation, and transportation (Focke et al., 2012). In this way the country will become energetically self-sufficient, with no fear of the depletion of petroleum reservoirs, it also brings the county to a green economy system. Environmentally it has also the advantage of decreasing the deposits from automobiles that use petroleum-based products, and wastes that are going to be released after usage. By doing so the first beneficiaries will be farmers who are going to prepare a farm for this plant and maximize agriculture in our country. Due to the source, and properties of mineral oil as well as advantages of the bio-lubricant, this paper possesses on the production of bio-based lubricants from *Citrullus colocynthis* (Bitter apple) seed oil, which has a significant area on society, the environment, and the country. The synthesized bio-lubricant can also be used as cutting fluid in machining. During machining the gradual breakdown of the machine tool as a result of the cutting operation, eventually leading to tool failure. To reduce such cracks of materials, cutting fluids are used in metal machining for a variety of reasons such as improving tool life, reducing work piece and thermal deformation, improving surface finish, and flushing away chips from the cutting zone by synthesizing bio-based lubricant (Susmitha et al., 2016).

1.6. Scope of the Study

In this work, extraction of crude oil from *Citrullus colocynthis* seed was performed. Then synthesis of FAME from Citrullus seed oil was done. In addition, bio-lubricant has been synthesized by the transesterification process. The synthesized sample has been characterized by using different techniques and its physio-chemical properties have been evaluated and compared with the standard. Moreover, an investigation of the effect of reaction temperature, alcohol to FAME molar ratio, and catalyst loading on bio-lubricant has been analyzed. Finally, the applications of bio-lubricant as cutting fluid were investigated, and also compare its surface finish with other cutting fluids such as water and mineral oil and the dry cutting process.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Introduction

A lubricant is a substance that is introduced between two surfaces that are moving relative to one another to minimize the friction between them and the wear and tear caused by contact of the surfaces (Cerón et al., 2018). Most lubricants are usually solutions or colloids that contain a lubricating solvent or base fluid together with certain components that improve their lubrication properties. Modern lubricant base fluids include animal oils, vegetable oils, synthetic esters, and mineral oils. Lubricants minimize wear and friction on moving surfaces (Nie, 2012). The term "lubricity" refers to a lubricant's capacity to decrease wear and friction. A lubricant increases a surface's operational lifespan by minimizing wear, and by lowering friction, it lowers the energy needed to move surfaces.

Additionally, lubricants lower the amount of heat generated by moving parts, prevent corrosion, and reduce the exposure of surfaces to corrosive substances and wear particles (Cerón et al., 2018). High viscosity index, good thermal and oxidative stability, good cold fluidity, and low volatility are all necessary for an effective lubricant base fluid (Owuna et al., 2020).

2.2 Historic Development of Lubricants

Since the beginning of civilization, people have used lubricants to help reduce the amount of energy needed to slide two objects against one another. Liquid lubrication was valuable as the first lubricant for transporting sleds in the Sumerian and Egyptian civilizations, and it is recorded that grease, oil, or mud have been used as a lubricant as early as 2400 B.C. (Nie, 2012). From the first century A.D., animal fats and plant oils were the principal lubricants used in machineries such as lathes, pulleys, and gears. Heavy industrial iron and steel machinery was widely adopted during the industrial revolution, around 1760. As lubricants, the usage of vegetable and animal oils from sources like palm and groundnut oil and sperm whale oil increased (Owuna et al., 2020).

2.3. Classification of Plant Oils

The fat obtained from plant sources is known as plant oil. Although we can also get oil from other sections of a plant, seeds are the main source of plant oil. The plant oils are categorized using the bases listed below (Han et al., 2019):

i) Classification based on source:

- tree crop oil: palm oil, coconut oil, and olive oil;
- annual crop oil: groundnut oil, sunflower oil, etc.;
- by-product oil: rice bran oil and soy bean oil.

ii) Classification based on availability:

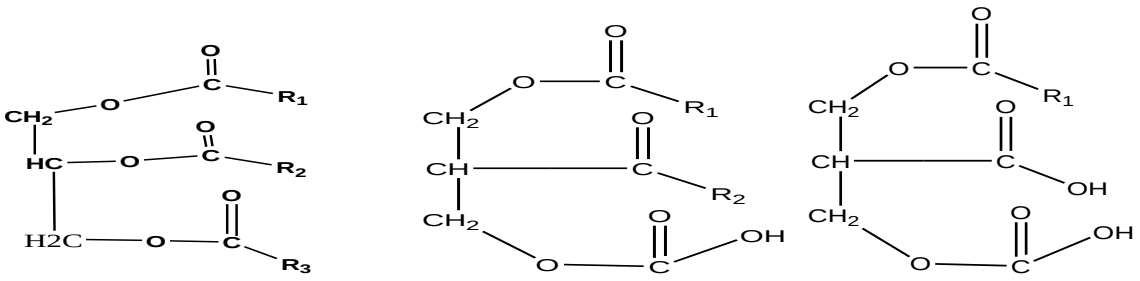
- major oil: coconut oil, groundnut oil, sunflower oil, soybean oil;
- minor oils: almond oil, apricot oil, avocado oil, and candlenut oil.

iii) Classification based on end use:

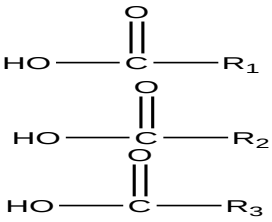
- edible oils: coconut oil, sunflower oil, soybean oil, and palm oil;
- non-edible oils: castor oil, Jatropha curcas oil, Jojoba oil, *Citrullus colocynthis*, etc.

2.3. Plant Oils Chemical Structure

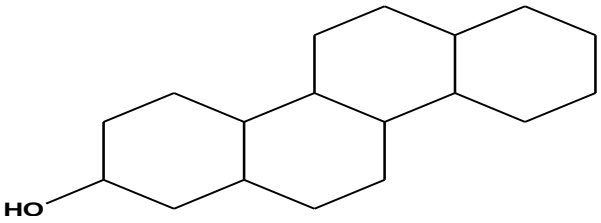
Plant oils differ from mineral oils in terms of their structure. Triacylglycerols (TAG) are the primary component of plant oils, accounting for 98% of total weight, and their fatty acid composition varies depending on the type of plant, crop, season, and growing conditions. Diacylglycerols (DAG), monoacylglycerols (MAG), fatty acids (FAs), sterols (0.3%), and tocopherols are the minor additions found in plant oils (0.1%) (Salih & Salimon, 2021). The majority of these small components are eliminated during processing, while some are useful byproducts. Fatty acids, which are long-chain molecules having 8–24 carbon atoms, are the building blocks used to describe the makeup of plant oils. Seed oils' chemical composition, which differs geographically from place to place, is what determines how effective they are. The majority of the Seed oils' physical and chemical qualities are caused by the constituent fatty acids because they produce larger amounts of triacylglycerol (Nor et al., 2019, Afifah et al., 2019).



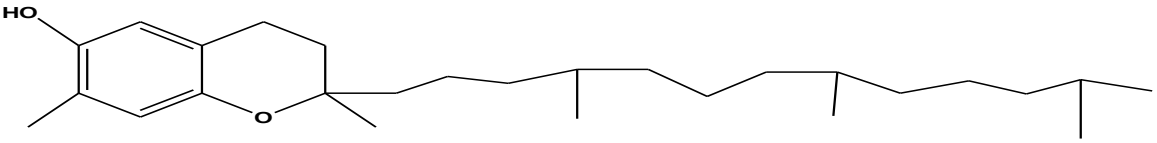
TGA DAG MAG



FAS



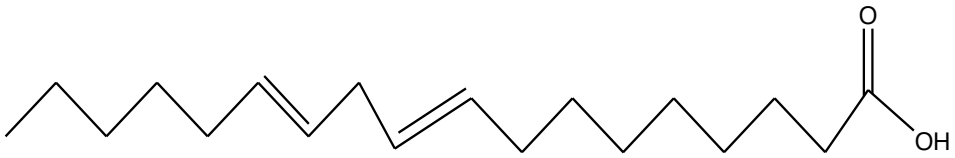
Sterols



Tocopherols

Figure 2.1. Systematic representation of the major component (TAG) and the minor components (DAG, MAG, FAs, sterols, tocopherols) of plant oils.

Where R_1, R_2, and R_3 represent the fatty acid of vegetable oil. For linoleic acid, its structure is as follows.



Linoleic acid

The saturated fatty acids are often found at the sn-1,3 positions of the TAGs found in oilseeds, while the sn-2 position of glycerol is esterified to an unsaturated or polyunsaturated acyl moiety. This is the outcome of the specialization of the distinct enzymes involved in their biosynthesis (Folayan et al., 2019). Tri-saturated fatty acids can be found in oils from tropical species, particularly in palm oil and lauric fats, although they are uncommon in plants growing in temperate environments (coconut and palm kernel fat). They should be removed from native oils using fractionation procedures because they may no longer be acceptable for lubrication due to their high melting points (Table 2.1). (Japir et al., 2021, Li, 2017).

Table 2.1. Properties of some common triacylglycerol species

TAG Name	Melting point (°C)	Viscosity at 80 ºC (cSt)	Reference
Glyceryl tripalmitine	66.4	13.17	(A. A. W. Japir et al., 2021)
Glyceryl tristearate	73.5	16.31	(Folayan et al., 2019)
Glyceryl distearate oleate	42.0	----	(Li, 2017)
Glyceryl distearate linoleate	37.0	----	(Zainal et al., 2018)
Glyceryl palmitate oleate stearate	37.0	----	(Zainal et al., 2018)
Glyceryl palmitate dioleate	18.5	----	(Bahadi & Japir, 2016)
Glyceryl palmitate dioleate	23.0	----	(A. A. W. Japir et al., 2017)
Glyceryl palmitate dilinoleate	-3.0	----	(Djomdi et al., 2020)
Glyceryl stearate oleate linoleate	-4.0	----	(Sagan et al., 2019)
Glyceryl trioleate	-5.0	12.22	Japir et al., 2021)
Glyceryl trilinoleate	-11.0	-----	Bahadi & Japir, 2016)
Glyceryl trilinolenate	-24.2	-----	(Djomdi et al., 2020)

2.4. Plant Oils' General Properties

Except for jojoba oil, which contains esters of fatty acids with long-chained alcohols, seed oils are esters of glycerol with fatty acids. These fatty acids typically have chains that range from C12 to C22. Fatty acids, therefore, make up about 85% of the weight of seed oils, determining their characteristics. Triacylglycerol's' fatty composition and the characteristics of plant oils are closely related to each other (Nie et al., 2020). Table 2.2. presents the fatty acid compositions of some commonly used seed oils.

Table 2.2. Fatty acid compositions of some plant oils

	Fatty acid name									
Plant oil	C12:0	C14:0	C16:0	C18:0	C16:1	C18:1	C18:2	C18:3	Others	Reference
Castor	….	….	0.5-1	0.5-1	….	4-5	2-4	0.5-1	83-85	(Sande et al., 2018)
Coconut	44-52	13-19	8-11	1-3	….	5-8	0-1	....	….	(Zainal et al., 2018)
Corn	….	….	11-13	2-3	0.3	25-31	64-60	1		(Bahadi & Japir, 2016)
Jatropha curcas	….	1.4	13-16	6-8	….	38-45	32-38	….	….	(Bahadi & Japir, 2016)
Karanja	….	….	11-12	7-9	….	0.08	13-21	73-79	….	(A. A. W. Japir et al., 2017)
Linseed	….	….	4-5	2-4	0-0.5	19.1	12-18	56.6	….	Zainal et al., 2018)
Mahua	….	….	28	23	….	41-51	10-14	……	….	(Sande et al., 2018)
Neem	….	….	18	18	….	45	18–20	0.5	….	(A. A. W. Japir et al., 2017)
Olive			13.7	2.5	1.8	71	10	0-1.5		(Bahadi & Japir, 2016
Palm	…..	1	37-41	3-6	0.4	40-45	8-10	….	….	Zainal et al., 2018)
Peanut	….	….	10-11	2-3	….	48-50	39-40	….	….	Zainal et al., 2018)
Rapeseed	….	….	4-5	1-2	0.21	56-64	20-26	8-10	….	Sande et al., 2018)
Safflower	….	….	5-7	1-4	0.08	13-21	73-79	……..	….	(Bahadi & Japir, 2016
Soybean	….	….	11-12	3	0.2	24	53-55	6-7	….	Zainal et al., 2018)
Sunflower	….	….	7	5	0.3	20-25	63-68	0.2	….	(Sande et al., 2018)

Saturated, monounsaturated, and polyunsaturated are the different degrees of unsaturation assigned to fatty acids, which are carbon chains having 4 to 24 carbon atoms (A. A. W. Japir et al., 2018). The fatty acids that don't have any double bonds between their carbon atoms are known as saturated fatty acids. Due to the structure of the molecule, they have the highest melting points and are the most chemically stable. Consequently, the melting point of the fatty acid will rise as the number of carbons in the chain increases (Agrawal et al., 2017). Stearic acid (C18:0), palmitic acid (C16:0), myristic acid (C14:0), lauric acid (C12:0), and butyric acid are examples of saturated fatty acids (C4:0). Fatty acids that only contain one double bond between the carbon atoms are known as monounsaturated fatty acids. The configuration of this double-bond can be trans or cis. They can be significantly resistant to rancidity and liquid at room temperature if stored appropriately. But compared to saturated fatty acids, they have substantially lower oxidation stability (Ashrafi et al., 2017). There are various monounsaturated fatty acids, such as Erucic acid (C22:1), oleic acid (C18:1), and palmitoleic acid (C16:1). At the same time, polyunsaturated fatty acids (PUFAs) are fatty acids that are typically liquid at room temperature and are distinguished by the presence of two or more double bonds in their carbon chain. Increased biological and oxidative instability of polyunsaturated fatty acids is implied by an increase in the number of unsaturations (Heikal et al., 2017). Tetracosapentaenoic acid (C24:5), docosatetraenoic acid (C22:4), docosapentaenoic acid (DPA) (C22:5), arachidonic acid (C20:4), linolenic acid (C18:3), and linoleic acid are examples of polyunsaturated fatty acids (C18:2). Different analytical techniques, such as nuclear magnetic resonance (NMR) spectroscopy, can be used to determine the fatty acid contents in the oils (Minami, 2017), gas chromatography (GC) (Al-Ardi, 2021).

Plant oils are extracted using various solvents, processing methods, or a combination of both from fruits, nuts, or seeds that contain oil (Ismail, 2015). Unrefined oils are subjected to several chemical and physical refining procedures after receiving them. The distribution of fatty acids affects the physicochemical characteristics of plant oils. The characteristics of the oil are significantly influenced by the various kinds of double bonds and their locations within the aliphatic chain. The characteristics of common plant oils and fatty acids are summarized in Table 2.3. The actual number of carbon atoms making up the aliphatic chains plays a much less significant function because most of these triacylglycerols have 18 and a minor number have 16 carbon atoms (Salih, 2021). The amount of oil and fat that is unsaturated is estimated by the iodine number. It is the number of iodine in grams consumed by 100 g of a chemical substance under investigation. Therefore, plant oils are categorized

into three groups mostly according to their iodine content. As a result, oils are classified as "drying" if their iodine value is greater than 130, "semi-drying" if it is between 90 and 130, and "non-drying" if it is less than 90 (Soares et al., 2017).

Table 2.3. Some specific physical properties of triacylglycerol's oils and fatty acids

Name	Viscosity (mpa.s)	Specific gravity	Melting point (ºC)	Reference
Oleic acid	3.41 at 110 ºC	0.850 at 80 ºC	16.3	(A. A.-W. Japir et al., 2018)
Stearic acid	2.79 at 110 ºC	0.839 at 80 ºC	69.6	(Agrawal et al., 2017)
Palmitic acid	3.47 at 110 ºC	0.841 at 80 ºC	62.9	(Ashrafi et al., 2017)
Myristic acid	2.78 at 110 ºC	0.844 at 80 ºC	54.4	(Heikal et al., 2017)
Sunflower oil	33.31 at 37.8 ºC	0.916 at 20 ºC	-17	(Minami, 2017)
Soybean oil	31.80 at 37.8 ºC	0.917 at 20 ºC	-16	(Pei et al., 2012)
Palm oil	30.92 at 37.8 ºC	0.890 at 20 ºC	35	(Sande et al., 2018)
Linseed oil	29.60 at 37.8 ºC	0.925 at 20 ºC	-24	(Zainal et al., 2018)
Castor oil	293.40 at 37.8 ºC	0.951 at 20 ºC	-18	(Bahadi & Japir, 2016)
Rapeseed oil	44.90 at 37.8 °C	0.920 at 20 °C	-10	(A. A. W. Japir et al., 2017)
Erucic acid	32.30 at 37.8 °C	0.912 at 20 °C	33.8	(A. A. W. Japir et al., 2021)
Ricinoleic acid	15.44 at 37.8 °C	0.940 at 20 °C	5.5	(Li, 2017)

There are numerous plant oils made from different resources. These cover the most widely used plant oils, such as soybean, cottonseed, peanut, and sunflower oils. Other common plant oils include palm, palm kernel, coconut, castor, and rapeseed oils. There are also contain a variety of less commonly known oils, such as rice bran oil, tiger nut oil, Patua oil, Niger seed oil, and many others. Their suitability for numerous purposes outside of edible usage is

determined by their yields, variable compositions, and consequently, their physicochemical qualities (Ismail, 2015).

2.5. Citrullus Colocynthis

The cucurbit family includes the colocynth (*Citrullus colocynthis*). It is a periodic trailing vine that can grow in tropical climates and is native to the Mediterranean Basin, subtropical Asia, and tropical Asia. It is notably grown for its wide range of use, including as fuel, medicine, antioxidant, and gel-forming agent. Because they produce a lot of oil, colocynth is a possible source of energy (bio-lubricant) (Al-Hwaiti et al., 2020, Feedipedia et al., 2022). A desert vine plant called *Citrullus colocynthis* grows on sandy, dry soils. It is indigenous to the Mediterranean Basin and Asia, and it is found on the west coast of northern Africa, eastward through the Sahara, Egypt, and India, as well as on the north coasts of the Mediterranean and the Caspian seas. Spain and the islands of the Greek archipelago are two southern European nations where it grows additionally. *Citrullus colocynthis*, often known as bitter cucumber, is a plant that bears fruit, and several cultures in Africa and middle Asia proudly use the seed oil from this plant for frying and cooking (Giwa et al., 2015). *Citrullus colocynthis* is a perennial trailing herbaceous vine that grows to 3 m long. It has a tuberous root system which allows its survival in arid areas. The stems are angular and rough. The leaves are stiff, 3- to 7-lobed, 5-10 cm long x 2.5–6.5 cm broad, and borne on 1-7 cm petioles. The flowers are monoecious (male and female distinct), solitary, borne on axillary buds, pentamerous, and greenish to bright yellow. The fruit is a globular drupe, 4-10 cm in diameter, about the size of a small orange, green and yellow variegated, becoming yellow when ripe. It has a hard rind, and a pulp that is toxic, bitter, light and spongy, easily broken, and light yellowish-orange to pale yellow. The pulp includes numerous smooth, edible seeds. They are egg-shaped, dark brown to light yellowish-orange in color, and 6-10 mm long (Bulbul & Nahar, 2011). The main chemical includes fruit pulp colocynthin (the bitter principle up to 14%), colocynthin (resin), colocynthetin, and pectin gum. The seeds are rich in fatty acids such as myristic, palmitic, stearic, oleic, linoleic, and linolenic acid. It is reported that the de-oiled cake may be included within the cattle feed of milking cows up to 25% and it did not exhibit a significant effect on the milk yield (Gurudeeban et al., 2016). The protein content of *Citrullus colocynthis* seeds turned into discovered to be 8.25% and rich in lysine leucine and sulfur-amino acids such as methionine. Colonythis seed includes oil 52%, protein 28.4%, fiber 2.7%, ash 3.6%, and carbohydrate 8.2%. These are good

sources of critical amino acids (such as arginine, tryptophan, and methionine) and nutrients (B_1, B_2, and niacin), and minerals (Ca, Mn, Fe, Mg, p, ok, and Zn) (Kamalakar et al., 2015). Cucurbitaceous is a massive plant family which consists of nearly 100 genera and 750 species. This plant family is thought for its super genetic variety and significant variation which includes tropical and subtropical regions, arid deserts, and temperate locations. Curcubits are known for their high protein and oil content (Alka et al., 2018). Seeds of cucurbits are assets of oils and protein with about 50% oil and up to 35 % protein. mainly for those reasons they are cultivated and consumed the world over. “Egusi” (*Citrullus colocynthis* L.) belongs to the species of the genus Citrullus of Cucurbitaceae family, which generally consists of a large number of varieties that are generally known as melons (Feedipedia et al., 2022).

Species of the genus Citrullus, belonging to the Cu- Cucurbitaceae family, generally encompass a large number of varieties that are typically referred to as melons. Melons are a major food crop in lots of tropical and subtropical parts of the world, mainly in sub-Saharan Africa. In West, East, and Southern Africa, several varieties of Citrullus lanatus and C. colocynth serve as first-rate food sources. Some varieties like watermelons are eaten as the result, whilst others (just like the tsama melon grown in the Kalahari Desert) serve as a good source of water during the dry seasons. Melon seeds are generally a rich source of oil. However, this resource is only used on a limited scale. For example, sesoswane seeds (from Botswana) and wrewre seeds (from Ghana) are extracted in a few rural areas for use as cooking oil (Gurudeeban et al., 2010).

A **B**

Figure 2.2. Citrullus Colonythis *(A, Fruits, B. Seeds)*

Citrullus colocynthis known as bitter cucumber is a fruit-bearing plant, seed oil is used for frying and cooking in a few African and middle eastern American countries owning to its unique flavor (Giwa et al., 2010). There is some confusion between this species and the carefully associated watermelon, whose seeds can be utilized in a great deal of identical manner. The seed flour is rich in micronutrients (vitamins and minerals), calcium, and niacin and could consequently be utilized in food formulations specifically in regions with low milk consumption like West Africa (Bakheit Mohamed Ahmed & Fath El-Rahman Ahmed Mohamed, 2020).s

Colocynth has long been used extensively in folk medicine. More recent pharmacological studies confirmed that *Citrullus colocynthis* is widely used in different parts of the world for the treatment of several diseases, including intestinal disorder, constipation, hypertension, and antidiabetic medication in many tropical and subtropical countries, as a remedy for sore throat and skin infection. *Citrullus colocynthis's* uncomplicated leaves demonstrated significant antibacterial, antioxidant, local painkiller, and anti-inflammatory activity (Biosci et al., 2015). Biodiesel is a liquid biofuel obtained by using chemical methods from plant oils or animal fat and alcohol that may be utilized in diesel engines, alone or blended with diesel oil. American Society for testing and materials (ASTM) defines biodiesel as a mixture of long-chain mono-alkylic esters from fatty acids received from renewable resources (Bakheit Mohamed Ahmed & Fath El-Rahman Ahmed Mohamed, 2020). Citrullus Colocynthis L., also known as Citrullus lanatus Thumb., Cucurbita Citrullus L., or Colocynthis Citrullus L., is a large plant family with almost 120 genera and 825 species. It is often referred to as the colocynth, bitter apple, bitter cucumber, egusi, or vine of Sodom. This plant family is renowned for its vast genetic adaptation to tropical and subtropical environments, arid deserts, and temperate regions. Curcubits are renowned for having high levels of oil and protein. Cucurbit seeds contain up to 35% protein and 50% oil, making them sources of both nutrients. Particularly because of these factors, they are grown and consumed everywhere. This food's therapeutic properties have only lately come to light. The majority of "melons" have medicinal and nutritional benefits, which have been well-documented in previous studies. Momordica charantia, an edible member of the Cucurbitaceae family that is also known as bitter melon or bitter gourd in English, is a tropical and subtropical vine that is widely cultivated in Asia, Africa, and the Caribbean for its edible fruit. There are numerous claimed medical benefits for this, including antiviral, antidiabetic,

antiulcerogenic, antioxidant, and hepatoprotective characteristics, as well as antihelmintic, antimalarial, anticancer, and cardiac protective properties (Nowak et al., 2019).

2.6. Properties of *Citrullus Colocynthis* Seed Oil

2.6.1. Density

The function of oil as a lubricant and the operation of machines are both critically dependent on density. The majority of systems are built to pump fluid with a particular density, therefore as that density changes, the pump's efficiency also changes (Samidin et al., 2021).

2.6.2. Acid Value

This is the number of a milligram of KOH required to neutralize the free fatty acid in 1 g of the sample (S, 2013, Kalam et al., 2012). The quantity of potassium hydroxide needed to neutralize one gram of sample is indicated by the acid value. It can also be used to calculate the acidity level. It can be determined through direct titration using potassium hydroxide. The assessment of acid value is frequently employed as a general indicator of the condition and edibility of oils since rancidity is typically followed by the development of free fatty acids. Oil service ability is indicated by the Acid Number (AN). The depletion of antioxidants helps monitor the accumulation of acid in oils. Oil oxidation produces acidic byproducts (S, 2013).

$$\text{Acid value} = \frac{\text{titre value} * \text{normality of KOH} * \text{molecular weight of the base}}{\text{Sample weight}} * 100 \ldots\ldots\ldots 2.1$$

2.6.3. Saponification Value

This is how much KOH is needed to saponify 1 g of fat or oil. The fatty acid's molecular weight is determined by the saponification value. A gram of fat can be saponified by using a certain amount of potassium hydroxide, which is known as the saponification value. The amount of ester linkage can be calculated using it. Potassium hydroxide back titration can be used to determine it (S, 2013).

$$\text{SPV} = \frac{\text{titre value} * \text{normality of KOH} * \text{molecular weight of the base}}{\text{Sample weight}} * 100\% \ldots\ldots\ldots\ldots\ldots 2.2$$

2.6.4. Percentage Free Fatty Acid (%FFA)

This is the weight-based percentage of particular fatty acid that is present in the oil.

The percentage of free fatty acid can be calculated by dividing it by two. FFA can behave as pro-oxidants in oils by accelerating the breakdown of hydrogen peroxide. Therefore, an oil with a high FFA level may oxidize further and develop an unpleasant flavor and taste. One of the most crucial issues in the refinement of edible oil is FFA content (S, 2013).

$$\text{Percentage of FFA} = \frac{Acid\ value}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.3$$

2.6.5. Iodine Value (IV)

The amount of unsaturation in a fat or oil is indicated by the iodine value (IV). It is described as the quantity of iodine that is absorbed by 100 grams of fat. The more C=C bonds are found in the fat the higher the iodine value. It will be fat if the iodine value is between 0 and 70, and it will be oil if it is greater than 70. Three categories of oil can be distinguished based on their iodine content (3). I). Non-drying (IV below 90, II). III) and semi-drying (between 90 and 130). Drying (IV between 130 and 200) (Sytar et al., 2013).

2.7. Biodiesel

Biofuels can be made directly from plants or indirectly from commercial, residential, household, and/or corporate wastes. Biodiesel, a substitute for diesel fuel made from vegetable oils and animal fats, is used in diesel engines and heating systems. Fatty acid methyl esters (FAMEs), which make up biodiesel, are a mixture produced from renewable resources and can either be in the form of fats or liquids (oils). Vegetable oils, animal fats, and short-chain alcohols serve as the primary raw ingredients for the synthesis of biodiesel.

The fact that no food is used to make fuel is another evident advantage of using non-edible oils for biodiesel manufacturing, in addition to its lower cost. Medium and large-scale biodiesel manufacturing trials have been carried out in several nations for these and other reasons, utilizing non-edible oils such as castor oil, cotton, jojoba, *Citrullus colocynthis,* and jatropha. Animal fat is another interesting option, especially in countries with an abundance of livestock resources. However, because of their strength, they require preparatory processing; also, extremely acidic grease from cattle, pork, poultry, and fish might be used (Hájek et al., 2021).

Due to their extremely high oil yield, microalgae appear to be a highly important alternative for future biodiesel production; nevertheless, only a few species can be used to produce biofuel (Oyinade & Damilare, 2020). Regarding the feedstock utilized in the manufacturing of biodiesel, however, fats and oils are frequently used interchangeably. Oil waste, such as frying oils and fats, can be utilized as one of the basic materials for the creation of biodiesel (Ghaly et al., 2014). Chemically, biodiesels are produced from the transesterification of triglycerides found in vegetable oils and fats (Menu, 2022).

One of the common organic reactions is transesterification, which is the sequential, reversible reaction of a triglyceride (fat or oil) with an alcohol to produce esters and glycerol. A small amount of alcohol is employed to change the equilibrium so that esters can develop (Oh et al., 2013). The most straightforward and effective method for producing biodiesel in large amounts is transesterification, as opposed to the less efficient, more expensive, and ultimately poor yield methods of pyrolysis and micro emulsification. Transesterification has consequently gained popularity and replaced other production techniques (Cerón et al., 2018). In the presence of the proper catalysts, transesterification is the reaction between oil and a fast chain of alcohol (methanol, ethanol, and propanol) (Felizardo et al., 2016). Oils with high free fatty acids content can be converted into biodiesel via a double-step transesterification process. In the first step, the oil is treated with an acid dissolved in methanol to reduce FFA content, whereas in the second step the preheated oil is trans esterified with methanol in the presence of a base catalyst to form ester and glycerol (Cerón et al., 2018).

2.7.1. Separation and Purification of Biodiesel

A critical step in the manufacture of biodiesel is the purification of the final product and its separation from other materials. Following transesterification, the initial step is separating the ester phase from the glycerol phase using either a gravity field or centrifugation, which is the most widely used technique in the sector (Atadashi et al., 2011). These phases differ in polarity and density; the GP, which contains particularly polar materials, has a higher density than the EP, which contains nonpolar ester. However, the separation is not complete, and some free glycerol and esters are still present in the EP and GP, respectively (ester losses). Moreover, the type of oil and alcohol used to affect the GP's ester content: is between 6 and 15 weight percent for methanol (Vávra et al., 2021). Ester loss during transesterification is correlated with the ester content in the GP, which lowers the yield of methyl esters (Hájek et al., 2018). The glycerol phase, which is a crucial step in the manufacture of biodiesel, goes unrecognized and is no longer properly examined because it is viewed as a waste product of transesterification. The transesterification process as well as the technique used to separate and purify the obtained esters determine the specific composition of the GP in most cases. Glycerol normally makes up 30–60 weight percent of the GP, along with other substances such as soaps, water, salts, alcohol, glycerides, the residual catalyst, and esters. The resulting glycerol is employed in numerous industrial processes. (Kosamia et al., 2020, Monteiro et al., 2018).

2.7.2. Properties of Fatty Acid Methyl Ester

The fatty acid composition of the raw materials hired in the transesterification method dictates, to a large quantity, the fuel properties of biodiesel produced. Distinctive feed stocks applied in biodiesel production have specific chemical compositions and undeniably have different fuel properties (Owuna et al., 2020).

The fuel properties of the biodiesels are as follows.

A. Density

Density is a crucial parameter for diesel fuel injection systems. A higher density for biodiesel consequences in the delivery of a slightly more mass of fuel since fuel injection equipment operates on a volume metering system (Owuna et al., 2020).

B. Kinematic viscosity

Kinematic viscosity is a very crucial fuel property and it represents the flow characteristics of fuel. One of the reasons why biodiesel is used as an alternative fuel in place of pure vegetable oils or animal fat is due to its reduced viscosity which enhances fuel flow characteristics. In addition, kinematic viscosity is an important parameter concerning fuel atomization and combustion in addition to gas distribution. The kinematic viscosity of biodiesel was measured at 40 °C and 100 ^{o}C (Verma et al., 2012). Kinematic viscosity increases with FA chain length and with an increasing degree of saturation of either the fatty acid or alcohol moiety in a fatty ester (José María Encinar & González, 2020).

C. Cloud Point

Cloud point is the temperature at which wax first becomes seen to the naked eye when the fuel is cooled. At temperatures under the cloud point, large crystals fuse and form agglomerations that finally become extensive and sufficient to prevent the pouring of the fluid and consequently affect the overall performance of fuel lines, fuel pumps, and injectors. The low-temperature behavior of biodiesel is significantly motivated by molecular structure. Low-temperature properties rely mostly on the saturated ester and the impact of unsaturated ester composition can be negligible (Pullen & Saeed, 2012).

D. Acid value

The acid value is a measure of the FFA content in the biodiesel and is measured as the milligram of KOH required to neutralize the FFAs in one gram of the sample. The acid value of biodiesel fuel depends on the type of feedstock and how well the fuel is processed. A high acid value makes the fuel prone to polymerization and also acts as a catalyst for hydrolysis (Bae & Kim, 2017, Popoola & Ikpambese, 2021).

2.8. Sources and Synthesis of Lubricating Oils

Conventional lubricants use high molecular weight hydrocarbons as base stocks, which are obtained from vacuum residue inside the refinery. Unsaturated fatty acids are used as base stocks in bio-lubricants, which may now be based mostly on vegetable oils. Due to their oxidizable functional groups, they have low heat stability and negative oxidation stability, making them unsuitable for use in lubricating oil applications. Vegetable oils can have their unsaturated fatty acid content decreased to make them appropriate for use in engines, making them equivalent to conventional lubricants. Chemical modification techniques that can be utilized include transesterification, epoxidation, and hydrogenation (Negi et al., 2021).

Figures 2.4 and 2.5 can be used to explain the life cycles of traditional mineral oil-based lubricants and bio-lubricants, respectively. In addition to improving the chemical and thermal stability of the final lubricant components, additives are also added to base stocks to improve the physicochemical and thermophysical qualities. The classification of lubricant additives, which includes friction modifiers and anti-wear or anti-oxidation compounds, is based solely on their function in lubrication systems. They could also be divided into groups based on how they operate and where they operate. Tribo-improvers, rheo-improvers, and maintainers are members of the main class. Tribo-improvers enhance the lubricant's tribological capabilities. The fluidity of the basic oil is influenced by rheo-improvers. Maintainers keep the lubricants and the device components in a desirable state by reducing the degradation of the materials used inside the lubrication device. The operating mechanism of the additives determines whether they are classified as chemical additives (if they undergo chemical reactions) or physical additives (if they operate without undergoing any chemical reaction) (Minami, 2017).

2.8.1. Esterification

The process of esterification is used to create esters, primarily from various alcohols and FFA. Numerous homogeneous and heterogeneous acid catalysts have typically been used in bio-lubricant synthesis through an esterification response (Bolina et al., 2021, Saboya et al., 2017). To prevent saponification in transesterification reactions carried out with alkaline catalysts, the esterification reaction utilizing homogenous acid catalysts, such as H_2SO4, has often been performed for TAG whose acidity value increases by more than 1%. Pre-transesterification therapy is the name given to this process phase (Ghafar et al., 2019, Gao et al., 2018).

2.8.2. Transesterification

Transesterification is a chemical reaction where an ester is changed into every other ester by substituting the alkyl group of an alcohol. In this method, several alcohols, particularly polyols like EG, TMP, PE, and NPG, are typically used to substitute the glycerol molecule in the structure of TAG. Several examples of TAG being employed as feedstocks for the transesterification-based synthesis of bio-lubricants can be found in the literature (Zainal et al., 2018, Cavalcanti et al.,2018, Sripada et al., 2013, Youssef et al., 2016). To avoid a saponification reaction, which interferes with the processes of separating and purifying glycerol and esters, TAG should have a low concentration of water and FFA. Alkaline transesterification uses catalysts, such as sodium and/or potassium hydroxides and alkoxides (Afifah et al., 2019, Gupta et al., 2020).

2.8.3. Alcohols

Low molecular alcohols like methanol, ethanol, and butanol are additional raw materials required for the synthesis of biodiesel. Because of its reduced cost and acceptable physical and chemical properties, methanol is specifically used. Both methanol and ethanol combine with oil to form a heterogeneous two-section system and are immiscible with it. Extreme stirring is necessary to ensure that the reaction proceeds at the interface (Hájek, Vávra, Mach, et al., 2020). Ethanol is the second most used alcohol, especially for homogeneous catalysts. Transesterification is often carried out at a lower temperature (25 – 30 ^{o}C) since saponification is simple to process at a higher temperature, making ethanol production from renewable resources possible and easy (Hájek et al., 2012). The larger number of carbons inside the alcohol chain results in decreased reactivity but a higher boiling point, meaning that the transesterification can be carried out at higher temperatures while the same strain is present. The caloric content of the esters also slightly rises as the carbon number rises (Hájek et al., 2017).

2.8.4. Types of Catalysis

When the alcohol is supercritical, the transesterification can be done without a catalyst at high temperatures and pressures (Hájek, Vávra, & Mück, 2020). Otherwise, it is necessary to use a catalyst (Zeng et al., 2017, Andreo-Martínez et al., 2018). Transesterification is often catalyzed by either chemical or enzymatic means. Chemical catalysts can be homogeneous or heterogeneous, which can then be classified as alkaline or acidic (Andreo-Martínez et al., 2018). The properties of each type of catalyst are shown in Table 2.4.

Table 2.4. Types of catalysts used in transesterification

Type of Catalyst	Advantages	Disadvantages	Reference
Homogeneous alkali	➢ Mild reaction conditions ➢ Less energy required ➢ Easy availability of catalyst ➢ The high reaction rate (4000 times faster than acid ones) ➢ High yields of reaction (99%)	• Using only quality oils (if the FFA content in the oil is more than 2%, saponification occurs) • irreversible loss of catalyst and decreasing of ester yield • produces more wastewater from purification	(Vyas et al., 2010)
Heterogeneous alkali	▪ Environmentally friendly - reusable ▪ Easy to separate from the reaction mixture ▪ The possibility of continuous production	➢ increases the energy requirements for the reaction (temperature, pressure) ➢ challenging catalyst synthesis ➢ catalyst instability ➢ lower activity in comparison with homogeneous ones	(Y. C. Sharma et al., 2011)
Homogeneous acid	✓ insensitive to FFA and water content in the oil ✓ esterification and transesterification occur simultaneously ✓ the easy availability of catalyst ✓ saponification can be avoided	✓ low reaction rate ✓ can lead to equipment corrosion ✓ irreversible loss of catalyst	(Vyas et al., 2010)
Heterogeneous acid	▪ insensitive to FFA and water content in the oil ▪ esterification and transesterification occur simultaneously ▪ recyclable	✓ low reaction rate ✓ high reaction conditions and longer reaction times ✓ higher energy requirement ✓ catalyst instability	(Jayakumar et al., 2021)
Enzyme	▪ Mild reaction conditions ▪ environmentally friendly and non-polluting ▪ reusable	✓ very slow reaction rate, ✓ high cost, ✓ sensitive to alcohol (methanol can deactivate the enzyme)	(Santos et al., 2020)

2.9. Production and Purification of Polyol Esters

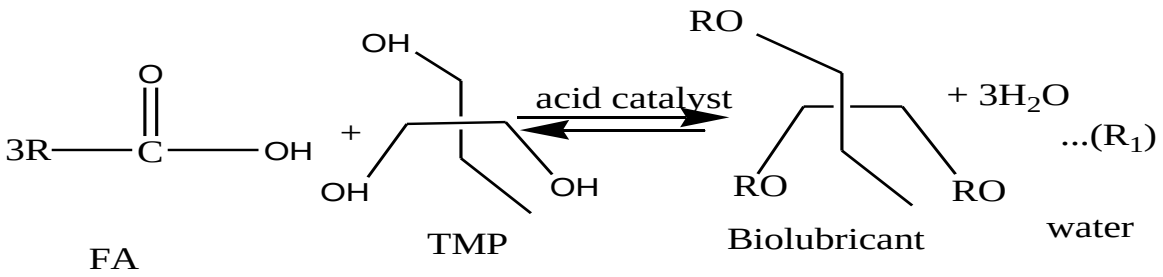
2.9.1. Production of Polyol Ester

Several synthetic approaches are available for the transesterification reaction between FAME and polyol, which produces polyol ester. Such reactions have been classified by the catalysts used in the reactions. Acid, base, or enzyme catalysts are used for esterification and transesterification reactions. The optimization of enzyme-catalyzed transesterification has been investigated in many studies; however, it is not commercially available (Nie, 2012).

2.9.1.1. Acid-catalyzed transesterification

Acid-catalyzed esterification of fatty acids with TMP is shown in reaction one (R_1).

Nie, (2012), investigated the iso- and n-valeric acid-catalyzed esterification of TMP. They claimed that when 7% sodium bi-sulfate was utilized as the catalyst, it transformed into bio lubricant when used at 110 –120 ^oC for 2 hours, while 1% sulphuric acid was used as the catalyst for a 60–hour reaction time, resulting in 83% of bio lubricant was received. Presently, Hafizah & Salmon, (2010) used a one-step, sulphuric acid-catalyzed esterification to produce TMP esters of Jatropha curcas oil. 55% of the reactants undergo partial conversion to TMP esters under the reaction conditions (4:1 mole ratio of fatty acids to TMP, 2% sulphuric acid as the catalyst, temperature of 150 ^oC for 3 h). The main issue with acid-catalyzed esterification is that it takes a long time for the reaction to complete and produces a low yield of trimethylol propane triester (TMP TE) (Afifah et al., 2019).



For base-catalyzed esterification of fatty acid with EG, the reaction is the same as reaction one. The reaction also takes a long time to complete and produces a low yield of ethylene glycol diester (EGDE).

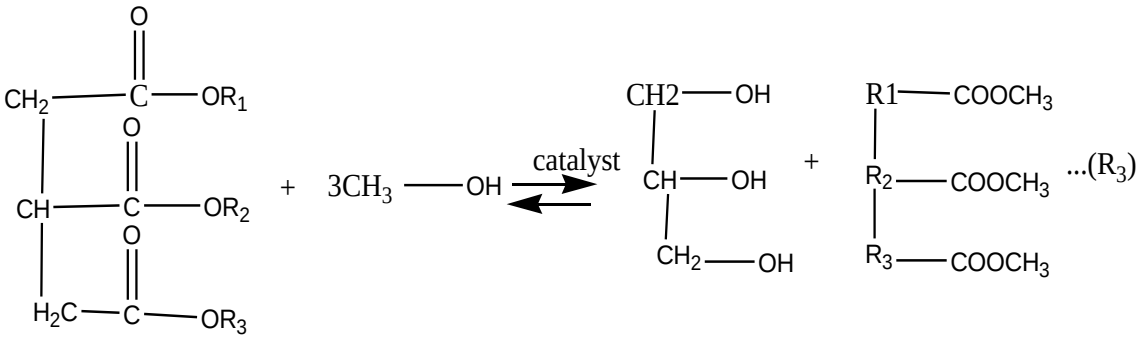
Where R: is the hydrocarbon group of the fatty acids

2.9.1.2 Base catalyzed transesterification

Stages of transesterification are often necessary for the base-catalyzed production of polyol fatty acid esters from TAG. The main transesterification method, as shown in reaction two (R_2), entails the employment of alcohol (often methanol or ethanol) in combination with a catalyst to physically separate the TAG molecules of raw vegetable oil into fatty acid esters.

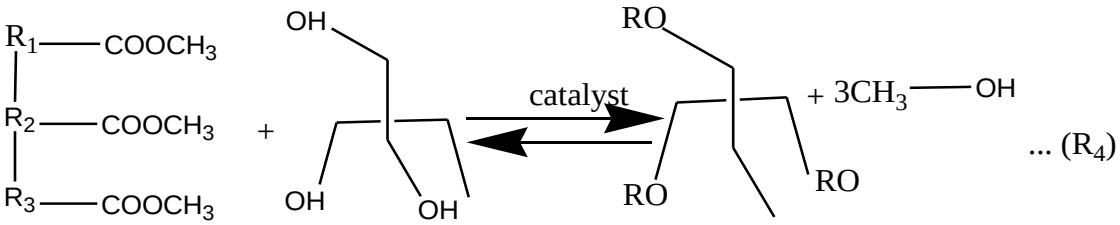
As shown in reaction three (R_2), this primary reaction produces glycerol as a co-product, and the second degree of the reaction produces methanol, which produces polyol fatty acid esters. Combining this reaction with a chemically resistant polyhydric alcohol (such as iso-sorbitol or neopentyl polyols, along with, EG, PE, TMP, or NPG) results in a substance that can be tested as a lubricant, (Nie, 2012).

Stage One:



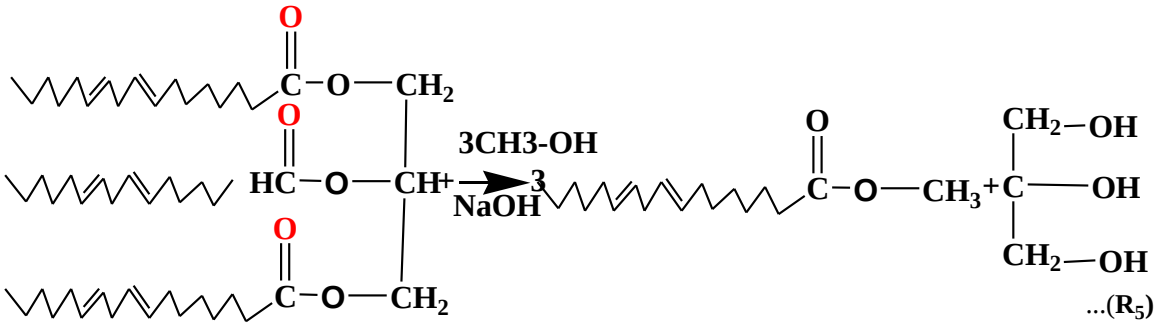
TG Methanol Glycerol FAME

Stage two:

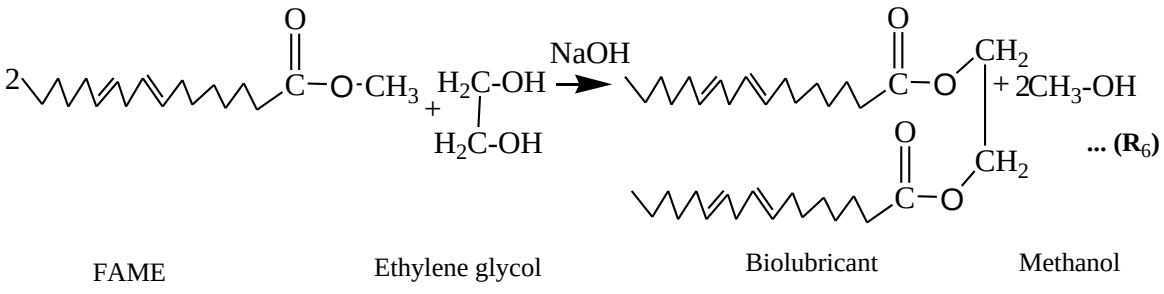


FAME TMP Biolubricant Methanol

When the polyol alcohol used is ethylene glycol the reaction looks as follows. The ethylene glycol di-esters (EGDEs) as bio-lubricants are produced from each oil-derived FAMEs for the different used vegetable oils using a transesterification reaction.



TG Methanol FAME Glycerol



2.9.2. Purification of Polyol Esters

The production of polyol esters of fatty acids from methyl esters and polyol produces a crude product mixture that includes unreacted FAME, fully esterified polyols, smaller amounts of partially esterified polyols, and catalysts. Commonly, these crude products could be washed with water and acid or alkaline solutions to remove the catalyst, and then further refined by distillation to remove the unreacted methyl esters. Heating the reaction mixture in an oil bath (180–200 ºC) under reduced pressure (0.2 mbar) enabled the removal of unreacted esters from the product (Nie, 2012).

2.10. Environmental Friendly Bio-lubricant

Most lubricants grow to be within the environment, either via leakage during transportation and equipment usage or by intentional disposal at the cease of their lifetimes. To minimize environmental damage, biodegradable bio-lubricants have attracted attention (Owuna et al., 2020). Bio lubricants are manufactured from a range of plant oils, including rapeseed, palm, sunflower, soybean, coconut, bitter apple, and canola. They are also sometimes referred to as bio-lubes, bio-based, green, ecologically friendly bio-lubricants, or plant-oil-based lubricants. Triacylglycerol (natural esters) makes up the majority of plant oils; its exact chemical makeup depends on the type of plant and strain used to make the oil (Sagan et al., 2019). In their natural states, plant oils can be employed as bio-lubricants. When taking into account industrial and equipment lubrication, they have various benefits. Plant oils are incredibly superior to mineral oils in terms of lubricity. Their lubricity is so strong that friction materials must be added to some applications, such as tractor transmissions, to lessen clutch slippage. In addition, plant oils have a relatively high viscosity index (VI). The high flashpoints that plant oils have are an essential characteristic (Reeves et al., 2017).

The attractive application of vegetable oils is as bio-lubricants that reduce machine wear and friction between surfaces. The mineral-based oils, which are obtained by refining crude oil and used to make lubricants, might be replaced with vegetable oils with remarkable success.

Because they introduce toxic materials, crude oil reserves are comparatively diminishing and contribute to increased environmental degradation (heavy metal, and sulfur compounds in the environment and air by their volatility (Hájek et al., 2021, Salih & Salimon, 2021). The key benefits of employing bio-lubricants are that they have a higher boiling point (reduced emission), are more biodegradable, lubricious, volatile, skin-compatible, have higher shear stability, have longer tool lives, have a higher viscosity index, and are safer on the shop floor (Salimon et al., 2010).

2.10.1. Characteristics of Bio-lubricant

Bio-lubricants have a wide range of advantageous physicochemical characteristics. Compared to those conventional petroleum-based lubricants, they provide technical advantages. Bio-lubricants have high VI, high flash points, high lubricity, and low evaporative losses (Usta et al., 2016).

2.10.1.1. Viscosity

A bio-lubricants viscosity is a measurement of its thickness or flow resistance. Viscosity is a measurement of the resistance to the flow of fatty acids and vegetable oils (Salimon et al., 2014). The viscosity of bio-lubricants will determine how thick they are and how much energy may be required to drive an object through them (Owuna et al., 2020, Salimon et al., 2014). The application of bio-lubricants is mostly influenced by viscosity. For vehicle transmission oils, low viscosity stocks are possible, however, diesel engine oils require higher viscosity stocks. The viscosity of the bio-lubricant is used in steel forming applications to assess how well a company can keep the work piece apart from the tools (to reduce friction and wear) (Salimon et al., 2014). At temperatures of 40 and 100 ^{o}C, the kinematic viscosity of bio-lubricants is measured and compared to an empirical reference scale (Hassan et al., 2019).

2.10.1.2. Viscosity Index

The viscosity index (VI) of a bio-lubricant is a measurement of how viscosity changes with temperature. A device that operates across a wide temperature range would need a lubricant with a higher viscosity index because the viscosity of a bio-lubricant is inversely related to its temperature. The effect of temperature on the viscosity of lubricating products is lessened by a higher viscosity index (Salimon et al., 2014).

2.10.1.3. Cloud Point

The temperature at which the main indicator of wax formation for bio lubricant can be found is called cloud point (CP) (Salimon et al., 2014). It is the temperature at which haziness first appears. The wax crystals that are produced can block apertures and filters, leaving depositing surfaces, such as a heat exchanger, and increasing the viscosity of the bio-lubricating oil (Owuna et al., 2020).

2.10.1.4. Acid or Neutralization Number (Value)

The acid or neutralization number shows the amount of acid or base content needed by a lubricant for neutralization. The acid value of lubricating oils must always be less than 1%. It happens because the acid value alters how the oxidation number, hydrolysis rate, and moisture content progress (Edith, 2012). It's important to know the acid value of a lubricant before using it on a machine. Mainly because with time, the lubricants in machines deteriorate, producing acidic waste products that might corrode the parts of the machines. The acid content of the oil or the amount of leftover alkalinity from additives in the oil must therefore be measured to track the acidity level in the oil as it ages (Samidin et al., 2021).

2.10.1.5. Anti-Wear Properties

For low-speed and low-pressure applications, lubricants work well. When oil viscosity is insufficient to prevent surface contact, boundary lubrication happens. To reduce wear, anti-wear additives offer a protective coating on contact surfaces. Standard laboratory studies can identify the anti-wear characteristic. Bio-lubricants based on vegetable oil have superior anti-wear characteristics to mineral oils (Mobarak et al., 2014).

2.10.1.6. Flash Point

The flash point temperature is one indicator of a test specimen's propensity to combine with air to generate a combustible combination under controlled circumstances. It is one of the characteristics that must be taken into account when determining the overall flammability danger of a substance. It quantifies and explains the characteristics of substances and goods in reaction to heat and an ignition source under regulated circumstances (Hassan et al., 2019).

2.10.1.7. Iodine Value

The iodine value is a measure of the number of double bonds in a particular sample of a bio lubricant molecule. It illustrates how vulnerable bio-lubricants are to oxidation processes. Since saturated bio-lubricants do not absorb iodine, they have zero iodine values. In contrast, unsaturated bio-lubricants do (Hussain et al., 2014). Seed oils have a special quality of iodine

value that makes them suitable as raw materials for the soap, food, lubricant, pharmaceutical, and cosmetics sectors (Owuna et al., 2020).

2.10.2. Advantages of Bio-lubricant

Bio lubricants are preferable for all applications rather than other petroleum lubricants due to the following properties.

High biodegradability, lower toxicity, Good lubricating properties, high viscosity index, high flashpoint, safer use due to inflammable nature, constant viscosity, less vapor, and oil mist production, Longer equipment life, reduction in oil losses through evaporation, and higher boiling points lead to fewer emissions, and cost-effectiveness due to reduced costs of maintenance, disposal, and storage (Saboya et al., 2017, Cecilia et al., 2020, Ho et al., 2019).

2.10.3. Factors Affecting the Cold Flow Behavior of Bio-lubricant

The composition of its esters has an impact on the bio-lubricants cold flow characteristics, as well as all of its other fuel characteristics. Triglycerides can be chemically transformed into trans esterified triglycerides, but this procedure doesn't alter the fatty acids' fundamental characteristics. As a result, the fatty acid composition of feedstock oils is crucial in establishing the characteristics of the bio-lubricant. Any type of oil or fat contains one of three types of fatty acids (Edith, 2012).

These are 1. Saturated fatty acids, 2. Mono-unsaturated fatty acids, 3. Poly-unsaturated fatty acid.

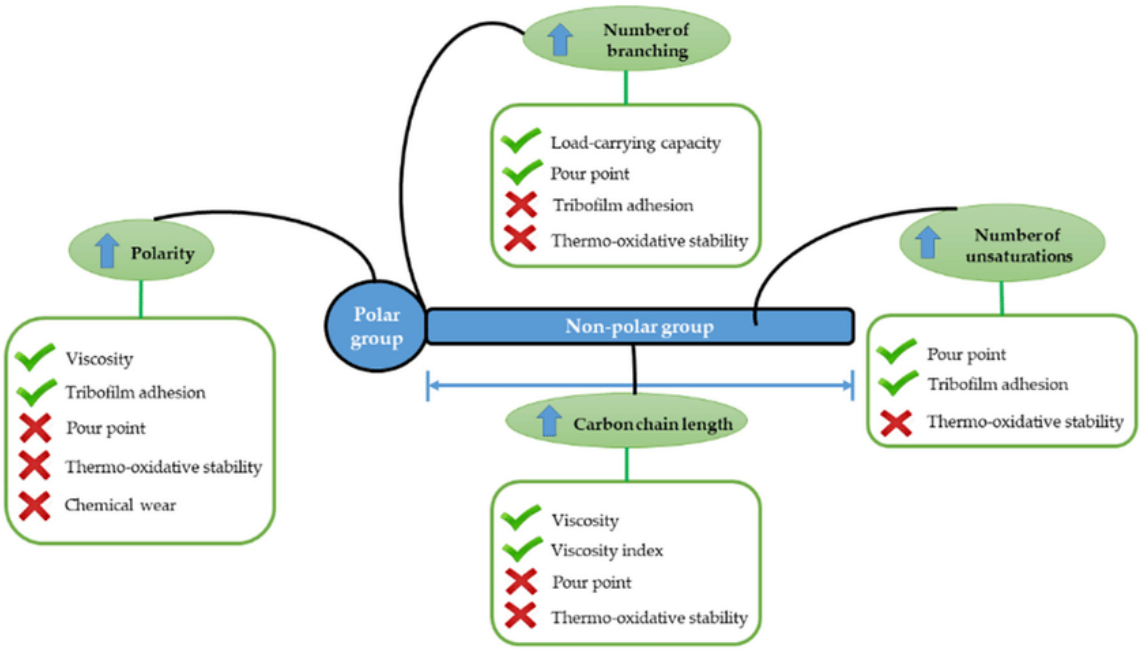


Figure 2.3. Molecular structure of vegetable oils and the relationships between the structure and the physicochemical properties, (Edith, 2012)

2.10.4. Biodegradability

Biodegradation is the chemical dissolution by which organic substances are broken down by the enzymes produced by living organisms. Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane and water. This means that bio-lubricants based on renewable raw materials derived from CO_2 and H_2O via photosynthesis, following their use, are ultimately returned to the earth as CO_2 and H_2O through biodegradation (Alfieri et al., 2018). Organic material can be degraded aerobically, with oxygen, or anaerobically, with-out oxygen. By definition, biodegradation is the chemical transformation of a substance by organisms. More importantly, Plant oils are biodegradable, generally less toxic, and renewable compared to petroleum oils (Reeves et al., 2017). Employing tests developed by the American Society for Testing and Materials (ASTM) and the Organization for Economic Cooperation and Development (OECD), oil is inoculated with bacteria and kept under controlled conditions for 28 days. The percentage of oxygen consumption or carbon-dioxide evolution is monitored to determine the degree of biodegradability (Ho et al., 2019). Most plant oils have shown to biodegrade more than 70% within that period, as compared to petroleum oils biodegraded at nearly 15 to 35%. For a test to be considered readily biodegradable, there must be more than 60% degradation in 28 days. Table 5. shows the biodegradation percentage for typical types of lubricants (Reeves et al., 2017).

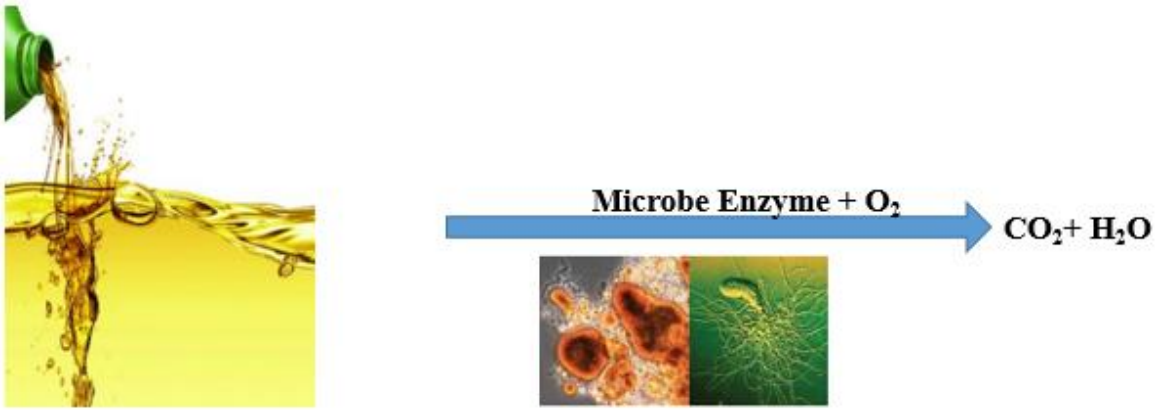


Figure 2.4. Biodegradation process of bio lubricant

Table 2.5. Biodegradation percentage (%) for typical types of lubricants (Reeves et al., 2017)

Lubricant types	Biodegradation percentage (%)
Plant oils	90 – 100 %
Plant oils-based esters	80 – 100 %
Polyols and diesters	55 – 100 %

Polyalkylene glycol (PAG)	10 – 20 %
Polyalphaolfien (PAO)	5 – 30 %
Polyether	0 – 25 %

2.10.5. Eco-toxicity

Eco-toxicity is an important parameter that must be controlled since some components of lubricant formulations are environmentally toxic and can irreversibly affect living things(Cecilia et al., 2020). Aqueous ecosystems are more prone to strong damage, therefore it is necessary to determine lubricant water toxicity and the potential to poison target organisms such as bacteria, algae, small fishes, or laboratory rats. A lubricant is considered to be degradable when it is biodegraded at least 80% within 28 days or at least 60% after 28 days. Eco-toxicity is measured using the LD_{50}, i.e., the required dosage to kill 50% of a population. A bio lubricant is not considered Eco-toxic when the LD_{50}, is above 1000 ppm (Reeves et al., 2017). The lethal dose (or LD_{50}) is defined as the dose of a test bio lubricant that is lethal for 50% of the animals in a dose group. The LD_{50} is one way to measure the short-term poisoning potential (acute toxicity) of a bio lubricant. LC values usually refer to the concentration of a bio lubricant in the air. LC_{50} value is the concentration of bio lubricant in the air at which 50% of the test animals die during the observation period (Cecilia et al., 2020).

2.11. Machining

Machining is one secondary manufacturing process that is performed to impart the desired shape, size, and surface finish by removing unwanted material from a solid 3-D blank. In conventional machining operations, the cutting tool compresses a thin layer of work piece material to gradually shear it off in the form of chips (Khandekar et al., 2012). The primary shear zone exists surrounding the concentrated shear plane along which work material undergoes shearing to become a chip. Initially, after forming, this chip flows under pressure over the rake surface of the cutting tool until it reaches the point of separation and finally leaves the cutting zone (R. P. Singh & Singhal, 2017). The presence of immense pressure and the relative velocity between the flowing chip and cutting tool gives rise to the secondary deformation zone. Both these zones (along with the flank wear zone) are sources of cutting heat; however, the secondary deformation zone accounts for 70 – 90% of cutting heat (Melkote et al., 2017).

This cutting heat increases the temperature of relevant parts (such as the machined part of the workpiece, cutting tool, and chip). The excessive cutting temperature has several detrimental effects on the cutting tool as well as the finished surface of the job (Song et al., 2017). Two possible ways to keep the cutting temperature within the limit are: (i) reducing the coefficient of friction between the chip and rake surface by lubricating the contact surfaces to minimize the rate of heat generation, and (ii) removing the generated heat from the cutting zone. Both effects can be achieved by delivering an appropriate cutting fluid in the proper orientation (cutting fluid acts as coolant and lubricant simultaneously) (Kannan et al., 2016). When machining is carried out in presence of cutting fluid, it is termed wet machining or wet cutting. If no cutting fluid is deliberately applied during machining, then it is termed dry machining or dry cutting. Various similarities and differences between dry machining and wet machining are given below in table format. Similarities between dry machining and wet machining (Ahmed et al., 2019, Sivaiah & Chakradhar, 2018)

- In most cases, the machining of a material can be carried out either in dry or wet conditions; however, their effects will be different. Some exceptions include wood cutting (only dry machining), cutting high strength, temperature resistant alloys (only wet machining), etc.
- Irrespective of the dry or wet cutting environment, the material is removed using a cutting tool and material removal takes place in the form of chips.
- The cutting force remains more or less the same in both cases (because cutting force primarily depends on work material, process parameters, and relevant features of the cutter).
- The same cutting tool can be employed for both cases; however, the cutter can be modified for efficient delivery of fluid and its enhanced action.

Cutting speed is defined as the speed at which the work moves concerning the tool (usually measured in feet per minute). **Feed rate** is defined as the distance the tool travels during one revolution of the part. Cutting speed and feed determines the surface finish, power requirements, and material removal rate. **Depth of Cut** is the total amount of metal removed per pass of the cutting tool. It is expressed in mm. It can vary depending upon the type of tool and work material. Mathematically, it is half of the difference in diameters (Kaladhar, 2020).

Table 2.6. Differences between dry machining and wet machining (Yıldırım et al., 2019, Guerrini et al., 2018, Feng et al., 2019)

Dry Machining	Wet Machining
✓ Machining is performed in absence of appropriate cutting fluid.	❖ Machining is performed in presence of appropriate cutting fluid.
✓ No cutting fluid delivery system is required.	❖ A proper fluid delivery system must be installed with the machine tool for controlled delivery of cutting fluid.
✓ No additional accessories for fluid delivery are required.	❖ Additional accessories like a storage tank, pump, pipeline, nozzle, recycle systems, etc. are required. So the machine becomes heavy and bulky.
✓ It is less hazardous to the workers. No such environmental pollution is associated with dry cutting.	❖ Prolonged exposure to cutting fluid sometimes turns hazardous to the operator. Moreover, its disposal contaminates the environment (water and soil).
✓ Problems associated with corrosion of machine tools are not prevalent here owing to the absence of cutting fluid.	❖ Some cutting fluids corrode various machine parts rapidly. Thus longevity of machine tools degrades.
✓ The rate of heat generation during machining is considerably more.	❖ For the same parameters and materials, the rate of heat generation is low due to the lubricating effect of cutting fluid.
✓ The cutting temperature remains very high during machining.	❖ Cutting temperature remains significantly low because of the reduced rate of heat generation and continuous removal of heat by cutting fluid.

✓ High cutting temperature sometimes limits the level of process parameters. Thus high cutting velocity, feed rate, and depth of cut cannot be utilized, which leads to low MRR and low productivity.	❖ Because of the low cutting temperature, high values of speed, feed, and depth of cut can be utilized without much problem. Thus high material removal rate (MRR) and improved productivity can be achieved.
✓ High cutting temperature accelerates the tool wear rate and thus reduces tool life. It also tends to deform the cutting edges plastically.	❖ For the same work-tool material combination and process parameters, the tool under wet machining exhibits prolonged life due to degraded wear rate. The tendency of plastic deformation is also meager.
✓ Sometimes finished surface oxidizes or burns due to excessive cutting heat. It changes the surface properties and appearance leading to rejected items.	❖ Cutting fluid can protect the finished surface from oxidation by maintaining the cutting temperature minimum.
✓ Due to excessive cutting heat, chip color changes undesirably.	❖ Chip color usually remains the same as that of work material.
✓ Workpieces and cutting tools are subjected to other thermal damages also.	❖ Wet machining reduces the tendency of thermal damage to work piece and cutter.
✓ Dry machining can be carried out while cutting soft materials like wood, polymer, soft metals, etc.	❖ Wet machining is preferred when cutting hard metals like steel, titanium, etc.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Overall Research Framework

This research was carried out to synthesize and characterize bio-lubricant from *Citrullus colocynthis* seed oil via double transesterification. The overall research methodologies are shown in Figure 3.1.

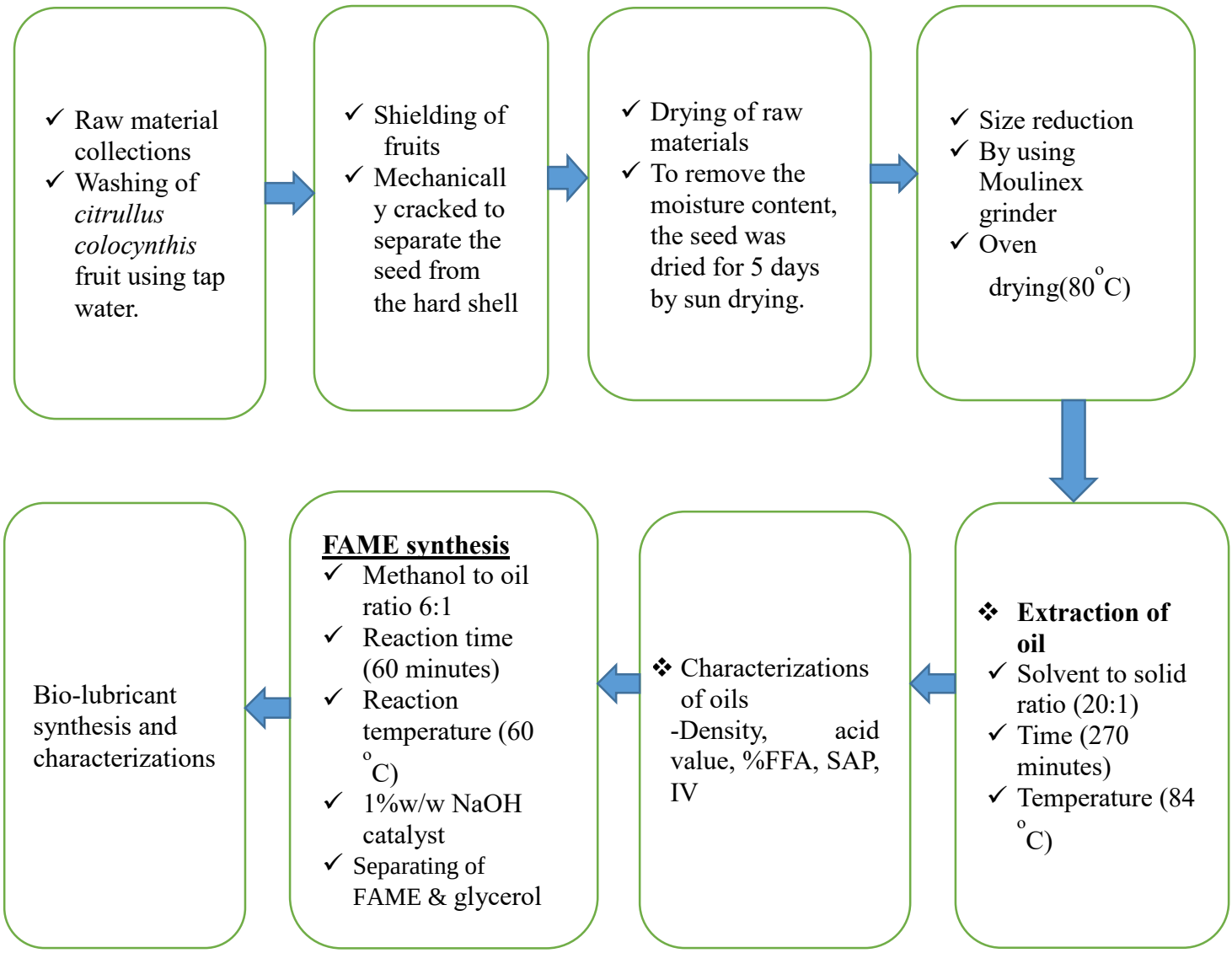


Figure 3.1. Overall the research frame work

3.2. Materials and Reagents

The **materials** and **reagents** that were used to conduct this study are as follow:

Table.3.1. Use of Chemicals and Reagents

Name	Uses
Crude *Citrullus colocynthis* oil	Raw material
Methanol (99%)	Synthesis of FAME and bio-lubricant
Ethanol (96%)	Extraction of oil
Potassium hydroxide	The catalyst for acid value, saponification value,
Sodium hydroxide	The catalyst for FAME synthesis
Hydrochloric acid	Titration for saponification value
Phenolphthalein indicator	For titration
Hexane	As co-solvent, purification and oil extraction
Absolute ethanol (99%0	For acid value determination
Ethylene glycol (EG) (98%)	Synthesis of bio-lubricant
Sodium thiosulphate	For iodine value determinations
Starch soluble	For iodine determinations
Iodine crystals	For iodine value determinations

3.3. Equipment and Instruments used

The **instruments** and **equipment** that were used in carrying out this thesis are Moulinex grinder, Soxhlets apparatus, Heating mantle, Viscometer, water bath, analytical balance, conical flasks, Graduated cylinders, Beaker glass 500 mL (pyrex), Erlenmeyer 250 mL (pyrex), three-neck round bottom flasks 500 ml (Duran), magnetic stirrer, Thermometer, pipettes, burette, burette withstand, test tubes, FTIR, GC-MS, NMR, TGA, Rotary evaporator, spatula, funnel, measuring cylinder, labeling, vacuum filter, round bottom flask, separatory funnel, viscometer, funnel, reflux condenser, chiller, distilling column, rounded spout, three-way adapter, Aluminum 6061-T6 work piece having (diameter 8 mm and length 100 mm), HSS cutter, spectrometer.

3.4. Methods

This section was categorized into three classes; raw material preparations, extraction and characterization of the crude oil, and finally, synthesis and characterization of biodiesel and bio-lubricant.

3.4.1. Raw Material Preparations

Citrullus colocynthis seed was used as the primary ingredient; however, the fruits were collected from Ethiopia, Afar region, Dubti woreda and the fruits contained contaminants such as sand and seed cover. Hand-picking was used to eliminate these contaminants, and tap water was used for washing. Beside the fruits had been mechanically shelled, to remove the seeds' tough shells (Cerón et al., 2018). The seeds moisture content was removed by using sun drying for 5 days. After drying, the seeds were ground into smaller pieces using a Moulinex grinder to obtain a fine powder. Finally, the fine powder were heated in an oven at about 80 ^{o}C for 15 minutes to remove the moisture created during size reductions to prepare it for extraction of oils (Attia et al., 2020). Additionally, the ash content of fine powder was determined by burning 5 g of seed materials at 600 ^{o}C for 8 hr. using furnace (Giwa et al., 2010).

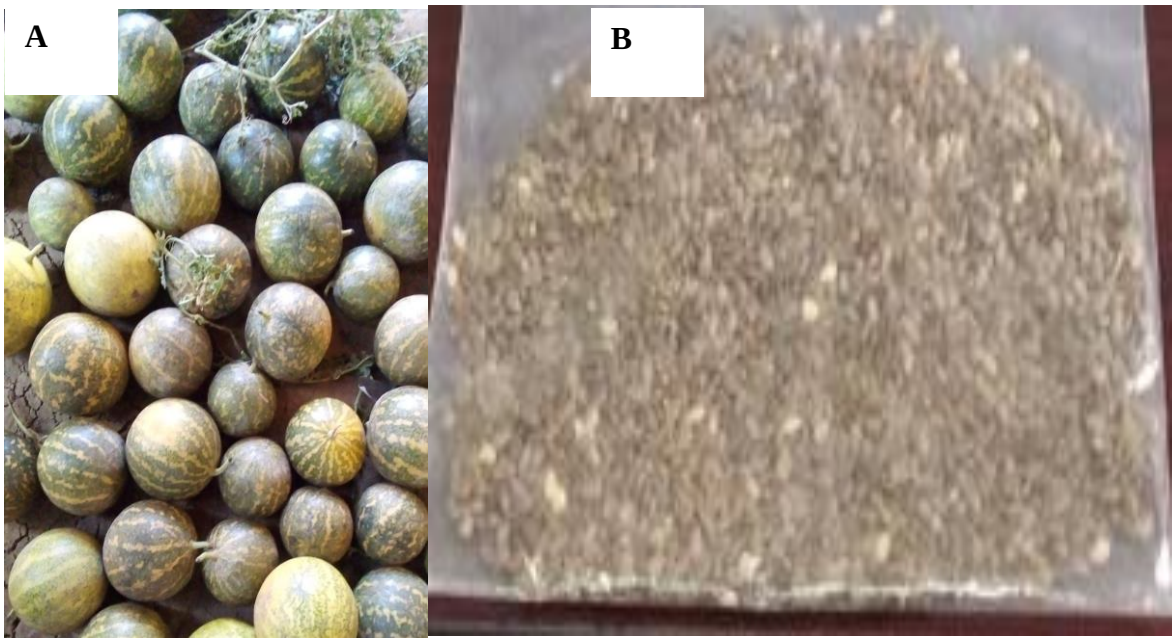


Figure 3.2. Raw material preparations *A). Fruits of Citrullus colocynthis B). Seed of Citrullus colocynthis C. Crushed sample*

3.4.2. Extraction of Oil from Citrullus Colocynthis Seed

A mass of 15 g of crushed *citrullus colocynthis* seed was weighed and placed in a 500 ml three neck flask of Soxhlet extraction system (Ali Elsheikh & Hassan Akhtar, 2014). Hexane and ethanol were the solvents used for the extraction of *Citrullus colocynthis* seed oil to select the solvent for extraction process. By carrying out solvent screening test the two solvents were selected to extract the crude oil based on the oil yield. The volume of solvent needed was determined by the ratio of 10:1. Beside reflux condenser was fitted and the mixture was heated at the boiling point of the solvent for three hours. 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, *citrullus colocynthis* crude oil was obtained. All experiments were done in duplicates and results were expressed on the basis of dry matter weight.

Table 3.2. The independent variables with their levels applied in this study

Independent variables	**Coded levels**		
	-1	0	1
Extraction temperature (^oC)	78	84	90
Extraction time (hrs.)	3	4.5	6
Solvent to solid ratio (ml/g)	10:1	20:1	30:1

3.4.3. Experimental Design for Response Surface Methodology (RSM) and Statistical Analysis

The extraction conditions of crude oil were optimized using a central composite design with Response surface methodology (RSM) applied to optimize the process variables which to achieve the highest extraction yield of crude oil from *citrullus colocynthis* seed. The parameters that could be optimized were extraction temperature (78-90 ^oC), extraction time (3-6 hrs.), and solvent to solid ratio (10:1- 30:1ml/g), with particle size, passed through a 10 mesh screen to achieve the highest extraction yield of crude oil from *Citrullus colocynthis* seed. From preliminary experiments, the range for each independent variable was selected. Each parameter was tested at three levels coded as (–1) for lower level, (+1) for higher level, and a central coded value considered as zero (0) as it is depicted in Table 3.2. The dependent variable chosen as response was extraction yield (Y, %). The coded and uncoded levels of different process variables used for optimization are indicated in Table 3.2. A second-order polynomial equation was used to fit the experimental data of the studied variables. The generalized second-order polynomial model used in the response surface analysis is shown in Eq. 3.1.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X^2_1 + \beta_{22} X^2_2 + \beta_{12} X_1 X_2 \quad \ldots\ldots (3.1)$$

where Y is the response (Y =percentage yield of oil); β_0 is a constant; β_1 and β_2 represent the regression co-efficient; while β_{11} and β_{22} are the quadratic coefficients; and β_{12} is the interaction coefficient. Design Expert software (version 13.1) was used for experimental design analysis and data processing. The different operating conditions of the experiments carried out in this study are presented in Table 3.3.

Then, the yield of extracted oil was determined by the following equations.

$$\%\text{Yield of oil} = \frac{\text{mass of extracted oil}}{\text{mass of the extracted sample}} * 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Table 3.3. Central composite design (CCD) for optimization of oil yield (Y1)

	Factor 1	Factor 2	Factor 3
Run	A:extraction temperature (°C)	B: extraction time (hr.)	C:solvent to solid ratio(ml/g)
1	74	4.5	20
2	84	4.5	20
3	78	3	30
4	78	6	30
5	94	4.5	20
6	84	2	20
7	84	4.5	3
8	90	3	30
9	90	6	30
10	90	3	10
11	84	4.5	20
12	84	4.5	37
13	90	6	10
14	84	4.5	20
15	84	7	20
16	78	3	10
17	78	6	10

3.4.4. Purification of crude Citrullus colocynthis Seed oil

The extracted oil was concentrated using a rotary evaporator at 80 °C to give a golden reddish oil and the solvent used recovered for 90 minutes (S, 2013). Moreover, to remove the dissolved ethanol, the crude oil was purified using a vacuum rotary evaporator at a temperature of 50 ° C for 30 minutes. Small amounts of precipitated particles were then removed by transferring the oil to a centrifuge and spinning it for about 30 minutes at 5000 rpm (X. Gao et al., 2019). The remaining ethanol traces were then removed from the crude oil by oven heating at 80 °C (S, 2013, Ali Elsheikh & Hassan Akhtar, 2014). Crude oil from *Citrullus colocynthis* seed was found at the end. Finally, the purified extracted crude oil was collected for analysis. The yield of extracted oil was determined by the equation, 3.1. (José María Encinar et al., 2020).

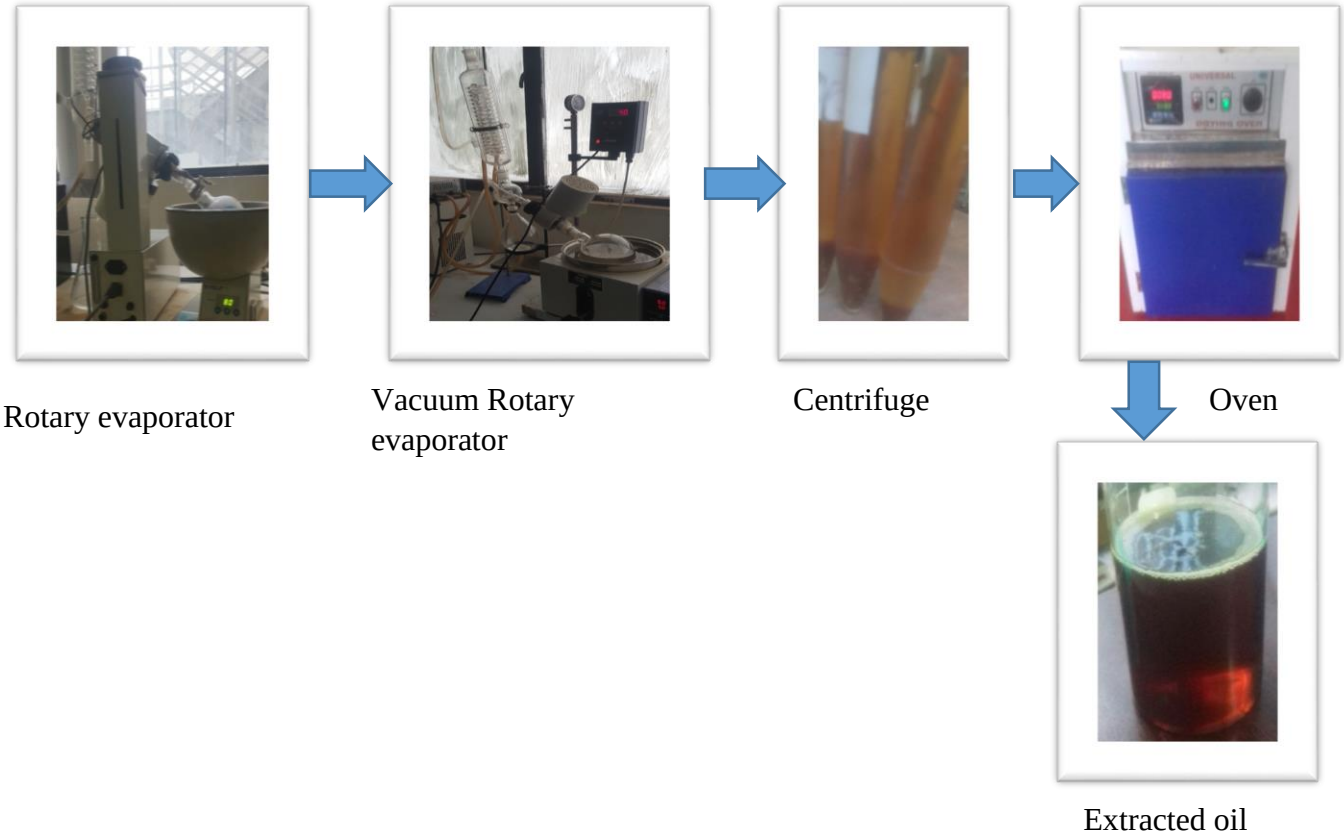


Figure 3.3. Purification of extracted crude oils

3.4.5. Fatty Acid Methyl Ester Synthesis

3.4.5.1. Transesterification of the Oils

The filtered oils obtained from oil seeds were converted to FAME using an alcoholic (methanol) transesterification process, followed by several purification steps and glycerol as a by-product. Transesterification reaction starts when the oil, alcohol, and catalyst are mixed and stirred in a reaction vessel. FAMEs are produced at optimum variables affecting transesterification reaction (Ambat et al., 2018, Kirubakaran & Arul Mozhi Selvan, 2018). The optimum process variables for high conversion transesterification are a molar ratio of methanol to the oil of 6:1, and 1.0%w/w of NaOH as a catalyst. A maximum fatty acid methyl ester yield was obtained at reaction time of 60 minute and reaction temperature of 60 °C (Nie, 2012). To synthesis fatty acid methyl ester, methanolysis of *Citrullus colocynthis* seed oil, 300 mL (267.66 g)) in the presence of 1%/w NaOH with a methanol to oil molar ratio of 6:1 was reacted. At a reaction temperature of 60 ^{o}C and reaction time of 60 minutes, the measured seed oil was transferred to a 500 ml three-neck round bottom flask to observe the conversion of oil into fatty acid methyl ester. After 60 minutes, carefully put the mixture into a separatory funnel, to separate fatty acid methyl esters and glycerol phases, by standing the mixture overnight. With a valve at the bottom of the separatory funnel, the glycerol phase (bottom phase) was transferred into a clean container. Entrained catalyst in the CCME was removed by successive rinses with hot distilled water. Then, residual water and methanol

present in the CCME was purified by oven-heating at 105 ^{o}C for a half-hour (Fischer et al., 2018). Finally, the purified FAME was obtained to be a raw material for the second transesterification.

The yield of methyl ester will be calculated using the following equation.

$$\text{Yield of ME} = \frac{\text{Vp}}{\text{Vs}} * 100\% \quad \text{.....(3.3).}$$

Where ME: methyl ester, Vp is the volume of product, and, Vs is the volume of sample oil used for the synthesis of fatty acid methyl ester.

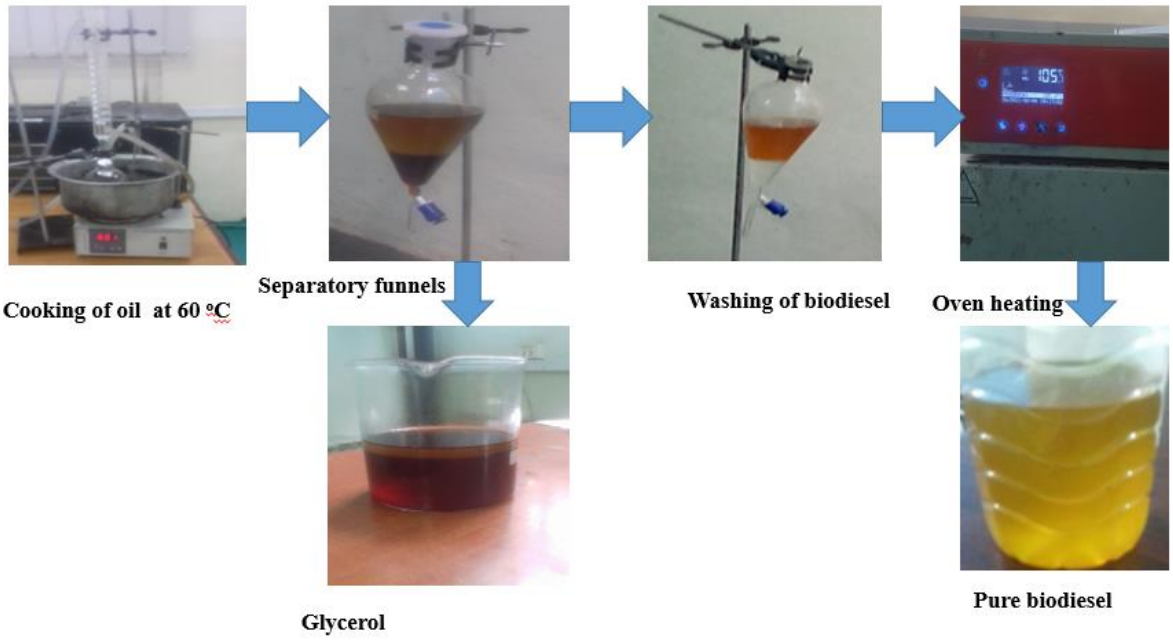
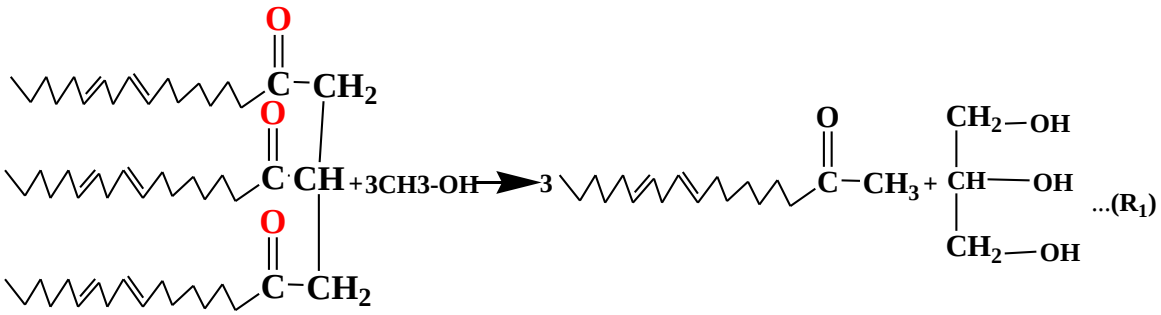


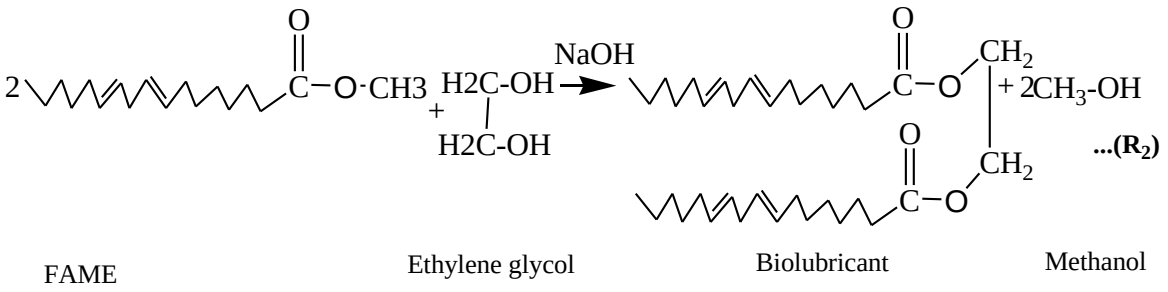
Figure 3.4. Fatty Acid Methyl Ester Synthesis



3.4.6. Synthesis of Bio-lubricants from oil-derived FAMEs

The ethylene glycol di-esters (EGDEs) as bio-lubricants were produced from each oil-derived FAMEs by using a second transesterification reaction. About 100 g of FAME was weighted and poured into a three-neck flask of 500 mL equipped with the reflux condenser, sampling port, and a thermometer (Soufi et al., 2015, Matthew Chukwudi Menkiti et al.,

2015). The effect of catalyst loading, temperature, and ethylene glycol to FAME molar ratio on the conversion of bio-lubricant was analyzed. The amount of ethylene glycol required was determined by the molar ratio of 1:1, 1:2, and 1:3. The amount of NaOH as the catalyst used was 0.5% (w/w),1% (w/w), 2% (w/w) of the weight of FAME and the reaction temperature were maintained at 160, 170,180 ^{o}C (Andreo-Martínez et al., 2018). The formed methanol as a byproduct of the reaction was immediately drawn from the reactor by heating the reaction vessel. The reaction was carried out for 120 minutes (José María Encinar et al., 2020). The released methanol from the reaction was collected and measured to calculate the transesterification conversion. The separated methanol was tested using a testing burner after bio-lubricant production, iodoform, miscibility with water, and boiling point. The testing burner and iodoform was used using the color of the flame and precipitate (Norton et al., 2019).



3.4.7. Purification of Polyol Esters

The production of polyol esters of fatty acids from methyl esters and polyol produces a crude product mixture that includes unreacted FAME, fully esterified polyols, smaller amounts of partially esterified polyols, and catalysts. The bio lubricant was washed with distilled water and a few drops of phosphoric acid to remove the residual, catalyst, and soap (X. Gao et al., 2019). The bio-lubricant was then refined by using a short path (vacuum) distillation to remove unreacted fatty acid methyl ester at a temperature of 150 ^{o}C by dissolving the sample with hexane, and purified at a temperature of 200 ^{o}C to remove residual water and ethylene glycol using oven drying. Finally, the purified bio-lubricant was collected for analysis (Dibal et al., 2017). The bio-lubricant yield is calculated by using the following equation (José María Encinar et al., 2020).

$$Yield\ of\ biolubricant = \frac{Vp}{Vs} * 100\% \quad \text{.....(3.4).}$$

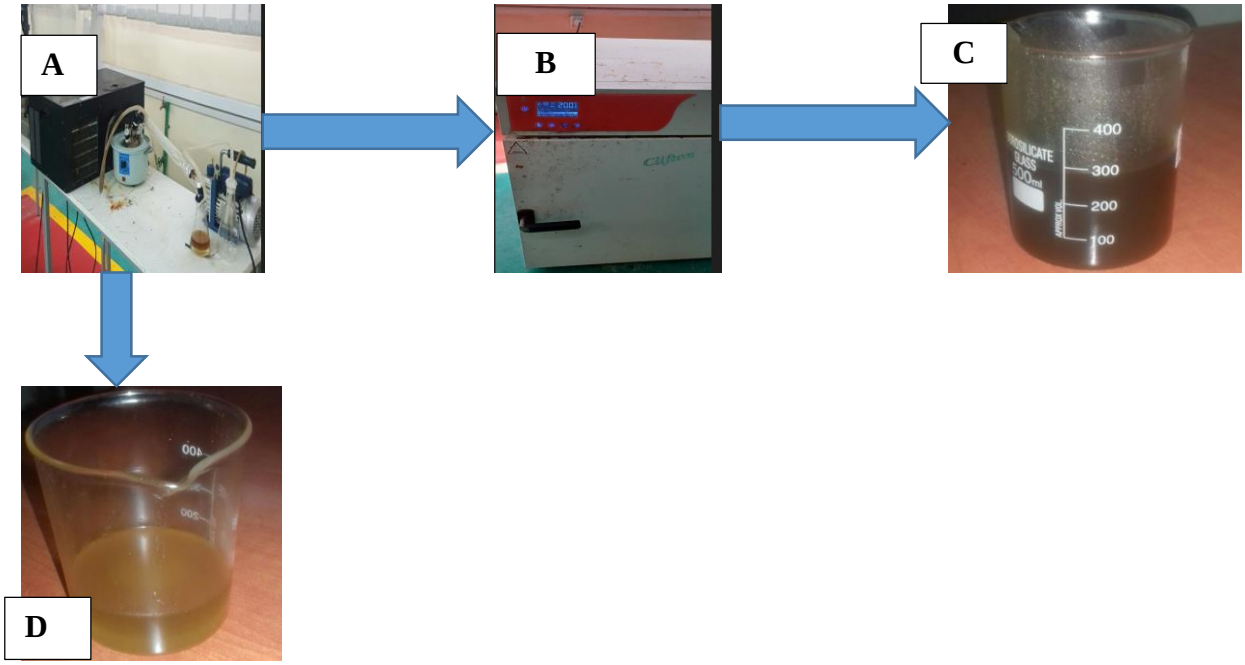


Figure 3.5. Bio-lubricant purification *(A, short path distillation, B. oven heating C. Synthesized bio lubricant, D. Unreacted product*

3.4.8. Analytical Characterization of seed oil, Fatty Acid Methyl Ester, and Bio lubricant

3.4.8.1. Gas Chromatography-Mass Spectroscopy (GC-MS)

The chemical compositions of seed oils were investigated using Gas Chromatography-Mass Spectrometry with helium gas as the carrier medium. This means that the fatty acid compositions of *C. colocynthis* seed oils, extracted by Soxhlets were investigated by using Gas Chromatography-Mass Spectrometry (Bireche et al., 2021).

3.4.8.2. Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure of the crude extracted seed oil, FAME, and Bio-lubricant were carried out using FTIR with wave numbers set at a range of 4000 to 400 cm^{-1} with 4 cm^{-1} resolutions and 32 mm/s scan rates. The FTIR spectrum of *Citrullus colocynthis* seed oil, fatty acid methyl ester, and ethylene glycol di esters (EGDEs) were analyzed (U. C. Sharma & Sachan, 2019).

3.4.8.3. Thermo-Gravimetric Analysis (TGA)

The thermal stability of seed oil, fatty acid methyl ester, and bio-lubricant was carried out using a thermogravimetric analyzer (TGA). Samples weighing ~8-10 mg were applied on alumina support under a nitrogen (N_2) atmosphere (40 mL °C min^{-1}) with a heating rate of 10 °C /min and heating range of 25 – 600 °C (Ali Elsheikh & Hassan Akhtar, 2014).

3.4.8.4. NMR analysis

The chemical structure of fatty acid methyl ester was investigated by ^{1}H NMR and ^{13}C NMR. The fatty acid methyl ester was dissolved in deuterated chloroform ($CDCl_3$) and filtered with a 0.25 μm filter and transferred to a 5 mm diameter NMR tube. For this case, the samples were completely dissolved in deuterated chloroform before the analysis (Atabani et al., 2019).

3.4.9. Physico-Chemical Properties of Citrullus Colocynthis Seed Oil, Fatty Acid Methyl Ester, and Bio-Lubricant

The physicochemical analyses of seed oil, FAME, and bio-lubricant were conducted according to the American Society for Testing and Materials (ASTM). The standard test method ASTM D-287 was used for the determination of the density at 20 °C, and 15 ^{o}C as well as specific gravity at 60 ^{o}F. Pour point, and cloud point were measured according to standard test method ASTM D97, and ASTM D2500 using KOEHLER apparatus respectively, ASTM D445 for viscosity measurement, and ASTM D6751 for flash point measurement. The physio-chemical properties of the crude seed oil, biodiesel, and bio-lubricant produced were evaluated using methods described compared to ASTM D 6751.

3.4.9.1. Determination of Density and Specific Gravity

The density of *Citrullus colocynthis* seed oil, fatty acid methyl ester, and bio lubricant were measured using an automatic density measuring device, the density meter DMA 4200 M. 3 ml sample was injected into the density meter by using a syringe. The sample's specific gravity at 60 ^{o}F and at 15 ^{o}C, along with its density at 20 ^{o}C and 15 ^{o}C, was shown by the Anton Paar DMA instrument after two minutes.

3.4.9.2. Determination of Acid Value

Acid value is determined by AOCS official method Cd 13-60. Briefly, extracted seed oil sample (15.6g) was weighed into a 250 mL Erlenmeyer flask equipped with a Teflon. Subsequently, 50 ml of absolute ethanol and phenolphthalein as indicators (two drops) were added to the flask (Mohammed-Dabo et al., 2012). Contents of the flask was then titrated with 0.1 N potassium hydroxide solution until the indicator turned light pink and the color persisted for a few seconds. The amount of titrant necessary to reach this endpoint was recorded, and the measurements obtained are utilized to calculate the acid value using equation 3.2. (S, 2013, Popoola & Ikpambese, 2021). The same procedure was used for fatty acid methyl ester with a sample mass of (20.2 g) and bio-lubricant (10.5 g).

$$\text{Acid value} = \frac{\text{titre value} * \text{normality of KOH} * 56.1}{\text{sample weight}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5).$$

3.4.9.3. Determination of Percentage of Free Fatty Acid (%FFA)

Percentage of free fatty acid is determined by AOCS official method Cd 13-60. Briefly, 11.47 g of the extracted seed oil was weight and transferred into Erlenmeyer flask equipped with a Teflon (S, 2013). Beside to this, 50 ml of absolute ethanol (Mohammed-Dabo et al., 2012) and phenolphthalein as an indicator solution (two drops) were added to the flask. It was then titrated with 0.1 N potassium hydroxide solution, and shaken constantly until a pink color persisted for few seconds. The percentage of free fatty acid is calculated using the equation below (S, 2013). Again we use the same procedure for fatty acid methyl ester with a mass of 11.47 g to determine the percentage of free fatty acid.

$$\%\text{FFA} = \frac{\text{titre value} * \text{normality of KOH} * 28.05}{\text{sample weight}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.6).$$

3.4.9.4. Determinations of Saponification Value

A sample of oil weighing 5.25 g was taken (Chowdhury et al., 2013) and transferred into a conical flask and 50 ml of ethanolic KOH was added to the sample. For 30 minutes, the oil and ethanolic KOH mixture was heated to saponify the oil (Chowdhury et al., 2014). After 30 minutes, remove the flask and check for the separated oil layer. When there was no visible oil layer and the mixture seemed transparent and clear, it was most likely the case that the oil and ethanolic solutions had been properly mixed. The saponification process ends when the mixture turns transparent (Ashrafi et al., 2017). 50 ml of ethanolic KOH has added to a blank flask once again (Chowdhury et al., 2014), and it was heated for 30 minutes. The unreacted KOH was then back titrated with 0.5 N hydrochloric acid using a phenolphthalein indicator solution (L. Wu et al., 2016). The SAP value of the samples was calculated by equation 3.6.

$$SAP = \frac{\text{titre value} * \text{normality of KOH} * 56.1}{\text{Weight of sample}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.7).$$

3.4.9.5. Determinations of Iodine Value

To determine the iodine value, a round-bottom flask was filled with 0.52 g of a weighted oil sample (Sytar et al., 2013). A blank flask was then made ready. The blank flask and flask containing the oil sample were filled with 25 ml of chloroform (Soares et al., 2017). The blank solution flask and the oil sample flask were each filled with 25 ml of 0.1 M iodine solution. Shake and rotate both flasks together for proper mixing. The sample flask and the

blank flask were titrated with 0.1 N sodium thiosulfate. Add 3 ml of 1% starch solution when the solution color is changed into lighter. Shake and resume the titration. Milky white color solution indicates the end-point of the titrations. Shake the flask vigorously. If the blue color comes back titrate again. Note the final burette reading (Tubino & Aricetti, 2013). Then, the IV can be calculated by the equation below.

$$IV = \frac{12.69(VB-VS)*0.1N}{WS} \quad \text{..... (3.8).}$$

Where IV= iodine value, V_B= Volume of blank, V_S= Volume sample, W_S = sample mass

3.4.9.6. Determination of Ester Value

The ester value of the bio-lubricant was obtained as a difference between the saponification value and the acid value (Popoola & Ikpambese, 2021).

Ester value = Saponification value – acid value……..……. (3.9)

3.4.9.7. Viscosity and Viscosity Index

Lubricant viscosity is the force keeping two moving surfaces apart to reduce friction conditions. The performance efficiency of lubricant depends on its viscosity and hence its viscosity index (Verdier et al., 2009). In this investigation, kinematic viscosities of the fatty acid methyl ester, and bio-lubricant were measured at temperatures of,40 ^oC, and 100 ^oC (Salimon et al., 2014). A temperature-controlled KVT-4000 automatic petroleum products kinematic viscosity test instrument (oil viscometer) was used to estimate the viscosity of the samples at 40 ^oC and 100 ^oC (Owuna et al., 2020). The viscometer automatically measures kinematic viscosity in accordance with the ASTM D-445 method whereas the viscosity index was measured following the ASTM D2270 method. The viscosity index shows the characteristic of the lubricant's viscosities when temperature changes were applied. The viscosity index (VI) is a parameter that measures the change of viscosity with temperature, mostly used to characterize the viscosity-temperature behavior of lubricating oils. The higher the VI of lubricant, the less viscosity decreases with an increase in temperature. On the other hand, lubricant with low VI tends to have viscosity loss with increments of temperature. The viscosity index indicates the extent of thickness or resistance to flow with temperature change (Alves et al., 2013, Mobarak et al., 2014).

3.4.9.8. Cloud Point and Pour Point

The pour point and cloud point were determined using an automatic pour and cloud point analyzer (KOEHLER IP-441), the instrument measures the pour point and cloud point in accordance with the ASTM D-2500 and ASTM D-97 methods respectively. The sample

movement is detected by the thermal probes (PT100 detection) placed above the sample surface which reacts if touched by the cooled sample. The fatty acid methyl ester and bio-lubricant samples were placed in a cooling bath at -35 ºC. However, the observations were taken from 9 ºC which is well above the expected cloud and pour points of the samples (Salimon et al., 2014). For cloud point reading, the samples were examined at intervals of 1 ºC, until a cloud is observed at the bottom of the test jar. For the case of the pour point, readings were taken for every 3 ºC decrease in the temperature until the sample ceased to flow (the sample is held in a horizontal position for 5 sec) (Mobarak et al., 2014).

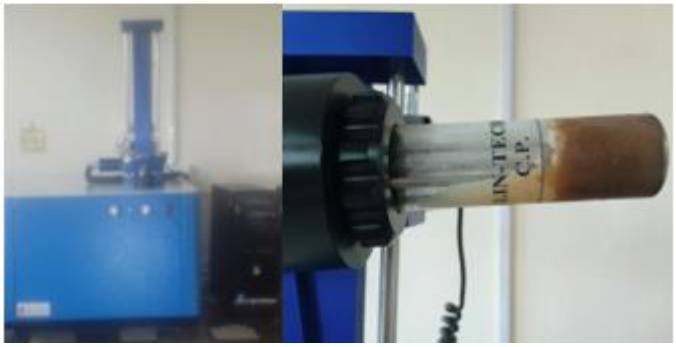


Figure 3.6. KOEHLER (Automatic Pour point and Cloud point analyzer)

3.4.9.9. Flash Point

For a flash point of fatty acid methyl ester, the biodiesel was poured into a beaker with a capacity of 100 ml. The hot plate was then opened and the beaker was put within it. A thermocouple was inserted inside the sample-containing beaker to detect the flash point (Hassan et al., 2019). The temperature of the biodiesel gives off enough vapors that ignite for a moment when a tiny flame was brought near to it was recorded (flash point). The lowest temperature at which the vapors of the FAME burnt continuously for at least five seconds when a tiny flame was brought near to it was recorded; i.e. (Fire point) (Mobarak et al., 2014).

Figure 3.7. Flash point and Fire point determination test (A. Flash, B. Fire point)

The flash point of a bio-lubricant was tested using a Cleveland open cup tester H-2085.4F conforming using ASTM D - 93. A lower flash point indicates high flammability (Mobarak et al., 2014). The temperature of the bio lubricant gives off enough vapors that ignite for a moment when a tiny flame was brought near to it was recorded (flash point). The lowest temperature at which the vapors of the bio-lubricant burnt continuously for at least five seconds when a tiny flame was brought near to it was recorded; i.e. (Fire point) (Owuna et al., 2020). It is the lowest temperature at which a chemical can vaporize to form an ignitable mixture in the air. It measures and describes the properties of materials, and products in response to heat and an ignition source under controlled conditions. The result of the test can be used for risk assessment which takes into account all factors that are pertinent to an assessment of the fire hazards of a particular end-use (Mobarak et al., 2014).

3.4.10. Determinations of Surface Roughness

The surface roughness of the material was determined using a surface roughness tester. To determine the surface roughness of the material, first, the turning and facing operations were performed using high-speed steel (HSS) cutter on Aluminum work piece materials. Before turning and facing operations of the aluminum workpiece materials, the chemical composition of the aluminum workpiece material was determined using a spectrometer to select the value of the input parameters for this experimental work. Those input parameters were cutting speed/spindle speed, feed rate, and depth of cut (Wang et al., 2020). According to Kannan et al., (2016), the range of operating parameters for Aluminum work piece machining with an HSS cutter are: cutting speed 1100 - 1500 mm/min., feed rate 500 - 900 mm/min and depth of cut 0.5 – 1.5 mm. Based on this range the values of the parameter for the turning operations were performed using HSS (high-speed steel) cutter on Aluminum

work piece materials. Those values were: cutting speed 1300 mm/min, feed rate 700 mm/min, and depth of cut 0.5 mm for our experiment. After that, determinations of surface roughness using dry cutting and wet cutting (water, mineral oil, and bio-lubricant) as cutting fluid were performed. During the machining process, a substance that had high surface roughness causes wear more rapidly and has greater friction coefficients. By comparing its surface roughness, selections of appropriate machining processes and cutting fluids were conducted (Krishnan et al., 2019).

Surface roughness is a component of surface texture and plays an important role in determining how an object will interact with its environment. Roughness is a good indicator of the performance of a mechanical component, since irregularities on the surface may form nucleation sites for cracks or corrosion (Croll, 2020).

Figure 3.8. Surface Roughness Tester

Table 3.4. Chemical composition of Aluminum 6061-T6

Aluminum							
Elements	Al	Si	Fe	Cu	Mn	Zn	Mg
%	97.59	0.60	0.27	0.11	0.45	0.11	0.62

Figure 3.9. Spectrometer

CHAPTER FOUR

4. RESULTS and DISCUSSION

The results obtained from experimental analysis of *Citrullus colocynthis* seed oil and synthesis of biodiesel and lubricants are presented in this chapter. These are explained under major three major headings namely: synthesis and characterization of *Citrullus colocynthis* crude oil, biodiesel, and bio-lubricant. This chapter contains the results of all laboratory activities, such as analyzing properties (density, acid value, percentage of FFA, saponification value, and viscosity) and characterization (FTIR, GC-MS) of *Citrullus colocynthis* seed oil. It also includes various analyses and studies on the optimization of the operating parameters in the extraction of seed oils by using Design Expert®13.0 software. The characterization results of the extracted *Citrullus colocynthis* seed oil were also discussed in this section. This extracted seed oil was characterized using, FTIR and GC-MS. In addition, characterization (FTIR, TGA, and NMR) and physio-chemical properties (density, acid value, %FFA, cloud point, pour point, viscosity, and viscosity index) were discussed. Similarly, characterization results and factor affecting bio-lubricant yield presented in this section.

4.1. Characterizations of Raw Materials

The characterizations of raw materials can be determined by determining the moisture content and ash content. The moisture content and ash content of seed was 4.24% w/w and 2.3% w/w respectively. Purpose of determining the moisture content of the raw materials was; it affects the color, quality and shelf life of the oil when it is at high level. Whereas, the ash content at high level causes health and environmental damages as well as reduces the calorific value. Based on the study carried out, the sample of *citrullus colocynthis* seeds have a good potential as a source of oil (Sytar et al., 2013).

4.2. Extraction of Citrullus colocynthis crude oil

The yield of crude oil obtained by using hexane and ethanol as a solvent was 40.1%, and 49.2% respectively at extraction time of 3 hrs., extraction temperature of at its boiling point, and solvent to solid ratio of 10 :1. Based on this analysis ethanol was the appropriate solvent used for extraction of *citrullus colocynthis* crude oil.

Table 4.1. Central composite design (CCD) and responses for the optimization of oil yield (Y1)

	Factor 1	Factor 2	Factor 3	Experimental value
Run	A: Extraction temperature (^oC)	B: extraction time (hr)	C:solvent to solid ratio(ml/g)	Oil yield (%)
1	74	4.5	20	40.8
2	84	4.5	20	51.6
3	78	3	30	43.5
4	78	6	30	48
5	94	4.5	20	40.1
6	84	2	20	46.5
7	84	4.5	3	39.2
8	90	3	30	43.2
9	90	6	30	45
10	90	3	10	41.2
11	84	4.5	20	52.1
12	84	4.5	37	50.3
13	90	6	10	42.5
14	84	4.5	20	51.8
15	84	7	20	51.7
16	78	3	10	41.3
17	78	6	10	45.6

The experimental values for response (extraction yield %) under different combinations of extraction conditions were shown in Table 4.2. Based on this, the optimum operating value for high yield of crude oil extraction were: extraction temperature 84 ^oC, extraction time of 4.5 hrs., and solvent to solid ratio of 20: 1(i.e., with 300 ml of ethanol and 15 gram of sample weight) with a particle size surpassed through 10 mesh. The obtained high yield of crude oil extracted from the sample was 52.1%. 52.1% oil yield means, from the sample weight of 15 grams the extracted oil was 52.1%. Theoretically, the crude oil extracted from *citrullus colocynthis* seed was 55.52%. While from experimental analysis the crude oil extracted from

citrullus colocynthis seed was 52.1%. So, from the total of 55.52% of crude oil 93.84% oil was extracted; while the rest (6.16%) of the oil was discharged with the residue.

4.2.1. Regression Analysis and Model Fitting

The adequacy of the developed models was tested at a 95 % confidence interval using the ANOVA technique, and the results of the linear and quadratic order response surface model fitting in the form of ANOVA are given in the table 4.3. The test for the significance of the regression models, the test for the significance of individual model coefficients, and the lack-of-fit test were performed using statistical Design-Expert 13.1. software package. By selecting the step-wise regression method, which eliminates the insignificant model terms automatically, the result is presented as shown tables 4.2 below.

Table 4.2. ANOVA analysis for the quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	306.61	9	34.07	39.37	< 0.0001	significant
A-extraction temperature	0.1511	1	0.1511	0.1746	0.6886	
B-extraction time	35.59	1	35.59	41.13	0.0004	
C-solvent to solid ratio	90.56	1	90.56	104.67	< 0.0001	
AB	2.31	1	2.31	2.67	0.1462	
AC	6.66	1	6.66	7.70	0.0275	
BC	0.0013	1	0.0013	0.0014	0.9707	
A^2	139.33	1	139.33	161.04	< 0.0001	
B^2	13.05	1	13.05	15.09	0.0060	
C^2	77.03	1	77.03	89.03	< 0.0001	
Residual	6.06	7	0.8652			
Lack of Fit	6.06	5	1.19	18.73	0.0515	not significant

Pure error	0.1267	2	0.0633
Cor .total	312.67	16	

The lack-of-fit test (P > 0.05) was used to examine the model's "fitness," which showed that it was suitable for correctly predicting the variation (Prasad et al., 2011). The degree to which the models fit the data is measured by lack of fit. The Lack of Fit F-value of 18.73 implies the Lack of Fit is not significant relative to the pure error. According to table 4.2, the lack of fit with a p-value (0.0515) greater than 0.05 (non-significant) suggests that the projected model reasonably represents the observed values, indicating that this model was capable of accurately predicting the appropriate response. There is a 5.15% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good for the model to fit. Therefore, the model adequately explained the response.

Table 4.3. Model adequacy measures for oil extractions

Std.Dev.	0.9302	R^2	0.9806
Mean	46.08	Adjusted R^2	0.9557
C.V.%	2.02	Predicted R^2	0.8550
		Adeq. Precision	16.6281

The predicted R^2 0.8550 of is in reasonable agreement with the adjusted R^2 0.9557 as one might normally expect; i.e. the difference is not more than 0.2. The difference between the adjusted R-square and predicted R- square is 0.1007 (i.e., they are close to each other) and this indicates the close fit of the model to the actual response data. According to several literature investigations, the model's suitability was demonstrated by the determination coefficient R-square value being greater than 0.75 (Subramonian et al., 2015). In the present study, the value of R-square for the developed correlation is 0.9806; this indicates that 98.06% of the extraction of oil is a success in the experimental studies. That indicates the model was adequate in this optimization study. The model's adjusted R^2 was extremely comparable to each of their respective R^2 values, demonstrating a strong correlation between the predicted and observed values. Adeq. Precision measures the signal-to-noise ratio and a ratio greater than 4 is desirable. Therefore, in this study, the ratio of 16.6281 indicates an adequate signal, and this model can be used to navigate the design space.

The degree of the data's dispersion is indicated by the coefficient of variation (CV). The coefficient of variation (CV) measures how much residual variation there is in the data with the size of the mean; smaller values of CV result in higher reproducibility. The model was repeatable, as shown by the coefficient of variation's (CV) value of less than 10 (Belhachat et al., 2018). The low CV showed that the experimental results were accurate and reliable (Table 4.4). A 2.02 % CV was observed.

4.2.2. Effect of Independent variable interactions on Oil Yield (Y)

Based on the predicted model, the effect of independent variable interaction (extraction temperature, extraction time, and solvent to solid ratio) are explained by plotting contour and three-dimensional (3D) plots. All other independent variables are expected at centered levels.

Second-order polynomial mathematical models for crude oil extraction were obtained by conducting a multiple regression analysis. These mathematical models were applied to develop a relationship between independent and response variables. The final quadratic polynomial equations for crude oil extraction were formulated by using the regression coefficient values with ignoring insignificant terms and are given by the following equations.

$$Y = 51.78 - 0.1052A + 1.61B + 2.58C - 0.5375AB + 0.9125AC + 0.0125BC - 3.52A^2 - 1.08B^2 - 2.61C^2$$

From this quadratic regression model equation, it was observed that the linear variables B, and C and the interaction variables AC and BC, have a positive effect on the extraction of crude oil yield, whereas other terms have a negative effect. The reason ethanol concentration creates a positive linear effect on oil yield is due to the hydroxyl group, which creates a hydrogen bond with oil, thus stimulating the solubilization of the solute in the solvent (Chouaibi et al., 2020).

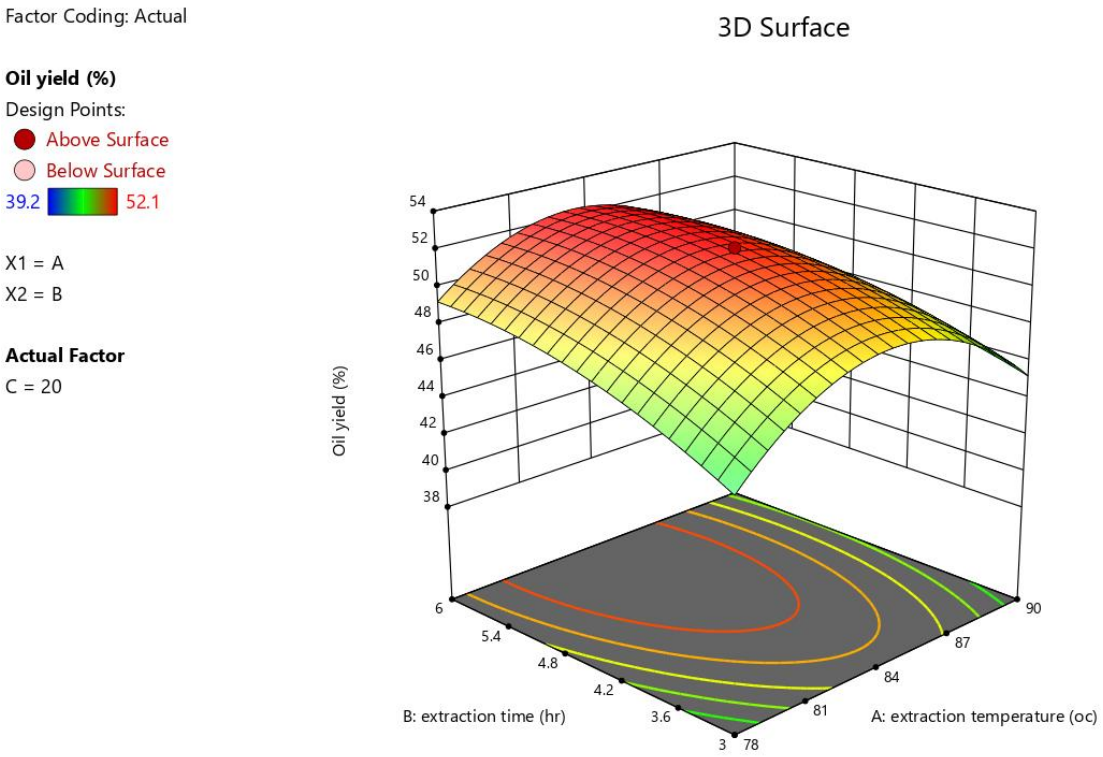


Figure 4.1. Response surface (3-D) plot for the interactional effect of extraction time and temperature on percentage yield of oil extraction

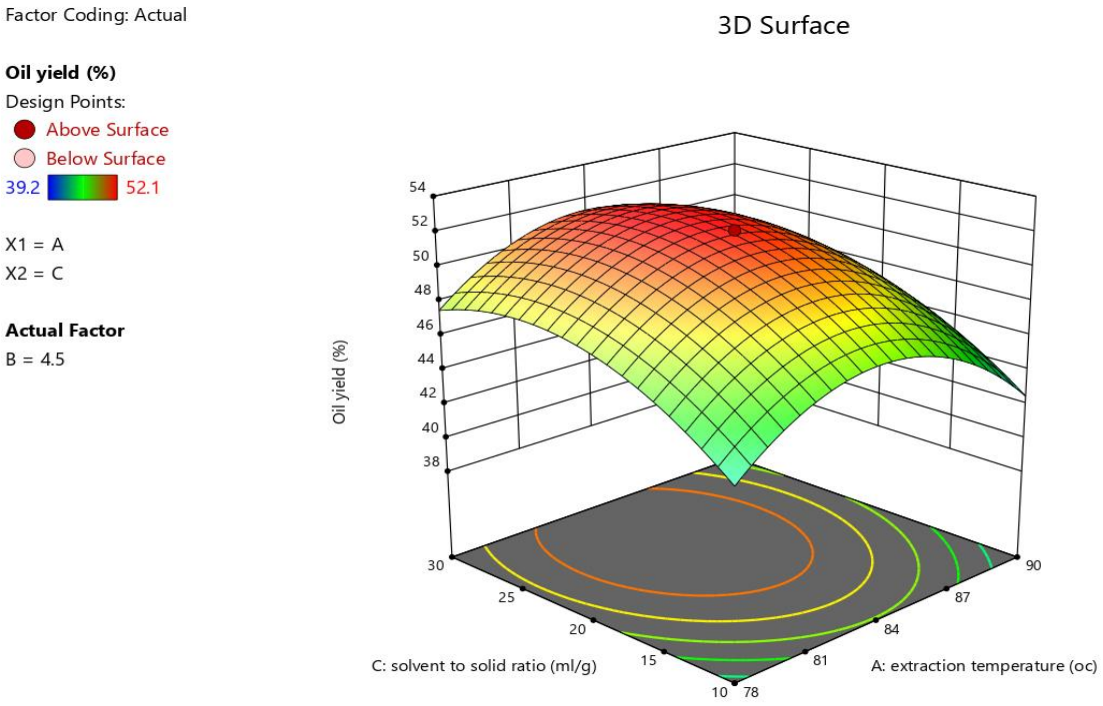


Figure 4.2. Response surface (3-D) plot for the interactional effect of extraction temperature and solvent to solid ratio on percentage yield of oil extraction

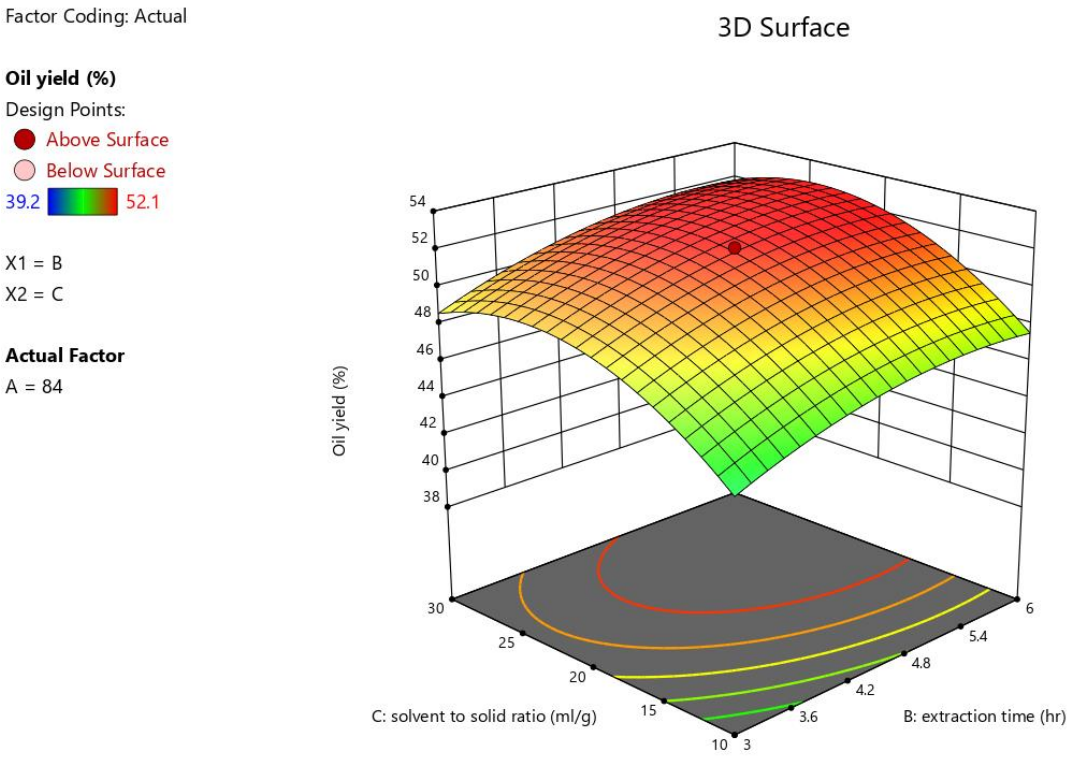


Figure 4.3. Response surface (3-D) plot for the interactional effect of extraction time and solvent to solid ratio on percentage yield of oil extraction

The three-dimensional (3D) responses for oil extractions are shown in Fig. 4.1, 4.2, and Fig.4.3, which indicates the effects of the significant terms on the tested response. The extraction parameters such as extraction temperature (X_1, 78 – 90 ^oC), extraction time (X_2, 3-6 hr.), and solvent to solid ratio (10:1 – 30:1 ml/g) influenced the oil extraction yield. The 3-D curves showed the main and interaction effect between two extraction parameters on the crude oil yield by maintaining the third parameter at zero level. Fig. 4.1,4.2. and 4.3, exhibited the main (X_1, X_2, and X_3) and interaction effect (X_1X_2, X_1X_3, and X_2X_3) on the yield of crude oil extractions.

From figure 4.1. as we see that at a constant solvent to solid ratio both extraction temperature and extraction time affect the extraction yield of oil in both interaction and quadratic manner. The extraction of crude oil achieved the highest value of 52.1% when extraction temperature and extraction time varied from 78 to 84 and 3.00 to 4.5 hr., respectively, and thereafter, the oil extraction yield was stable when extraction time and temperature surpassed the optimum value. Initially, the crude oil yield increased significantly as extraction time increases because of the more extraction time, oil pockets are diffused out due to the higher boiling point, followed by a stable as further increasing the extraction time. The results is in good

agreement with previous work (Zhang et al., 2012). When the extraction temperature rises to a certain point, the formation of cavitation bubbles, on the other hand, will be extraordinarily high which strengthens the energy dissipation between cavitation bubbles and causes its insufficient collapse, resulting in decreased energy transfer efficiency and crude oil yield. This finding is in good agreement with previous work (Zheljazkov et al., 2014, Kusuma & Mahfud, 2015). However, the linear effect of extraction temperature (X_1) was found to be not significant; while extraction temperature (X_1) was significant. Both extraction time and extraction temperature had a non-significant interaction effect while a significant quadratic effect on the extracted crude oil yield.

Fig.4.2, showed the 3D response curve of the main and interaction effect (X_1X_3) of solvent to solid ratio and extraction temperature on extraction of oil yield at constant extraction time. The extraction yield of crude oil significantly increased with an increase in solvent to solid ratio from 10:1 ml/g to 20:1 ml/g, and extraction temperature from 78 to 84 ^oC, and thereafter both the crude oil yield decreased. However, using a lot of solvents could mean that it takes longer and more energy to condense the extraction solution, which was in good agreement with work of Jeyaratnam et al., (2016). Increasing the amount of solvent will result in a higher concentration gradient at the interface between the solid particle and solvent (ethanol) for the crude oil that is present in the combination. The amount of solvent, however, no longer affected the crude oil yield once the solute inside of the C. colocynthis seed particles had been completely extracted (Yingngam & Brantner, 2015). This was most likely caused by some volatile components being susceptible to degradation in the presence of a high solvent (ethanol) concentration (Zhang et al., 2012). On the other hand, this decrease is probably elucidated by the solubilization of lipids (fatty acids and triglycerides), and also when the extraction temperature increases, the ethanol density is reduced and reduces its solvation power, which was in good agreement with previous work (Muangrat & Jirarattanarangsri, 2020). Solvent to solid ratio has a significant on crude oil extraction while extraction temperature has non-significant effect on crude oil extraction yield. Both solvents to solid ratio and extraction temperature have significant interaction and quadratic effects on the yield of crude oil extractions. A higher yield of oil extraction is strongly favored when a high solvent-to-solid ratio is employed for a certain time of extraction (B) and temperature (A). The 3D (figure 4.2 and 4.3) indicates that the extracted oil increased when solvent to solid concentration increased. Therefore, the solvent to solid ratio is a fundamental variable in the extraction of oil (Ocholi et al., 2018).

Fig. 4.3. showed the 3D response curve of the main and interaction effect (X_2X_3) of solvent to solid ratio and extraction time on the extraction of oil yield at constant extraction temperature. The extraction yield of crude oil significantly increased with an increase in solvent to solid from 10:1 ml/g to 20:1 ml/g, and extraction time was 3.00 to 4.5 hrs. Initially, crude oil yield increased significantly as extraction time increases because of the more extraction time, oil pockets are diffused out due to the higher boiling point, which was in good agreement with the previous work (Zhang et al., 2012). The extraction yields started stable when the extraction time surpassed the optimum value. However, when all of the solute inside solute particles has been extracted, the quantity of solvent no longer changed the yield of the crude oil (Yingngam & Brantner, 2015). When the solvent to solid ratio was more than 20:1, the yields of the extractions began to decrease. This was probably due to some volatile components being susceptible to dissociate under a high proportion of solvent (ethanol). And also, this yield reduction is accredited to the solute which did not have contact time to be dissolved, which was in good agreement with previous work (Chouaibi et al., 2020). Both solvents to solid ratio and extraction time have significant linear, interaction and quadratic effects on the extractions of yield of crude oil.

In addition, the regression model was used to explore the interaction effects of three independent parameters for the extraction of oil extraction yield. According to the 3D response surface analysis, the linear term (X_2, and X_3), interaction term (AC), and quadratic terms (X_1, X_2, and X_3) had a significant effect on the extraction yield. Indeed, the quadratic effect of temperature and solvent to solid ratio is the most significant factor on oil extraction yield ($P < 0.0001$) as well as the linear term of solvent to solid ratio is the most significant factor on crude oil extraction yield, which was in good agreement with work done before (Belhachat et al., 2018).

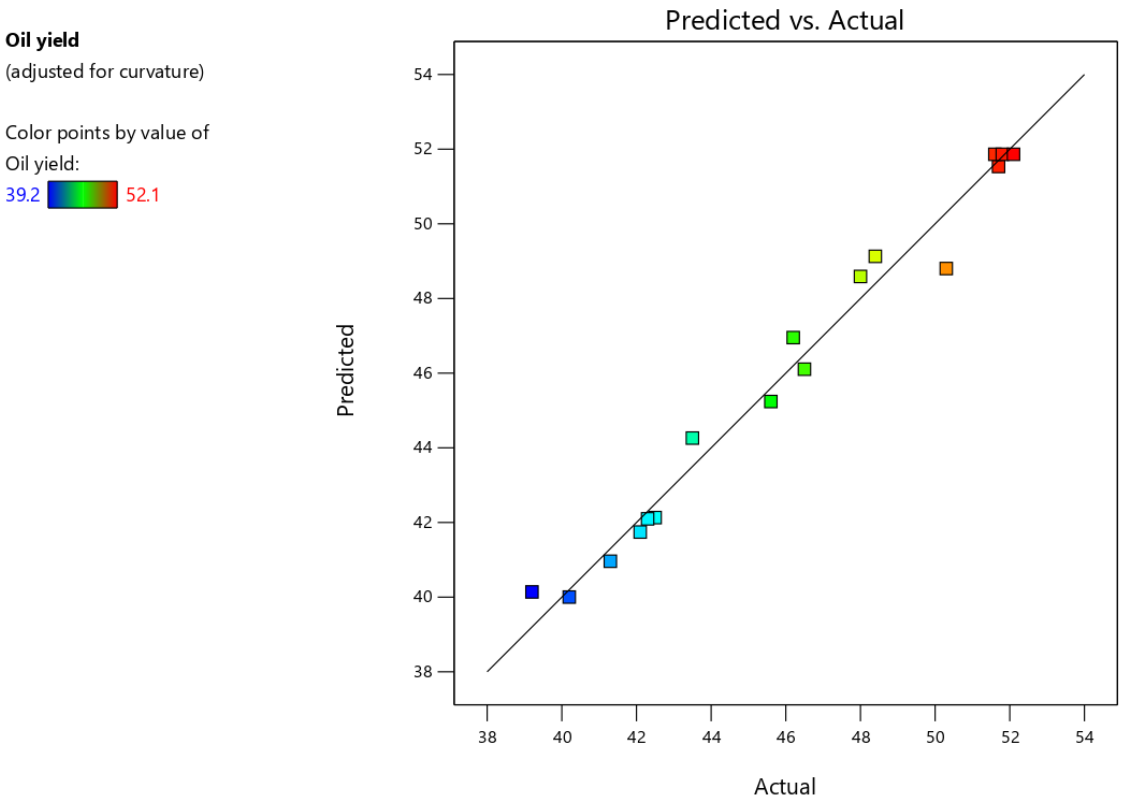


Figure 4.4. Predicted vs actual value of oil extraction

The sufficient approximation of the second-order polynomial model can be checked by comparing experimental value and predicted data by plotting the relationship between the predicted values and the experimental values of crude oil extraction yield. The comparison of this values was performed by generating a fitted-line plot for the results obtained, showing how close it was or how far it deviated from the fitted line. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4.4. above. Second-order polynomial equations were used to mathematically model the impact of extraction variables and their interactions on crude oil yield. By comparing and visualizing the experimental value and predicted value of extracted crude oil, the second-order polynomial model's suitability was examined. The plotted in figure 4.7. demonstrated that the regression model equation provided by an accurate description of the experimental studies, in which all the points are very near to the line of the perfect fit. This result shows that the relationship between the three independent process variables (extraction temperature, extraction time, and solvent to solid ratio) and the reaction was successfully captured (Zhang et al., 2012). That means, the experimental values were close to a straight line of the predicted values, there is in agreement between this values, the determination coefficient R^2 for the crude oil yield extraction of C. colocynthis seed was 0.9890, this result

indicated that the response surface model in this study was suitable to be used for optimization of the independent process variables and was adequate for predicting the yield of crude oil extraction of C. colocynthis seed. This predicted vs. actual plotted data also concluded that the proposed response surface model was suitable to optimize the conditions for crude oil extraction.

4.3. Properties of Extracted Citrullus Colocynthis Crude Oil

Crude oil from the seeds of Citrullus colocynthis was used in this experiment. As indicated in table 4.5, the quality of Citrullus colocynthis seed oil (CCSO) was evaluated in terms of a few specific physicochemical properties, such as acid value, percentage of free fatty acid, saponification value, density, iodine value, and ester value.

The density of the crude oil extracted from Citrullus colocynthis seed was 0.9196 g/cm^3 (ASTM D 287). According to the data of EN 14214 standard, the standard limit of Citrullus colocynthis seed oil is in the range of (0.905 – 0. 926 g/cm^3). The density of Citrullus colocynthis seed oil obtained to be in good agreement with the limits specified by EN 14214 standard. And also, the density of Citrullus colocynthis seed oil was in good agreement with the previous work (Ivanova et al., 2022).

The acid value of the *Citrullus colocynthis* crude oil was 0.72 mg KOH/g. The obtained result of acid value for *Citrullus colocynthis* seed oil was in close agreement with Alloune et al., (2018). With the acid value of 0.72 mg KOH/g content, transesterification of the oil was conducted directly (using a single-stage reaction process (Giwa et al., 2010). According to Pillai & Kumar, (2020), the acid value of Custard Apple Seed Oil was 2.28 mg KOH/g of oil, whereas according to S, (2013), the acid value of jatropha oil was 29.06 mgKOH/g of oil. When the acid value is greater than 2%, the process needs esterification with an acid. So, for further process, both of them need esterification of the oil with acid catalyst conducted, because it causes rancidity and corrosion (Nie, 2012). The extracted crude oil does not need esterification with an acid due to the result obtained was within the range.

The percentage of free fatty acid was 0.36 mg KOH/g. The value of the percentage of free fatty acid can be in close agreement with the study conducted by Ivanova et al., (2022). But, from this result, we concluded that if the percentage of free fatty acid was greater than 2%, the process needs an esterification process for further processes, and also it indicates the rancidity of the extracted seed oil. So, the percentage of free fatty acid is less than 2% and it does not need esterification of the extracted seed oil for further processes. Moreover, it has

been reported that < 0.5% FFA required for successful transesterification to avoid soap formation resulting from high free fatty acid (Demirbas, 2009). The result obtained was within the range.

The saponification value of seed oil obtained was 176.3143 mg KOH/g. This indicates the amount of KOH required to saponify one gram of oil sample (Alloune et al., 2018). The saponification value of *Citrullus colocynthis* seed oil was observed to be in good agreement with the limits specified by EN 14214 standard (192 ± 43.7). According to Pillai & Kumar, (2020), the saponification value of Custard Apple Seed Oil was 197.795 mgKOH/g of oil, and according to, S, (2013), jatropha oil was 198.76 mgKOH/g of oil. A value for which its saponification value was very high; it was used for soap making. Compared to those two oils the saponification value of CCO was slightly less. So, it is used to synthesize a better bio lubricant than the other two. Agbede et al., (2012), reported that oils with saponification values greater than 300 mgKOH/g are generally suitable for soap production. Based on the result obtained, the synthesized crude oil was within the range, and used as a synthesis of good quality of lubricant.

The iodine value of the *Citrullus colocynthis* seed oil was 78.1 g I/100 g oil. This indicates the degree of unsaturation of fat or oil (Alloune et al., 2018). Primarily based on their iodine value, plant oils are subdivided into three categories. Consequently, oils are classified as "non-drying" if their iodine value is below 90, "semi-drying" if the component comprised is between 90 and 130, and "drying" if the iodine value is greater than 130 (Salih & Salimon, 2021). Based on these criteria, the iodine value of CCO is below 90. So, the CCO is classified as a non-drying oil. Drying and semi-drying oil were not used for the synthesis of bio lubricant. Non-drying oil is used for the synthesis of bio-lubricant.

The ester value of the *Citrullus colocynthis* crude oil was 175.5943 mg KOH/g of oil. The high value of ester value indicates the presence of a high amount of ester and low molecular weight of fatty acid content.

Therefore, all the properties of synthesized seed oil were in good agreement with the standards.

Table 4.4. Comparison of Properties of Citrullus seed oil with Custard Apple Seed Oil (Pillai & Kumar, 2020), Jatropha crude oil (S, 2013), and standard value

Properties	**Citrullus seed oil (Our work)**	**Custard Apple**	**Jatropha crude oil**	**Standards EN 14214**

		Seed Oil		
Density (g/cm^3) at 20 ^{o}C	0.9196	0.922	920.4	0.905 – 0. 926
Density (g/cm^3) at 15 ^{o}C	0.9228			
Specific gravity at 60 ^{o}F	21.775			
Acid value (mg KOH/g oil)	0.72	2.28	29.06	< 2%
Percentage of free acid (mg KOH / g oil)	0.36	1.14	14.6	< 2%
Saponification value (mg KOH / g oil)	176.3143	197.795	198.76	< 300
Iodine value (g I / 100 g oil)	78.1	60.213		< 90
Ester value (mg KOH/g of oil)	175.5943			

4.4. Transesterification of Crude Oil and Characterization of Fatty acid methyl ester

The FAME was synthesized by transesterification of *Citrullus colocynthis* seed oil with methanol. Theoretically, a reaction between one mole of TAG and three moles of alcohol should result in three moles of FAME; while an excess of alcohol is necessary to shift the equilibrium towards the formation of esters. According to Ren et al., (2017) a molar ratio of 6:1 should be utilized to maximize the conversion of FAME. When the methanol to oil molar ratio was increased from 3:1 to 6:1, the production of FAME improved significantly from 64.67 to 97.33% (v/v), which is in total conformity with those obtained by previous work (Nie, 2012).

4.4.1. Characterization of C. Colocnythis Oil Methyl Ester (CCOME)

The fuel properties of the CCOME were determined and compared with diesel and biodiesel of ASTM standard.

Density is an important parameter for diesel fuel injection systems. It is the weight of a unit volume of fluid. A higher density for biodiesel results in the delivery of a slightly greater mass of fuel since fuel injection equipment operates on a volume metering system. The density of synthesized FAME obtained was 0.885 g/cm^3 (ASTM D 287). This result was close to the limits of the ASTM D6751 standard which was 0.88 g/m^3 for biodiesel and 0.823 g/cm^3 for diesel fuel (Babakura et al., 2019, Bakheit Mohamed Ahmed & Fath El-Rahman Ahmed Mohamed, 2020). That means the obtained density was within the limits specified by ASTM D-6751 standards (0.875 – 0.9 g/cm^3). The density of FAME at 15 ^{o}C was 0.8882 g/cm^3. This result fits into the limits specified by EN 14214 standard (860–900 kg/m^3).

Moreover, the density of CCOME was observed to be in good agreement with that of conventional methyl esters, egusi melon oil methyl ester (884 kg/m^3) obtained by Giwa et al., (2010). From the result obtained, the density of methyl ester was decreased when compared to that of the *Citrullus colocynthis* crude oil, because it passed through a series of modifications through transesterification processes. And also, the non-polar methyl ester molecules making up the FAME do not mix with the polar glycerol molecules (Ishola et al., 2020).

The acid value of FAME synthesized from *Citrullus colonythis* seed oil was 0.55 mg KOH/g. This result almost fits into the limits specified by EN 14214 standard (0.5 max). The results obtained were in good agreement with previous works (Bakheit Mohamed Ahmed & Fath El-Rahman Ahmed Mohamed, 2020, Babakura et al., 2019). The acid value is one of the most important parameters used to check biodiesel quality. According to Nisar et al., (2017), the acid value of jatropha FAME was 0.629 mgKOH/g. When the determined acid value of FAME was large it causes the rancidification of FAME (Aworanti et al., 2019). When we compare it with that of jatropha FAME, the FAME synthesized from *Citrullus colocynthis* seed oil the C. colocynthis seed oil methyl ester does not cause rancidification, and does not accelerate wear and rust formation as well as corrosion, because it was in close agreement with the limits specified by EN 14214 standard. Therefore, the acid value of CCOME satisfies this specification and hence, is an indication of good FAME quality.

The specific gravity of CCOME in this study was 27.64 at 60 ^oF (ASTM D 287), or 0.894 at room temperature. It is somewhat in agreement with the limit of biodiesel rather than diesel standard whose ranges were 0.88 – 0.90 and 0.82 – 0.88 The results observed in this finding were in good agreement with the works of Bakheit Mohamed Ahmed & Fath El-Rahman Ahmed Mohamed, (2020).

The flash point of a fuel is the temperature at which it will ignite when exposed to a flame. The flash point of FAME is higher than diesel fuel, which makes it safer for transportation purpose. The FAME produced from Citrullus colocynthis seed oil had a flash point of 181 °C, which was observed to be in good agreement with Kaisan et al., (2020). The minimum specifications of flash points for biodiesel and diesel are 130 ^oC, and 120 ^oC, which are the limits specified by ASTM D-6751, and EN 14214 standards. This finding was in good agreement with the standards. The fire point of CCOME was 195 ^oC, which is the lowest temperature at which the vapors of the oil burnt continuously for at least five seconds when a tiny flame is brought near to it, in which The flash point of a fuel is the temperature at

which it will ignite when exposed to a flame. The flash point of biodiesel is higher than diesel fuel, which makes it safer for transportation purposes. The flash point and fire point of the CCOME were found to be 181 °C and 195 °C, respectively which is higher than that of jatropha biodiesel at 73 ^{o}C which was obtained by previous work (Kaisan et al., 2020). According to Giwa et al., (2010), the flash point of egusi melon oil methyl ester was 142 ^{o}C. The synthesized FAME from *citrullus colocynthis* seed oil was higher than that of egusi melon oil methyl ester. Biodiesel which had a low value of flash points causes hazards, and with a high value of flash points had a significant hazard, or does not cause a hazard. Based on this comparison, the FAME synthesized from *Citrullus colocynthis* seed oil was less hazardous than jatropha biodiesel. It was in good agreement with the results of Encinar & González, (2020).

Kinematic viscosity is a very important fuel property and it represents the flow characteristics of fuel. The kinematic viscosity of synthesized FAME measured at 40 and 100 oC was 10.28 cst, and 6.79 cst respectively. According to ASTM D-6751 standard the range of biodiesel is between 1.9 - 6.0 and diesel fuel 1.9 - 4.1, and for EN 14214 the range of biodiesel is in the range of 3.5-5 cSt (Bakheit Mohamed Ahmed & Fath El-Rahman Ahmed Mohamed, 2020). The obtained result was higher than the acceptable viscosity ranges for biodiesel. This is due to biodiesel having a larger fatty acid chain length causing an increase in kinematic viscosity. In addition when the alcohol constituents in fatty acid ester may increase the kinematic viscosity (Verma et al., 2012). The viscosities of the biodiesel at 40 and 100°C are very important fuel properties; they are useful in determining the fluidity of the fuel at low and high temperatures. They also show the thermal stability of the fuel. A crucial aspect of fuel is its kinematic viscosity, which describes how fuel flows. One of the reasons why biodiesel is used as an alternative fuel instead of pure vegetable oils or animal fats is result of its reduced viscosity which enhances fuel flow characteristics. In addition, kinematic viscosity is an important parameter regarding fuel atomization and combustion as well as fuel distribution (Giwa et al., 2010).

The pour and cloud point of synthesized *Citrullus colcoynthis* seed oil methyl ester was -3 and 9 ^{o}C respectively. The pour point is defined as the lowest temperature at which the biodiesel can be poured under the prescribed test conditions. Cloud point is the temperature at which wax first becomes visible to the naked eye when the fuel is cooled. At temperatures below the cloud point, bigger crystals combine to create agglomerations that eventually become large enough to block the flow of the fluid, affecting the efficiency of fuel pumps,

injectors, and lines. According to ASTM D-6751 and EN 14214 standards, no limit is specified for pour and cloud point. This may probably be due to the fact that the climate conditions world over vary to a great extent, thus affecting the needs of FAME consumers in each particular region. Most of the time, the standard value of pour point by using ASTM D-97 and cloud point using ASTM D-2500 was between -15 to 16 ^{o}C, and -3 to 12 ^{o}C respectively (Ambat et al., 2018). Based on this standard the result obtained was within the specification; this indicates the synthesized FAME was in good agreement with the standard limit indicating the acceptability of the synthesized FAME.

Table 4.5. Properties of Citrullus colocynthis oil methyl ester, *Jatropha FAME (Nisar et al., 2017), compared to the standard*

Properties	**CCOME (our work)**	**Jatropha biodiesel**	**USA (ASTM D6751), (EN 14214)**
Density (g/m^3) at 20 ^{o}C	0.885	869 (ASTM D 4052)	0.875 – 0.9
Density (g/cm^3) at 15 ^{o}C	0.8882		0.86 - 0.9
Specific gravity at 60 ^{o}F	27.64		
Acid value (mg KOH/g)	0.55	0.629	0.5 max
Flashpoint (^{o}C)	181	73 (ASTM D 93)	130 min, 120 min.
Fire point (^{o}C)	195		
Viscosity @ 40 ^{o}C (cSt)	10.28	2.45	1.9 - 6.0
Viscosity @ 100 ^{o}C (cSt)	6.79		
Pour point (°C)	-3 (ASTM D 97)		-15 to 10
Cloud point (°C)	9 (ASMT D 2500)		- 6 to 13

4.5. Synthesis and Purification of Bio-lubricant

4.5.1. Synthesis of Bio-lubricant

The bio-lubricant was synthesized by using process parameters such as reaction temperature, catalyst concentration, alcohol to FAME ratio, and Co-solvent with a fixed reaction time of 120 minutes. Based on the effect of operating conditions (reaction temperature 160,170 ^{o}C and 180 ^{o}C, catalyst loading of 0.5% w/w, 1% w/w and 2% w/w, and FAME to ethylene glycol molar ratio of 1:1,1:2 and 1:3) on bio-lubricant yield, the optimum condition was temperature 170 ^{o}C, FAME to ethylene glycol ratio 1:3 and catalyst loading 1% w/w at a fixed reaction temperature of 120 minutes which gives a maximum yield of bio-lubricant of 92,15%.

4.5.2. Effect of Operating Conditions on Bio-Lubricant Synthesis

4.5.2.1. Effect of temperature

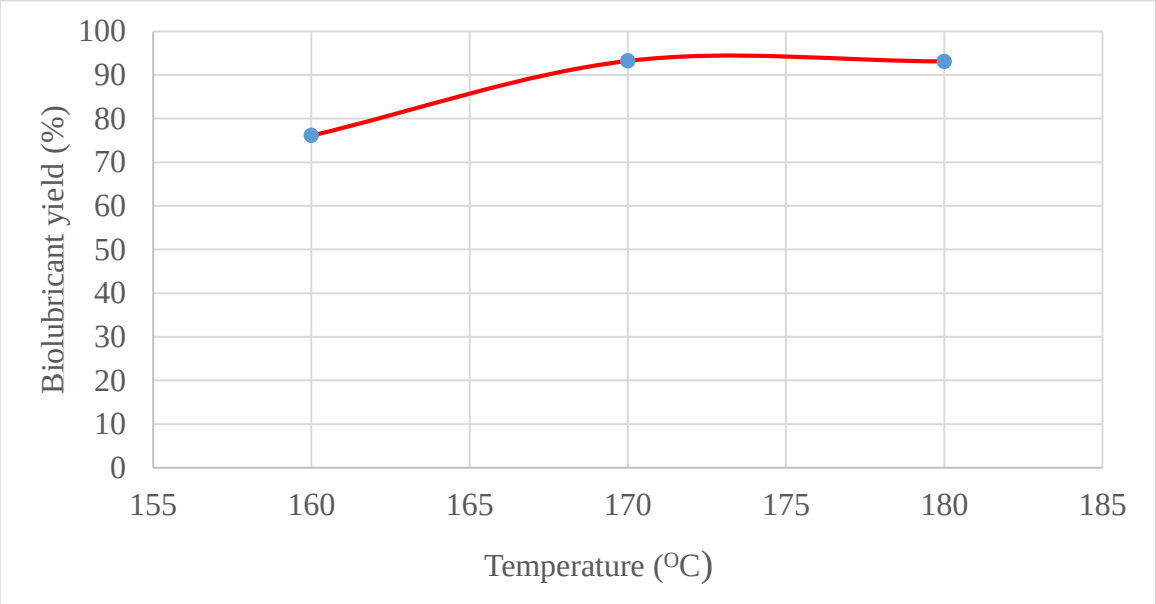


Figure 4.5. Effect of temperature on synthesis of bio-lubricant: (Catalyst,1% w/w; alcohol to ethylene glycol molar ratio, 3:1)

Regarding the effect of temperature on bio-lubricant yield, it can be shown from Figure 4.8, that 160 ^{o}C had the worst results, yielding 76.1% at the end of the experiment. Over 90% of the reactions at 170 and 180 ^{o}C were synthesized in 120 minutes, with final yields of 92.15 and 92.1% in each case, albeit the reaction at 180 ^{o}C was kinetically faster. That means as the temperature increases, the yield of bio-lubricant can also increase from 76.1% to 92.15%. An increase in temperature implied higher conversion values at the end of each experiment, increasing the reaction rate at the beginning of the reaction. This could be due to the endothermic nature of the reaction, increasing chemical product generation with

temperature, as observed for the production of bio-lubricants from different sources and alcohols (Farag et al., 2018,Moura et al., 2021). This increase is due to the increase in reaction temperature which can increase the reaction rate and accelerate reactant particle collisions. The reaction at a temperature of 180 ºC may cause the more volatile FAME component to vaporize and reduce the total residence time that decreasing the yield of bio-lubricant, which was in close agreement with previous work (José María Encinar et al., 2020). The color of the final lubricant product mixture was found to be affected by the temperature as well and it losses it's property. The color of bio-lubricant was gradually changed from brown to dark brown when the temperature changed from 170 ºC to 180 ºC; in addition, it changes into grease lubricating oil as similar findings have been reported by Singh, (2011). Since the product darkened at higher temperatures and changed into grease lubricant, 170 ºC was chosen as the optimum experimental temperature. Therefore, the optimal reaction temperature was 170 ºC which gives maximum bio lubricant yields.

4.5.2.2. Effect of Ethylene glycol/FAME Molar Ratio

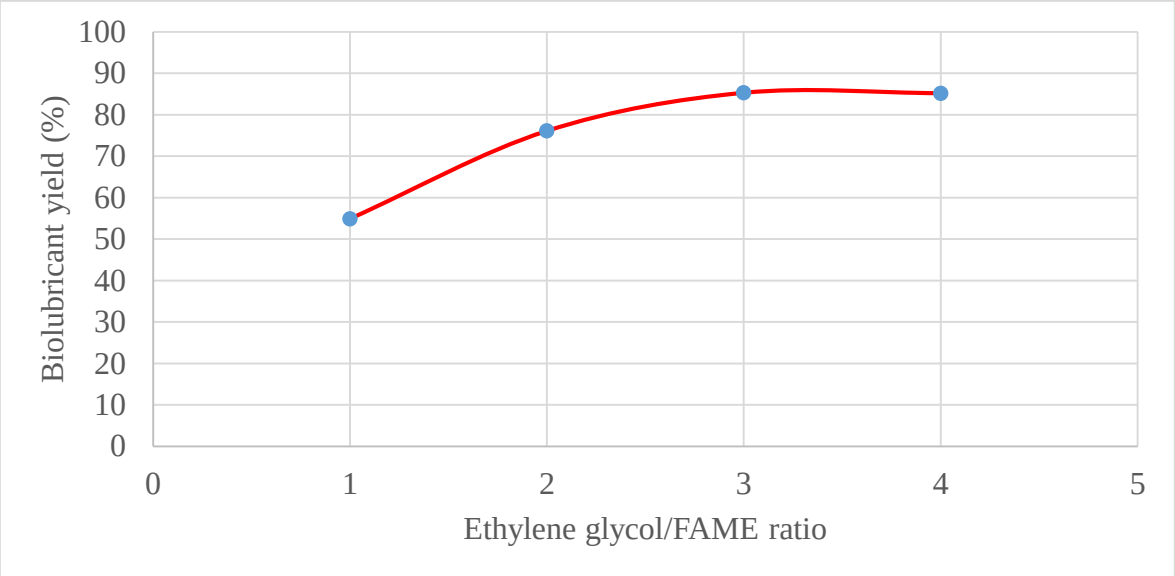


Figure 4.6. Effect of Ethylene glycol/FAME molar ratio on synthesis of bio-lubricant: (Catalyst, 1% w/w; temperature: 170 ºC), time 2 hours)

From figure 4.9, we see that there was a variation in the yield of bio-lubricant concerning ethylene glycol to FAME, particularly for the 1:1 molar ratio. With this figure, conversion was only about 54.9%, although the yield was better with 2:1, 3:1, and 4:1. (76.6%, 85.3%, and 85.2, respectively). These findings demonstrated that increasing alcohol concentration, shifting the process in the direction of bio-lubricant production. The concentration of alcohol had a positive effect on kinetics, increasing the rate at which the end product formed.

Because of this, several authors suggest using a slightly greater alcohol concentration than the 1:1 molar ratio in transesterification reactions using FAME as the substrate (Jose & Anand, 2016). It was equally observed in other studies, as in the case of polyol ester bio-lubricant produced from safflower whose yield increased with the amount of alcohol (pentaerythritol) (J. M. Encinar et al., 2022). Therefore, too much alcohol caused reaction products to be produced. Kleinaite et al., (2014) claim that when FAME is utilized as an intermediate substrate in a transesterification reaction, the alcohol concentration is larger than 1:1. Based on this, the optimum molar ratio, which provides the highest yield of bio-lubricant, was 3:1.(85.3 %). That means the best molar ratio in this scenario was 3:1.

4.5.2.3. Effect of catalyst loading

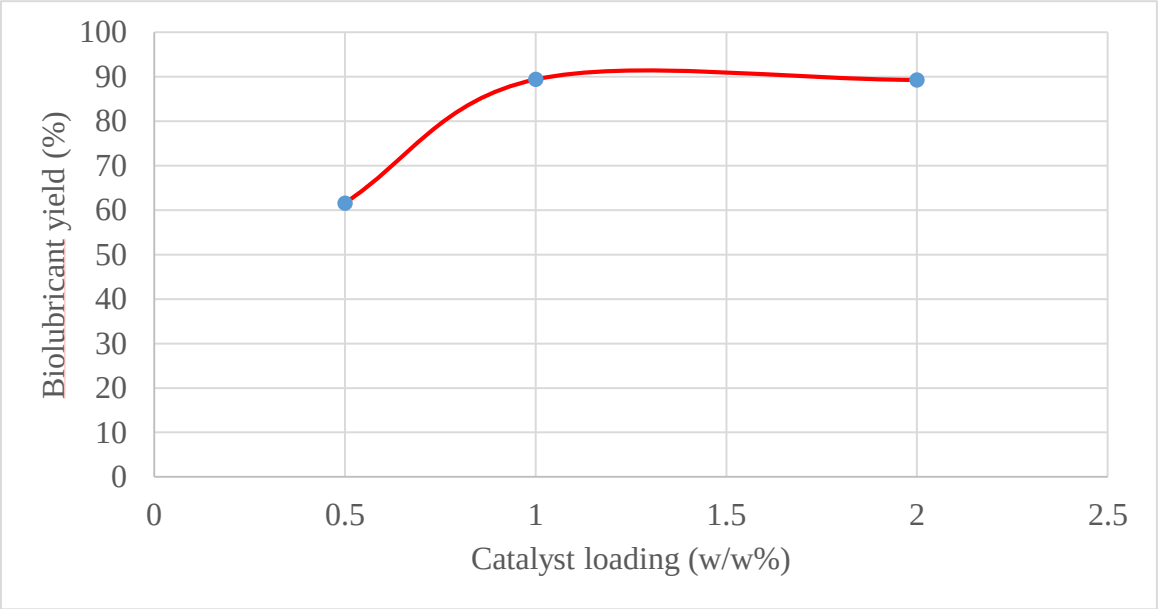


Figure 4.7. Effect of catalyst loading on synthesis of bio-lubricant: (Temperature, 170 ºC; ethylene/FAME ratio,3:1, time of 120 minutes)

From figure 4.10, the concentration of the catalyst had a favorable kinetic impact on the rate of the reaction. With 0.5% catalyst (w/w), the final conversion was too low (under 65%) which was 61.6%, compared to 1 % and 2 %, taking into account the bio-lubricant yield (90.40% and 90.16%, respectively). A catalyst speeds up a chemical reaction by lowering the amount of energy needed in the synthesis of bio-lubricant. As the concentration was increased the bio-lubricant yield was also increased until it reaches an equilibrium. More catalyst reveals more active sites which participate in the reaction and catalyze the production of lubricant (Talukder et al., 2010). With a further increase in the catalyst loading to 2%w/w, the rate of fatty acid methyl ester conversion remained the same, i.e. the reaction

rate reached a maximum for catalyst loading of 1%w/w. In this case, the optimum catalyst concentration was 1% that giving the maximum bio-lubricant yield of 90.40%, after that increasing the catalyst concentration does not have an impact on bio-lubricant synthesis rather than the formation of soap. Due to this from figure 4.10, using a maximum concentration of catalyst below which conversion enhancement was not seen. Based on this, 1%w/w was determined to be the optimum catalyst concentration, this finding was in close agreement with the work of Encinar et al., (2020).

Taking into mind, the discussion above for the synthesis of bio lubricant yield, the present experimental design was done following the classical approach of parametric study (one parameter at a time). The optimum physical-chemical conditions to achieve maximum conversion for such transesterification reaction of FAME with ethylene glycol were found to be: Temperature = 170 ^{o}C, FAME to ethylene glycol molar ratio = 3: 1, catalyst loading of = 1%w/w with a reaction time of 120 minutes.

The separated methanol was characterized using a **testing burner**, **iodoform test, miscibility with water,** and **boiling point**. The test burner produced a flame that was bluish and seemed colorless. The color of the flame looks colorless using testing burner whereas yellow precipitate using iodofrom test. Additionally, it was boiling at 65 ^{o}C, and also miscible with water. These standards allow for the identification of the bio-lubricants byproduct (i.e., methanol).

4.5.3. Properties of Synthesized Bio-lubricant

The bio-lubricant was subjected to certain property tests to determine its relevancy as lubricating oil. The physical-chemical properties of bio-lubricant include density, kinematic viscosity (40 ^{o}C), kinematic viscosity (100 ^{o}C), viscosity index, acid number and pour point as shown in Table 4.6. Table 4.6, shows the comparison of bio-lubricant and lubricant (ISO VG-460). The major lubricating properties of the bio-lubricant produced are presented in table 4,6, standards for light gear application according to ISO VG-460 specification.

The synthesized bio-lubricant had a density of 0.947 g/ml at a temperature of 20 ^{o}C and 0.9498 g/ml at 15 ^{o}C using ASTM D 287. The specific gravity of bio-lubricant at 60 ^{o}F was 17.39. According to the data of ASTMD-6751, the standard density of bio-lubricant is 0.91 – 0.95. The obtained result was following the standard. When compared to the density of the crude oil sample, it was also seen that the lubricant had a greater density. This may be ascribed to the various alterations it undergoes, including the double transesterification

processes that caused the lubricant to be higher than the crude oil and so increase its lubricity (Sarma & Vinu, 2022). The higher the density of a lubricant, the thicker it becomes; which increases the amount of time it takes for particles to settle out of suspension. This may be explained by the various modifications it has undergone, which caused the lubricant to rise above the crude oil and thereby increase its lubricity. Based on the result obtained the synthesized lubricant was used as gear lubricant, which was in good agreement with the standard value of gear lubricant.

In comparison to lubricant (ISO VG 460), the kinematic viscosity of bio-lubricant was 408.45 cSt, and 66.62 cSt, correspondingly at 40 ^{o}C and 100 ^{o}C respectively. The Viscosity index of the bio-lubricants 239. The ISO VG-460 kinematic viscosity of bio lubricant at 40 ^{o}C was between 414 -506 cSt, while for that at 100 ^{o}C was greater than 41 cSt, and VI was greater than 90. The kinematic viscosity of bio lubricant at 40 ^{o}C is almost the same as the minimum value of ISO VG- 460 and the kinematic viscosity of bio lubricant at 100 ^{o}C and VI is within the specification. Ashrafi et al., (2017) reported the viscosity index of sunflower oil-based bio lubricant was 122. According to Afifah et al., (2019), the standard viscosity index needed for lubricants can range from 30 to 240 for automobiles. Due to this result, our result was in good agreement with this standard. The lubricants' high viscosity index will enable them to maintain their lubricating characteristics at greater temperatures. A good multi-purpose lubricant keeps its viscosity constant as the temperature fluctuates. The bio-lubricant's high viscosity index is a sign that variations in viscosities at higher temperatures will be limited; the greater the value, the better the lubricant (Salih et al., 2017). Based on the kinematic viscosity result, the synthesized bio-lubricant is gear lubricant. It is formulated to withstand heavy loads and severe conditions resulting in very good micro pitting resistance.

The result of the acid value of bio-lubricant produced was 0.48 mg KOH/g. However, the acid value for the ISO of lubricant was 0.5 mg KOH/g maximum. The result observed that the acid value of synthesized bio lubricant was below the maximum limit of the standards, and hence, is an indication of good bio lubricant quality. Another concern is that bio lubricant does not contain any additives that would prevent it from oxidizing (Putra et al., 2020). A high acid value makes the bio-lubricant prone to polymerization, and also acts as a catalyst for hydrolysis. A high acid value is not recommended for bio-lubricants due to oxidation

which can accelerate wear and rust formation as well as corrosion (Popoola & Ikpambese, 2021). The percentage of free fatty acid for bio lubricant was 0.26 mg KOH/g.

The results of pour point of bio-lubricant were -6 ^{o}C. The pour point is the lowest temperature at which oil flows when its container is tilted for a predetermined amount of time. It is essential for oils that must flow at low temperatures (Salimon et al., 2014).. It is among the most important characteristics that affect how well lubricants work. When compared to *Citrullus colocynthis* oil methyl ester, the synthetic *Citrullus colocynthis* seed oil bio-lubricant's pour point was noticeably higher. The pour point changed from the initial pour point of biodiesel, from -3 to -6 °C. This is due to the effect of polyol alcohol (ethylene glycol). In this case, the fatty acid is removed from glycerol and attached with more stable polyol alcohol of ethylene glycol as reported by (Matthew C. Menkiti et al., 2017). The bio-lubricant's cloud point was -1 ^{o}C. The cloud point is, the point at which wax (paraffin) starts to separate begins to occur. This cloud point is a crucial sign of how well automotive applications will work in low temperatures. These values are comparable with the pour point and cloud point values of other bio-lubricants as reported by Menkiti et al., (2017), and S, (2013). Based on this finding, when the weather condition was cold, the bio-lubricant operate until the temperature of the bio-lubricant was reached – 6 ^{o}C. Based on this finding it is good according to the weather condition of our country. The coldest place in Ethiopia is Adis Ababa, with a minimum coldest average temperature of 7.4 ^{o}C (Kifle Arsiso et al., 2017). Due to this reason, the synthesized bio-lubricant was in good agreement with the weather condition of our country, Ethiopia.

The flash point and fire point of the bio-lubricant synthesized were 272 ^{o}C and 281 ^{o}C respectively and the value is above the minimum requirement of the bio-lubricant flash point standard (ASTM D6751). The flash point of a chemical is the lowest temperature where it will evaporate enough fluid to form a combustible concentration of gas. The flash point is an indication of how easy a bio lubricant may burn. Materials with higher flash points are less flammable or hazardous than chemicals with lower flash points (Tulashie & Kotoka, 2020).

The fire point is the temperature to which the product must be heated under the prescribed conditions of the method to burn continuously when the mixture of vapor and air is ignited by a specified flame. Menkiti et al., (2017) described the fire point of a lubricant as the lowest temperature at which sufficient vapor is produced continuously for burning after ignition for

at least 5 seconds. The flash and fire points provide information about a material's volatility, fire resistance, and the highest temperature at which it may be utilized, which aids in determining its suitability for shipping and safety. A good lubricant should have fire and flash points that are higher than its working temperature (Popoola & Ikpambese, 2021). Shah et al., (2019), also noted that mineral oil SAE 40 has a flash point of 204°C and a fire point of 209°C. Ashrafi et al., (2017), reports that the flash point of sunflower oil-based bio-lubricant was 295 ^{o}C. Chen et al., (2019), report that the flash point of mustard seed oil bio lubricant was 200 ^{o} C. The results show clearly that the bio-lubricants have excellent flash and fire points when compared to standard SAE 40 lubricants. According to the findings, bio-lubricants can be transported in both wet and dry climates without much risk of explosion. These values are in close agreement with the results of Ashrafi et al., (2017) and causes very low hazards comparatively.

Table 4.6. Hazard and flash point (Tulashie & Kotoka, 2020)

Flashpoint (^{o}C)	**Hazard**
> 93	Very low hazard
66 to 93	Moderate low hazard
38 to 66	High to moderate hazard
-18 to 38	Extreme to high hazard
< (-18)	Extreme hazard

Based on the above criteria, the flash point of Citrullus colocynthis bio lubricant is higher than 93 ^{o}C. So, a flash point with a high value indicates that the bio lubricant is less flammable or hazardous.

Table 4.7. Physico-chemical properties of Citrullus colocynthis seed oil bio-lubricant comparison with other plant lubricant and standard

Physico-chemical properties	**Citrullus seed oil Bio lubricant**	**Sunflower lubricant** (Ashrafi et al., 2017)	**Mustard seed oil Lubricant (**Chen et al., 2019)	**Standard ASTM D751,ISO VG 460**	**ISO VG 320**
Density (g/mL) at 20 ^{o}C	0.947 (ASTM D-287)	0.9884 (ASTM D-1298)	875	0.910 – 0.950	0.915-0.95
Density (g/mL) at 15 ^{o}C	0.9498 (ASTM D-287)	----	-----	0.90 – 0.950	0.90 – 0.950
Specific gravity at 60 ^{o}F	17.39 (ASTM D-287)	-----	-----	Not available	
Kinematic viscosity at 40 ^{o}C (cst)	408.45 (ISO VG-460),	462 (ASTM D-445)	8.6	414 - 506	288 - 352
Kinematic viscosity at 100 ^{o}C (cst)	66.62 (ISO VG-460),	35 (ASTM D-445)	2.8	> 4.1	>4.1
Viscosity index	239 (ASTM D2270)	122 (ASTM D-2270		>216	>198
Acid number (mg KOH/g)	0.48	----	12.2	0. 5 Max.	
% FFA (mg KOH/g)	0.26	----	6.1		---
Pour point (^{o}C)	-6 (ASTM D97)	-9 (ASTM D-92)	-5	Not available	
Cloud point (^{o}C)	-1 (ASTM D2500)	----	----	Not available	
Flashpoint (^{o}C)	272	295 (ASTM D-93	200	130 Min.	
Fire point (^{o}C)	281	------	----		

4.5.4. Analytical Characterization of Citrullus Colocynthis Crude Oil, Fatty acid Methyl Ester, and Bio-lubricant

In this context, the extracted seed oils, fatty acid methyl ester, and bio-lubricants were analyzed by using TGA, and FTIR. Additionally, the seed crude oil was analyzed using GC-MS; whereas both fatty acid methyl ester and bio lubricant were analyzed using NMR.

4.5.4.1. Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

The fatty acid profile of the oil extracted from the Citrullus colocynthis seed has been presented by GC-MS analysis as follows and also it provided accurate information about the most abundant compounds of this group in table 4.5. below. The most abundant fatty acids were linoleic acid, oleic acid, hexadecanoic acid (palmitic acid), and stearic acid. Detailed analysis of the relative contribution of each fatty acid to the complete profile revealed that linoleic acid (C18:2n-6) was the most abundant fatty acid, constituting 43.01% of the total fatty acids, followed by oleic acid (C18:1n-9), which represented 32.50% of the total fatty acid content; other mono and polyunsaturated fatty acids were found at much lower concentrations. Concerning saturated fatty acids, palmitic (C16:0) and stearic (C18:0) acids accounted for 10.21% and 6.25% of the total content, respectively. In addition, it was found that unsaturated and saturated fatty acids, described in Table 4.5, accounted for 83.5 % and 16.5 % of the total content, respectively (Bireche et al., 2021).

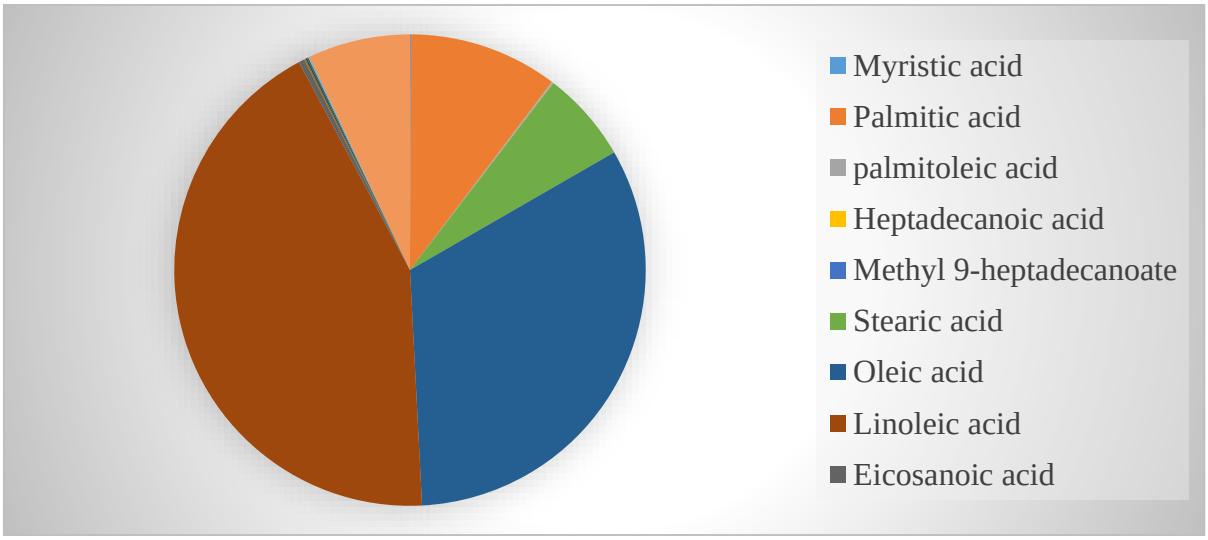


Figure 4.8. Percentage of fatty acid profiles of Citrullus colocynthis seed oil

Table 4.8. Fatty acid (%) composition of C. colocynthis seed oils

S.N.	Compound name	Formula	RT	Area	%Area
1	Myristic acid	$C_{14}H_{28}O_2$	9.33	138,559	0.07
2	Palmitic acid	$C_{16}H_{32}O_2$	10.38	20,741,948	10.21
3	palmitoleic acid	$C_{16}H_{30}O_2$	10.66	161,917	0.08
4	Heptadecanoic acid	$C_{17}H_{34}O_2$	10.87	87,110	0.04
5	Methyl 9-heptadecanoate	$C_{18}H_{34}O_2$	11.17	54,417	0.03
6	Stearic acid	$C_{18}H_{36}O_2$	11.51	12,703,333	6.25
7	Oleic acid	$C_{18}H_{34}O_2$	11.82	66012498	32.50
8	Linoleic acid	$C_{18}H_{32}O_2$	12.33	87358714	43.01
9	Eicosanoic acid	$C_{20}H_{38}O_2$	12.66	813,099	0.4
10	Linolineic acid	$C_{18}H_{30}O_2$	12.90	205,812	0.1
11	Erucic acid	$C_{22}H_{42}O_2$	13.01	218,312	0.11
12	Docosanoic acid	$C_{23}H_{34}O_2$	14.11	195,977	0.1
13	Tetracosanoic acid	$C_{25}H_{50}O_2$	16.23	193,153	0.1
14	cholesterol	$C_{27}H_{46}O$	27.90	14,212,842	7

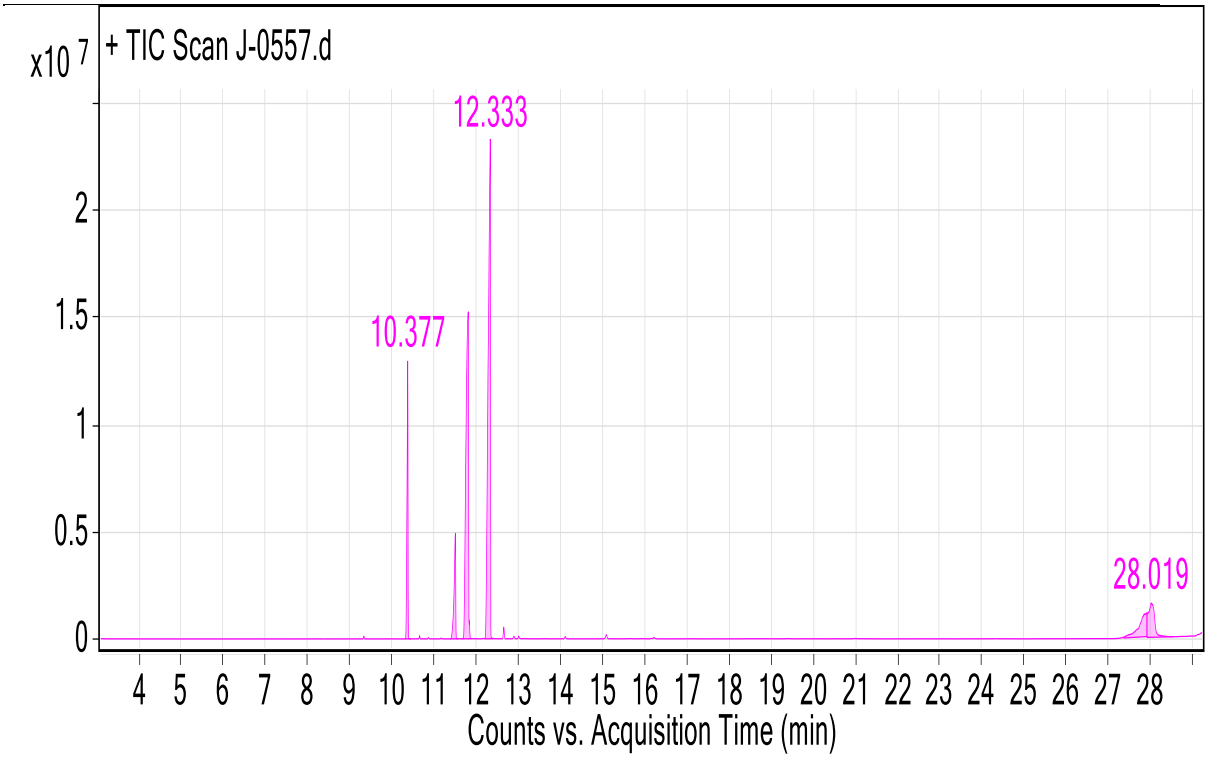


Figure 4.9. GC-MS analyses of C. colocynthis seed oils

4.5.4.2. NMR Analyses of Synthesized Biodiesel

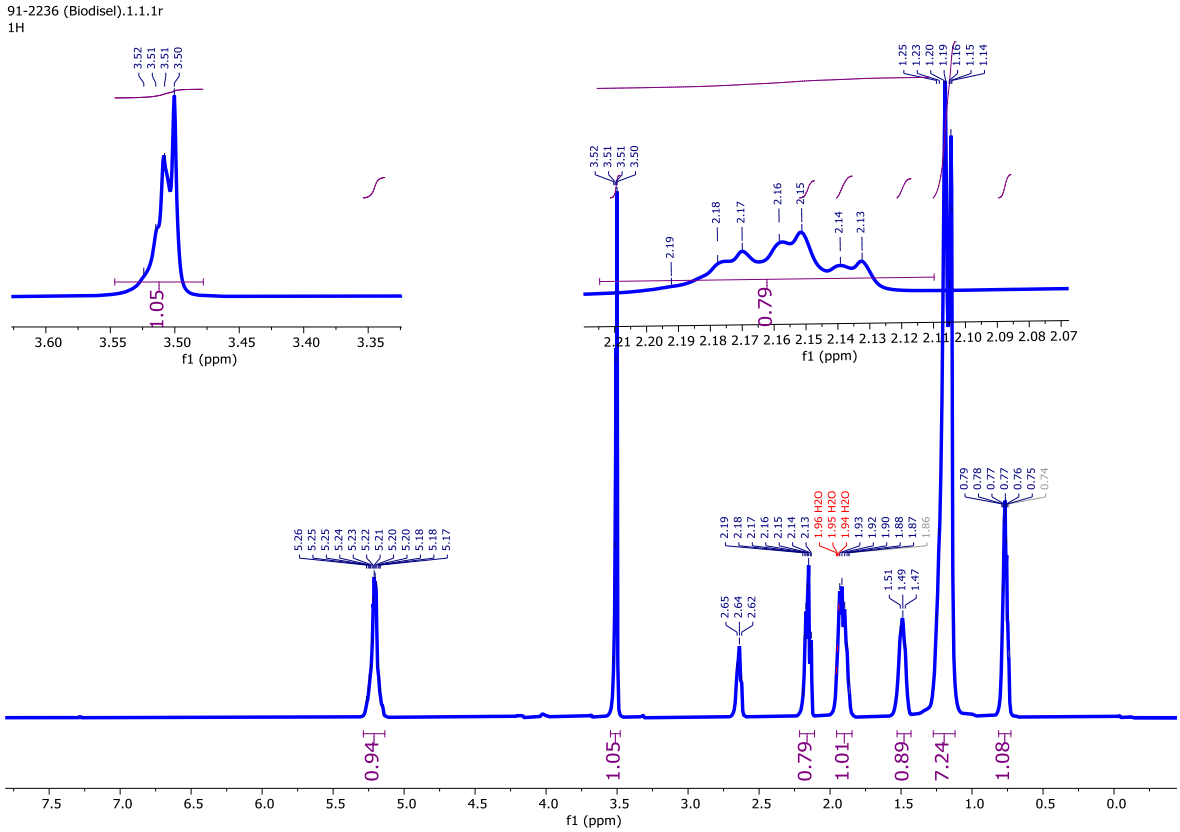


Figure 4. 10.[1] H-NMR spectra of CCOME

In this study, the sample has been characterized by ^{1}H NMR spectroscopy and their spectra are shown in Fig.4.13. The characteristic peaks of methoxy protons δ (-O-CH_3) had been observed as a singlet at around 3.50 ppm, for CCOME. These chemical shifts indicate the presence of methyl esters in biodiesel. Other observed peaks as triplets had been around 0.78 ppm of the terminal methyl δ (-CH_3) protons. It was in close agreement with the previous works (Atabani et al., 2019) and a large signal at 1.2 ppm was observed clearly which was assigned for methylene protons of carbon chains, which was in close agreement with works done before (Ali Elsheikh & Hassan Akhtar, 2014). The peaks at 1.2 and 1.90 ppm represent the acryl group of (-OCO-CH_2-CH_2-) and (-CH_2-CH=CH-), which was in close agreement with previous work (A. Usman. K.U. Aliyu, Itodo, et al., 2021). Certain characteristic signals protons α- to the methylene carbonyl group δ (-CH_2-C=O-) to the ester group were observed at 2.16 ppm (Samanta & Sahoo, 2021). The peaks at 2.64 ppm were responsible for diallelic methylene proton δ (-C=C-CH_2-C=C-), which was in good agreement with previous work (Atabani et al., 2019). The absence of peaks between 4.0 and 4.3 ppm suggested that no glycerol traces were present in CCOME. This finding is in good agreement with Ali Elsheikh & Hassan Akhtar, (2014). The characteristic peaks of olefinic protons and carbons δ (-

CH=CH-) as doublet were observed at around 5.21 pp, which was in close agreement with work done before (Kundu & De, 2021).

The ^{1}H nuclear magnetic resonance (NMR) spectroscopy was used to monitor the conversion of glycerides to methyl esters and the yield of the reaction product. The relevant signals used to monitor and quantify this conversion are that described by (Madhuvilakku & Piraman, 2013). The signals used for the conversion of the transesterification process are the integration value of methoxy groups in the methyl esters at 3.50 ppm (singlet) and that of the α-carbonyl methylene groups present in all fatty esters derivatives at 2.18 ppm (triplet) labeled" X" according to equation 4.3.

$$\%Yield\ of\ ME = \frac{2Z}{3X} * 100\% \quad \text{.....4.3}$$

Where X= the integration value of α-carbonyl methylene groups presents in all fatty esters derivatives = 0.79, and Z = the integration value of methoxy groups in the methyl esters = 1.05.

By substituting the value of X and Z, in equation 4.3, the reaction conversion efficiency of oil into biodiesel is 89% as checked by proton is NMR spectroscopy.

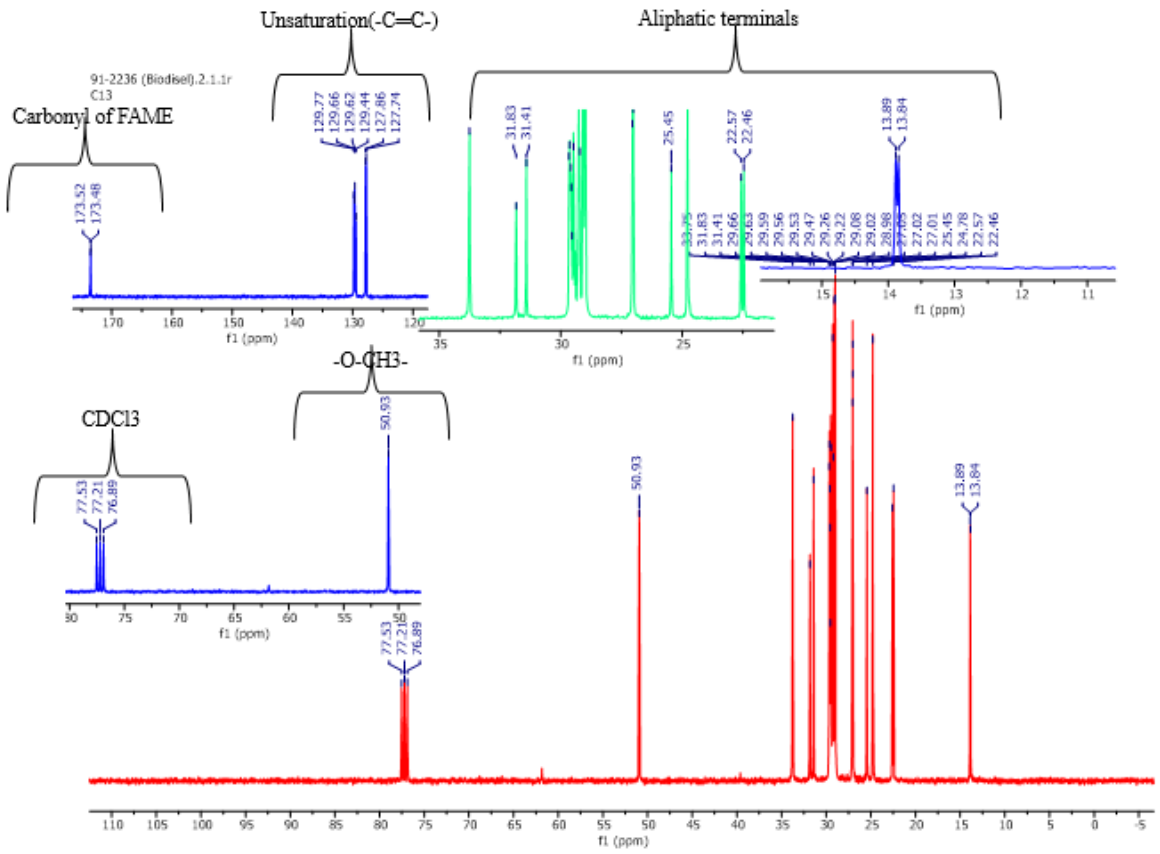


Figure 4.11. ^{13}C-NMR spectra of CCOME

A representative spectrum of ^{13}C-NMR of the sample is shown in Fig. 4.14. The peaks at 173.208, and 172.801 ppm conform to the characteristic peaks of ester and carbonyl groups δ (-COO-) and δ (-C=O-) respectively, which was in close agreement with the previous work (Atabani et al., 2019). The peaks around 127.672 and 130.125 ppm indicate the unsaturation in methyl esters. Other peaks at 13.793 – 14.143 ppm are related to the terminal carbon of methyl groups δ (-CH_3) and signals at 22.3422 – 34.116 ppm are related to methylene functional group δ (-CH_2-) of long carbon chain in FAMEs. The peak at 51.145 ppm is related to the methoxy group of methyl esters, which has also been done previously (Kumar et al., 2016), and the peak at 173.854 ppm is related to the carbonyl carbon, which was in good agreement with the last works (Kundu & De, 2021).

4.5.4.3. Fourier transform infrared (FTIR) analysis (oil, FAME, and Bio-lubricant)

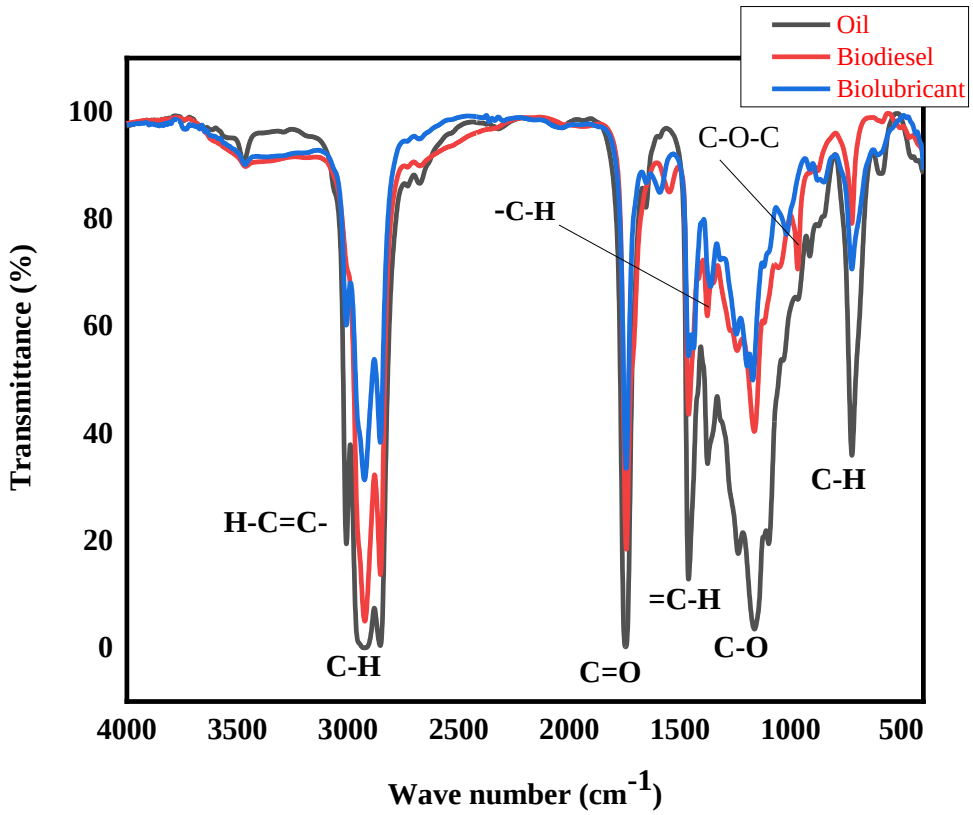


Figure 4.12. FTIR spectrum of oil, biodiesel, and bio lubricant

The Fourier transform infrared spectroscopy (FTIR) method is efficient in determining whether functional groups are present in the sample.

The oil spectra of the *Citrullus colocynthis* are depicted in Fig. 4.15. The absence of the -OH group in the oil, FAME and bio-lubricant spectrum confirmed that the transesterification

reaction had been carried out successfully. The absorption peak at wavelengths 2933 cm^{-1} and 2859 cm^{-1} represents the presence of the -CH3 and $–CH_2$ groups with asymmetric and symmetrical stretching vibrations in the atoms of carbon-bound hydrogen. Unsaturated hydrogen stretches (C=C-H) are shown by the absorption peaks at 3011 cm^{-1}. *Citrullus colocynthis* seed oil absorption peak at 1748 cm^{-1} is correlated with stretching of the C=O carbonyl groups (Fig. 4.15). The absorption peaks at 1462 $cm^{-1}$and at 1370 cm^{-1} correspond to the vibration of the C-H deformation, and the range from 1231 cm^{-1} to 1153 cm^{-1} is due to the vibrations of the ester group. The absorption peak appearing at 727 cm^{-1} corresponds to the strain vibration of $-CH_2$, which can be also in good agreement with the last works (Freitas de Medeiros et al., 2019, Bruno et al., 2022).

The absorption peaks at 2928 cm^{-1} and 2857 cm^{-1}, respectively, are under the -C-H-stretching vibration of the terminal methyl group of the fatty acid chain and methylene, which can also be studied by Kumar et al., 2016, Bruno et al., (2022). Accordingly, it denotes the symmetric and asymmetric stretching vibrations of C-H alkane groups, respectively. They may be methyl ($-CH_3$) or methylene ($-CH_2$) groups in the esters chains of the biodiesel, and they need more energy to create stretching vibrations within their bond than typical C-H bending vibrations of alkene groups, which are visible at low energy and frequency ranges (Babakura et al., 2019). The stretching band = C-H is seen at a wavelength of 3011 cm^{-1}. The C=O ester group's stretching vibration is what causes the absorption peak to appear at 1746 cm^{-1}. This indicates that the characteristic peak of C = O group stretching for methoxy ester (CH_3O-CO-) appears at 1746 cm^{-1}, and the absorption peak at 1192 cm^{-1} relates to an ester group (C-O), which can also be in good agreement with the works done before (Ullah et al., 2015, Babakura et al., 2019, Bruno et al., 2022). The asymmetric bending vibration of $-CH_3$ found in the biodiesel spectrum is represented by the absorption peak at 1437 cm^{-1}. Usually, the absorbance peak at 1168 cm^{-1} represents the methoxy group ($O-CH_3$) stretching vibration, which denotes biodiesel synthesis. The rocking, and bending vibration of methylene groups is also shown by the absorption peak at 726 cm^{-1} ($-CH_2-$), which was in good agreement with the previous works (Khan et al., 2020, Bruno et al., 2022).

The FTIR spectra of the produced bio-lubricant were comparable to those of biodiesel. This shows that the second transesterification did not cause any harm to the CCOME's molecular structure. (Attia et al., 2020). The presence of a vibration absorption band was seen at 1742 cm^{-1}, similar to carbonyl (C=O), indicating the presence of fats; 1158 cm^{-1}, corresponding to the vibration of the C-O, indicating the presence of ester; and its shoulders at 1170 cm^{-1}

and 1235 cm^{-1}, which was in close agreement with works done before (Menkiti et al., 2017, Ocholi et al., 2018). The CH_3 and CH_2 stretching vibrations may be seen at 2854 cm^{-1} and 2928 cm^{-1}, respectively, as it was in good agreement with work done before (do Valle et al., 2018). Since there are no longer any processes taken on to get rid of the double bonds in the carbon chain, the band at 721 cm^{-1} is caused by the stretching of olefinic carbon. The absorption band at 1456 cm^{-1} indicates the presence of C-H bending vibrations, this shows that the functional group of an alkane in their molecular structure is the same, in close agreement with research done before (Heikal et al., 2017).

When we summarized the FTIR spectrum, CCO has an ester group (C=O) at 1748 cm^{-1}, FAME has one at 1746 cm^{-1}, and bio-lubricant has one at 1742 cm^{-1}. The FAME is produced by the first transesterification, according to the shift from 1748 cm^{-1} to 1746 cm^{-1}. The fatty acid ethylene glycol esters (bio-lubricant), which are produced by the second transesterification, are indicated by a substantial change from 1746 cm^{-1} to 1742 cm^{-1}. Since fatty acid ethylene glycol esters are only found in ethylene glycol-based lubricants, the C=O (ester) group has a specific wavelength of 1742 cm^{-1}. The CCO, FAME, and bio lubricant all contain the function group C-O (ester), which is located at 1153 cm^{-1}, 1168 cm^{-1}, and 1170 cm^{-1}, respectively. The C-O (ester) at 1051 cm^{-1}, however, only shows up in bio-lubricant. The C-O (ester) group's specific wavelength for ethylene glycol-based lubricants is 1051 cm^{-1}. It was in close agreement with the works done before (Chowdhury et al., 2014, Putra et al., 2020).

From FTIR figure 4.15, the peak of the hydroxyl group (-OH) at 3462 cm^{-1} in oil, biodiesel and bio-lubricant was very small and even could be neglected, indicating that the transesterification reaction was considerably close to completion, which was in close agreement with the work done before (Y. Wu et al., 2013). The complete disappearance of C=C double bonds at wavelength 1604 cm-1 in CCO and the formation of C-O-C bands at 963 cm^{-1} and 1026 cm^{-1}, respectively, in biodiesel and bio lubricant, indicated the conversion of the majority of double bonds in the feedstock. It was in close agreement with works done before (U. C. Sharma & Sachan, 2019).

4.5.4.4. Thermogravimetry Analysis (TGA)

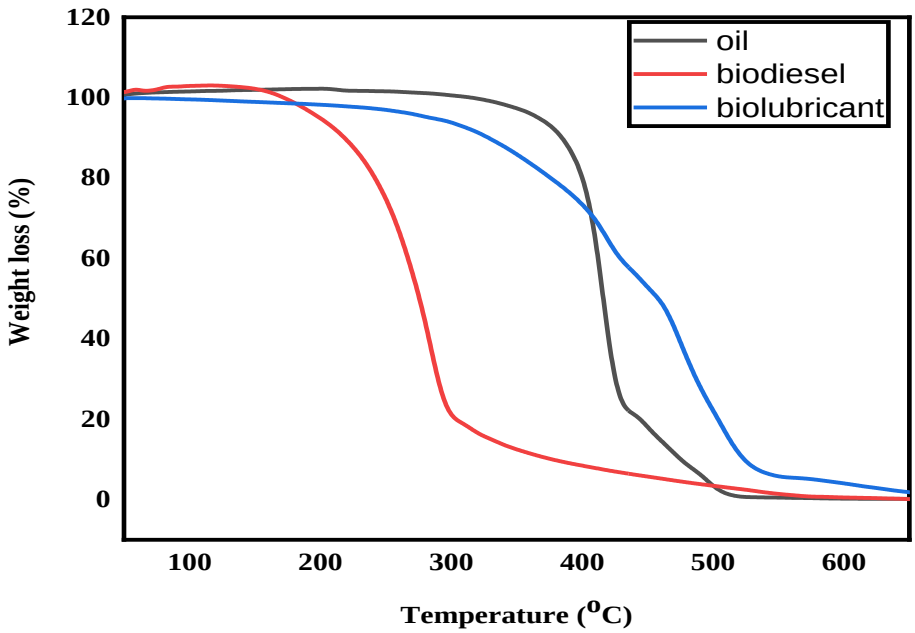


Figure 4.13. Thermogravimetric profile of Crude oil, FAME, and bio-lubricant

From the TGA curve of Figure 4.16, the onset temperature (To, and decomposition peak temperature (Td) for FAME were 192 ^{o}C, and 281 ^{o}C respectively. That means the maximum degradation rate occurred at a temperature of 281 ^{o}C where the rate of weight decreased. Slower weight loss reductions were observed at higher temperatures. The onset temperature and decomposition temperature of the crude oil was 384, and 417 ^{o}C respectively. Whereas, for that of synthesized bio-lubricant onset and decomposition temperature was 361, and 445 ^{o}C respectively. A higher onset decomposition temperature suggested higher thermal stability of the substance. A large difference in thermal stability of *Citrullus colocynthis* seed oil, biodiesel, and bio-lubricant is because the oil is consisting of larger molecules than that of FAME, and bio-lubricant. Oil is primarily composed of triacylglycerol; while FAME and bio-lubricants are composed of methyl linoleate, and ethylene glycol dilenoleate respectively (Y. Wu et al., 2013).

Table 4.9. Onset and decomposition temperature of oil, FAME, and bio-lubricant

Items	Onset temperature (^{o}C)	Decomposition temperature (^{o}C)
C.colocynthis seed oil	384	417
FAME	192	281
Bio lubricant	361	445

4.5.4.5. Unreacted Product Characterization (FTIR)

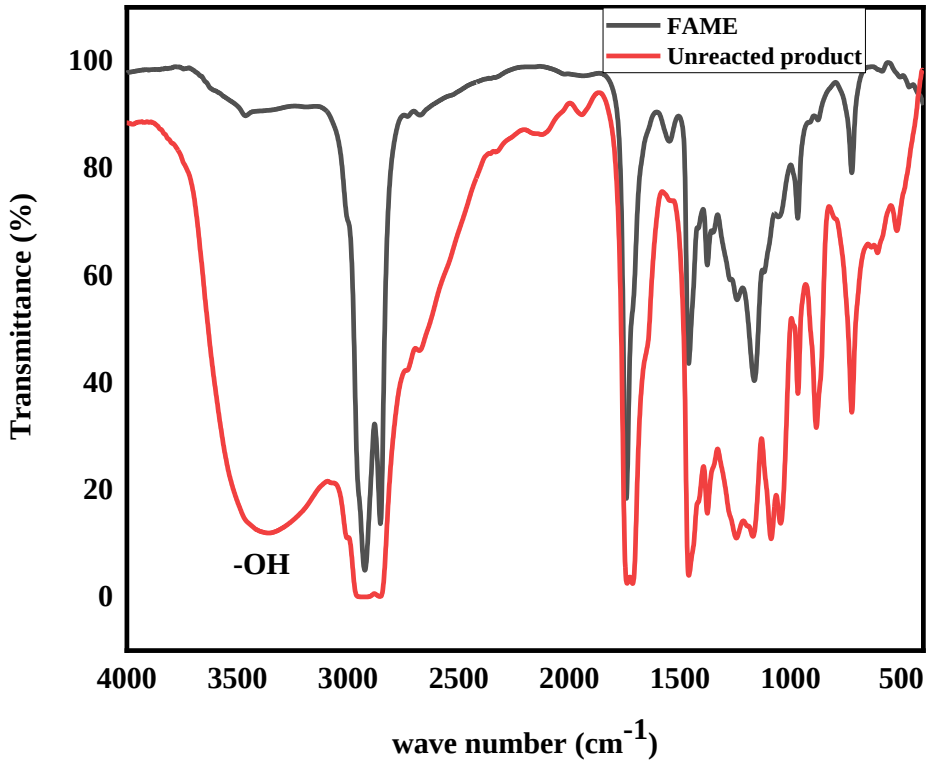


Figure 4.14. Fourier transform infrared spectroscopy for unreacted product

From figure 4.15, we have seen that the alcohol group (-OH) stretching vibration in biodiesel was absently confirming that the transesterification reaction had been carried out successfully. But from figure 4.20, alcohol group (-OH) stretching (3500-3100 cm^{-1}) corresponds to the peaks at wavelengths 3388 cm^{-1} in the unreacted product spectrums. This indicates that the unreacted alcohol was removed with an unreacted product. That means during removal of unreacted fatty acid methyl ester from bio-lubricant by using vacuum distillation column some unreacted alcohol was going with unreacted fatty acid methyl ester as we compare with FTIR of fatty acid methyl ester.

4.5.4.6. Determination of Surface Roughness

Surface roughness is a measure of the texture of a surface and plays an important role in determining how an object will interact with its environment. Roughness is a good indicator of the performance of a mechanical component, since irregularities on the surface may form nucleation sites for cracks or corrosion. In tribology, rough surfaces wear quickly and have a higher friction coefficient (Kannan et al., 2016).

Table 4.10. Comparison of cutting fluids

Machining	Surface Roughness value (μm)
Dry machining	2.96
Water cutting	2.05
Mineral oil cutting	1.83
Bio-lubricant cutting	1.49

Based on the result obtained, the bio-lubricant had a low value of surface roughness. Since roughness is a good indicator of the performance of a mechanical component; i.e., a value in which its surface roughness is low is more desirable, free from severe damages, has reduced tool wear, accelerates tool life, and good machinability. Based on the result obtained the bio-lubricant has a more selective and appropriate substance used for machining materials used as cutting fluids to reduce the wear, coefficient of friction, and heat generated between two surfaces compared to dry cutting, and other wet cutting fluids such as water and mineral oil. In addition, when the surface roughness of the material was high, it indicates the gradual breakdown of the machine tool as a result of cutting operations, eventually leading to tool failure. And also, the lower the roughness values, the more the corrosion resistance. A rough surface increases corrosion rate by increasing surface area which involves in distribution of electrochemical reactions (Sivaiah & Chakradhar, 2018). Based on this analysis bio-lubricant was a good cutting fluid than the other.

CONCLUSIONS and RECOMMENDATIONS

CONCLUSIONS

In this study, response surface methodology was used to investigate the optimum process parameters that could obtain a maximum yield of crude oil from bitter apple seed. Three independent variables, namely extraction temperature, extraction, and solvent-to-solid ratio have been tested. The findings showed that the most significant impact on oil seed yield was caused by solvent to solid ratio. The optimum conditions determined by RSM were: extraction temperature 84 ^{o}C, extraction time 4.5 hrs., and solvent to solid ratio 20:1, with a particle size that surpassed through mesh size 10. Under these optimal conditions, the oil yield (Y1) of around 52.1% was obtained. It has been established that the seeds of *C. colocynthis* are highly oil-rich, which has significant economic relevance. The extracted oil was characterized, and its physiochemical properties were also compared to the ASTM standard. The results of GC-MS indicate the major fatty acid composition of *Citrullus colocynthis* seed oil was linoleic acid (43.01%), oleic acid (32.5%), and palmitic acid (10.21%). After extraction of oil at optimum variables, the biodiesel was synthesized by using a transesterification process at a reaction temperature of 60 ^{o}C, a reaction time of 1 hr., methanol to oil ratio was 6:1, and catalyst concentration of 1%w/w (NaOH). Under these optimum conditions, the biodiesel yield of 97.33% was obtained. The synthesized biodiesel was characterized and its physiochemical properties were compared to the ASTM standard. Bio-lubricant was synthesized by using a double transesterification process from Citrullus colocynthis seed oil methyl ester. The production of bio-lubricants (conversion) was influenced by temperature, concentration of catalyst (sodium hydro-oxide), and alcohol/FAME molar ratio. As reaction temperature, ethylene to FAME and catalyst concentration increased the biolubricant yield also increased and further increase of those parameters may not affect the bio-lubricant yield significantly. A maximum yield of 92.15% of bio-lubricant was achieved at the optimum reaction conditions: reaction temperature 170 ^{o}C, ethylene glycol to FAME ratio 3:1, and catalyst loading 1%w/w (NaOH), at a fixed reaction time of 120 minutes. The synthesized bio-lubricant was characterized, and compared to the ASTM standard. The FTIR results indicate, when transesterification reaction occurs, the absorption band of triacylglycerol is shifted to lower wavelength due to the formation of methyl esters of smaller chains than those of starting triesters present in oils in C = O bond and the appearance of C-O-C in biodiesel and bio-lubricant. The extracted of oil, biodiesel and bio-lubricant were thermally stable up to 384,192, and 361 ^{o}C respectively

based on thermogravimetric analysis (TGA). The viscosity of the bio-lubricant synthesized was 408.45 cSt. Based on this result the viscosity of the bio-lubricant synthesized was close to the standard viscosity grade of 460 (ISO VG - 460), which has a range of 414 – 506 cSt. The viscosity grade of ISO VG-680, 460, 320, 220, 150, and 100 are categorized as gear lubricants. Based on this the synthesized bio-lubricant was categorized as a gear lubricant (gear lube). Therefore, these oils protect gear drives and provide high film strengths which contribute to the minimization of wear and extended systems life. More importantly, it helps protect critical internal components in automotive and mechanical gear systems from wear and heat damage. Additionally, the density of the synthesized lubricant was 0.947 g/cm^3, which was within the specified standard of ASTM D 6751 (0.91 – 0.95 g/cm^3). The flash point of synthesized bio-lubricants was around 272 ^{o}C which is better than mineral lubricants. The practicability of synthesized bio-lubricant was also evaluated as a good cutting fluid during machining which resulted in a better surface roughness of 1.49 µm compared to water, mineral oil, and dry machining (dry cutting). Hence, the synthesized bio-lubricant can favorably serve as a substitute of petroleum based lubricant.

RECOMMENDATIONS

- In the future, for a detailed investigation of the lubricant qualities, it is recommended to use standard testing equipment for lubricants' anti-wear and antifriction properties, such as the High-Frequency Reciprocating Rig (HFRR) and also study rheological analysis.
- It is recommended to incorporate an optimized procedure for the preparation of an enzymatic nano-catalyst to produce a bio-lubricant from *Citrullus colocynthis* seed oil, and also study the kinetic models, and thermodynamics for transesterification of *Citrullus colocynthis* oil methyl ester with polyol alcohol for the synthesis of bio-lubricant.
- It is suggested to describe and compare the effect of different Co-solvent on the synthesis of bio-lubricant, and the ester content by using a homogeneous and heterogeneous catalyst as well as on the cold flow properties of bio-lubricant.
- It is also important to optimize machining parameters of facing and turning operation for Aluminum with HSS cutter using Response Surface Methodology and Further, this work can be extended to other types of machining processes such as milling, drilling to find the best optimal parameters. It also recommended to investigate the effect of adding nanoparticles on a cutting fluid on surface finish and material removal rate.

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APPENDIX

Appendix A: (Sample Calculation)

Molecular Weight (MW) Calculation of Reactants

MW of methanol=32.04 g/mol

MW of NaOH= 40.1 g/mol

MW of KOH= 56.1 g/mol

MW of TG = 874 g/mol

MW of ME = 294 g/mol

MW of EG = 62 g/mol

The first step of transesterification

Mass of vegetable oil = 267.66 g (300 ml)

Mole of vegetable oil =267.66 g / 874 g/mol = 0. 3063 mol

A mole of methanol = 6 × mole of vegetable oil = 0.3063 × 6=1.84 mol

Mass of methanol = 32 g/mol ×1.84 mol = 58.8 g

Mass of NaOH= Mass of vegetable oil ×1%w/w = 2.7 g

Moisture contents Determinations

Initial mass (W_1) = 20 g

Dry mass (W_2) = 0.848 g

$$\%m = \frac{W1-w2}{w2} * 100 = 4.24\% w/w$$

Ash content determination

Sample mass (W_1) = 5 g

Mass of ash (W_2) = 0.115 g

$$\%ash = \frac{W2}{w1} * 100 = 2.3\% w/w$$

Soxhlet Extraction Setup

The second step of transesterification

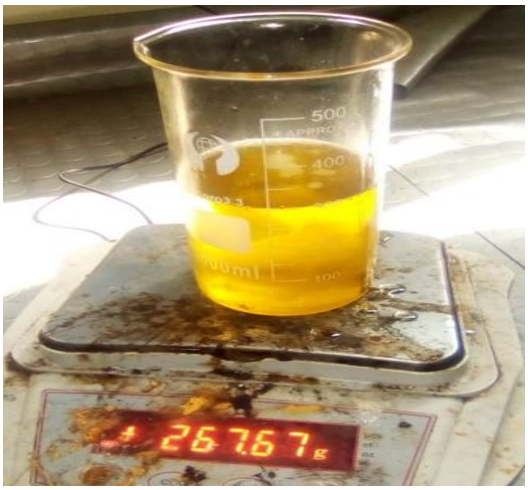
Mass of FAME = 100 g

$$\text{Mole of FAME} = \frac{100}{294} = 0.34 \text{ mol}$$

Mass of EG = 62 x 0.34 x 3 = 63.3 g, for molar ratio of 3:1

$$\text{Mole of EG} = \frac{63.3}{62} = 1.02 \text{ mol}$$

Mass of FAME for bio-lubricant synthesis



Mass of oil for FAME synthesis

Experimental setup for bio-lubricant synthesis

Appendix B: (Percentage yield determinations)

For oil

A: wt. of sample = 20 g

B: wt. of extracted oil =10.42 g

$$\%\text{Yield of oil} = \frac{\text{mass of extracted oil}}{\text{mass of the extracted sample}} * 100\%$$

$$\%\text{Yield of oil} = \frac{10.42\ \text{g}}{20\ g} * 100\%$$

= 52.1% (percent yield of oil from a sample)

For biodiesel

$$\text{Yield of ME} = \frac{\text{Vp}}{\text{Vs}} * 100\%$$

Vp is the volume of product = 292 ml,
Vs is the volume of sample oil used for the synthesis of biodiesel = 300 ml,

= 97.333% (v/v), when molar ratio of methanol to oil was 6:1, and 64.67% (v/v), with molar ratio of 3:1.

For bio-lubricant

$$\text{Yield of biolubricant} = \frac{\text{Mp}}{\text{Ms}} * 100\%$$

Mp = mass of synthesized bio lubricant: 92.15 g

Ms = mass of biodiesel or sample used: 100 g

$$\text{Yield of biolubricant} = \frac{92.15}{100} * 100\%$$

= 92.15%

Appendix C: (Determination of properties of oils)

I. Acid value determinations

A: titre value = 5 ml -3 ml = 2 ml

B: sample weight = 15.6 g

C: normality of KOH = 0.1 N

$$\text{Acid value} = \frac{\text{titre value} * \text{normality of KOH} * 56.1}{\text{sample weight}}$$

= 0.72 mg KOH/g

II. Determinations of the percentage of free fatty acid (% FFA)

A: titre value = 2 ml

B: sample weight = 15.6 g

C: normality of KOH = 0.1 N

$$\%\text{FFA} = \frac{\text{titre value} * \text{normality of KOH} * 28.05}{\text{sample weight}}$$

= 0.36 mg KOH/g

III. Determinations of iodine value

A: Sample weight(W_S)= 0.52g

B: the volume of sodium thiosulfate for blank was (V_B)= 41ml – 1ml=50 ml

C: the volume of sodium thiosulfate for sample was (V_S) = 20 ml – 2 ml = 18 ml

$$\text{IV} = \frac{12.69(\text{VB} - \text{VS}) * 0.1\text{N}}{\text{WS}}$$

= 78.1 g I/100 g oil

IV. Determinations of saponification value

A: sample weight(Ws) = 5.25 g

B: V_B = Volume of blank solutions = 57 ml

C: V_S = Volume of sample's = 24 ml

$$SV = \frac{28.05(VB - VS)}{Ws}$$

= 176.3143 mg KOH/g of oil sample

V. Determination of ester value

ESTER value = saponification value – acid value

= 176.3143 mg KOH/g - 0.72 mg KOH/g

= 175.5943 mg KOH/g of oil

Appendix D: (Determination of properties of biodiesel)

I. Determination of acid value

A: titre value = 4 ml – 2 ml = 2 ml

B: sample weight = 20.2 g

C: normality of KOH = 0.1 N

$$\text{Acid value} = \frac{\text{titre value} * \text{normality of KOH} * 56.1}{\text{sample weight}}$$

= 0.55 mg KOH/g of biodiesel

II. Determination of percentage of free fatty acid (% FFA)

A: titre value = 4 ml – 2 ml = 2 ml

B: sample weight = 20.2 g

C: normality of KOH = 0.1 N

$$\%\text{FFA} = \frac{\text{titre value} * \text{normality of KOH} * 28.05}{\text{sample weight}}$$

= 0.277 mg KOH/g of biodiesel

III. Determination of acid value of bio-lubricant

A: titre value = 1.9ml – 1 ml = 0.9 ml

B: sample weight = 10.5 g

C: normality of KOH = 0.1 N

$$\text{Acid value} = \frac{\text{titre value} * \text{normality of KOH} * 56.1}{\text{sample weight}}$$

= 0.48 mg KOH/g of bio-lubricant

Table: Appendix E: Simplified Infrared Correlation Chart

	Type of vibration	**Frequency(cm^{-1})**	**Intensity**
C-H	**Alkanes (stretch)**	3000-2850	strong
	-CH_3 (bend)	1450 and 1375	medium
	-CH_2 bend	1465	medium
	Alkenes stretch	3100-3000	medium
	Out of plane bend	1000-650	strong
	Aromatics (stretch)	3150-3050	strong
	Out of plane bend	900-690	strong
	Alkyne stretch	3300	strong
	Aldehyde	2900-2800	week
C-C	Alkane is not interpretatively useful	2800-2700	week
C=C	Alkene	1680-1600	medium
	aromatic	1600 and 1475	week
C≡C	Alkyne	2250-2100	medium
C=O	aldehyde	1740-1720	strong
	Ketone	1725-1705	strong
	Carboxylic acid	1725-1700	strong
	Ester	1750-1730	strong
	Amide	1670-1640	strong
	anhydride	1810 and 1760	strong
	Acid chloride	1800	strong
C-O	Alcohols,ethers,esters,carboxylic acid,anhydrides	1300-1000	strong
O-H	Alcohol, phenol		
	stretch	3500-3100	Medium
	bend	1640-1550	strong
C-N	Amines	13500-1000	Medium
C=N	Imines and oximes	1690-1640	weak
C≡N	Nitriles	2260-2240	medium
X=C=Y	Allenes, ketenes, isocyanates	2270-1950	strong
N=O	Nitro(R-NO2)	1550 and 1350	Strong
S-H	Mercaptanes	2550	week

S=O	Sulfoxides	1050	strong
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375-1300	strong
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1200-1140	strong

(Source: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table)

Appendix F: GC-MS analysis report of seed oil

JIJE LABOGLASS

JIJE Analytical *Testing* Service Laboratory

Doc. No: JATSL/FS.10-3.1 | Page 1 of 1 | Ver. No: 04 | Effective Date: July 08, 2017

Analytical Test Report

Customer Name:	Ababu Girma	Test Report No:	157
Contact Person:	Ababu Girma	Report Date:	21/05/2022
Sample Type:	Plant Oil	Test Request No:	Not Specified
Sample Source:	Not Specified	Tel (Mob):	+251922847566
Sample Collected By:	Ababu Girma	Fax:	Not Specified
Sample Collection Date:	27/04/2022	E-mail:	Ababugirma2012@gmail.com
Sample Receiving Date:	27/04/2022	Tested By:	JATSL
Sample Condition:	Normal	Dates Tested	05/05/2022

Lab No. J-0557/2704/22 | Customer ID: -

S/N	Compound Name	Formula	RT	Area	%Area
1	Methyl tetradecanoate	C15H30O2	9.33	138559	0.07
2	Hexadecanoic acid, methyl ester	C17H34O2	10.38	20741948	10.21
3	9-Hexadecenoic acid, methyl ester, (Z)-	C17H32O2	10.66	161917	0.08
4	Heptadecanoic acid, methyl ester	C18H36O2	10.87	87110	0.04
5	Methyl 9-heptadecenoate or 9-17:1	C18H34O2	11.17	54417	0.03
6	Methyl stearate	C19H38O2	11.51	12703333	6.25
7	Oleic acid, methyl ester	C19H36O2	11.82	66012498	32.50
8	Linoleic acid, methyl ester	C19H34O2	12.33	87358714	43.01
9	Eicosanoic acid, methyl ester	C21H42O2	12.66	813099	0.40
10	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	C19H32O2	12.90	205812	0.10
11	Methyl 13-eicosenoate	C21H40O2	13.01	218312	0.11
12	Docosanoic acid, methyl ester	C23H46O2	14.11	195977	0.10
13	Tetracosanoic acid, methyl ester	C25H50O2	16.23	193153	0.10
14	Cholesterol	C27H46O	27.90	14212842	7.00

Remark:

1. This test report is only for specific sample(s) which has been tested by JIJE Analytical *Testing* Service Laboratory.

Verified by
Name: Tesfaye Gezahegne | Signature | Date: 21/05/2022
Technical Signatory

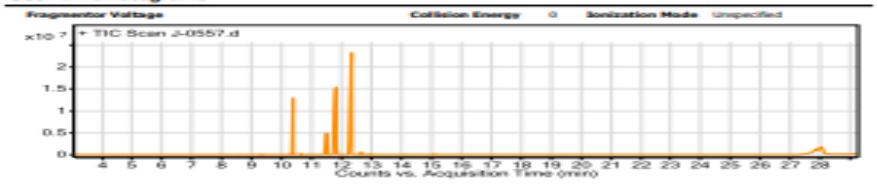
Authorized by
Name: Mulugeta Tesfa | Signature | Date: 21/05/2022
Laboratory Manager

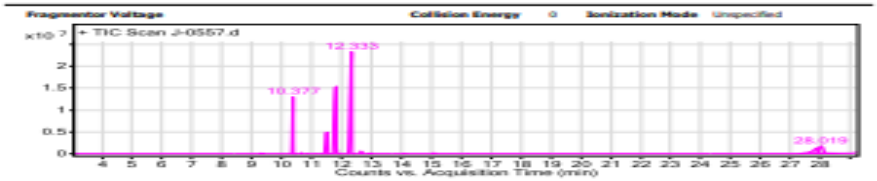
Tel: +251-37207 01/ 02
Fax: +251-011-372 07 03
P.O. Box: 70877
Email: info@jijelabglassplc.com
Web site: www.jijelabglassplc.com
Physical Address: Nifas Silk Lafto Sub City, Woreda 01, Lebu, Feziana Building 6th Floor, Infront of Varnero Real Estate, Addis Ababa, Ethiopia.

Qualitative Analysis Report

Data Filename	J-0557.D	**Sample Name**	FAP-ME
Sample Type		**Position**	15
Instrument Name	GCMS_IEE	**User Name**	IEE
Acq Method	Fatty Acids_Beef_2.M	**Acquired Time**	5/5/2022 12:40:47 AM
IRM Calibration Status	Not Applicable	**DA Method**	default.m
Comment			
Expected Barcode		**Sample Amount**	
Dual Inj Vol	1	**TuneName**	ATUNE.U
TunePath	D:\MassHunter\GCMS\1\5977\	**MSFirmwareVersion**	6.00.25
OperatorName	IEE	**RunCompletedFlag**	True
Acquisition SW Version	MassHunter GC/MS Acquisition B.07.03.2129 18-May-2015 Copyright © 1989-2014 Agilent Technologies, Inc.		

User Chromatograms

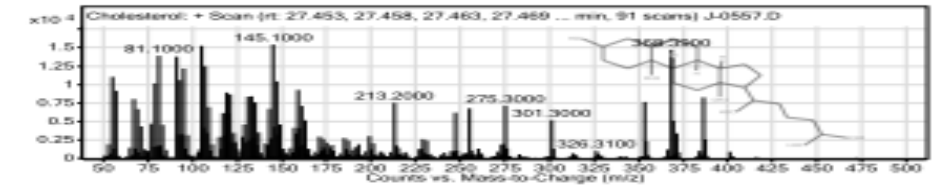




Integration Peak List

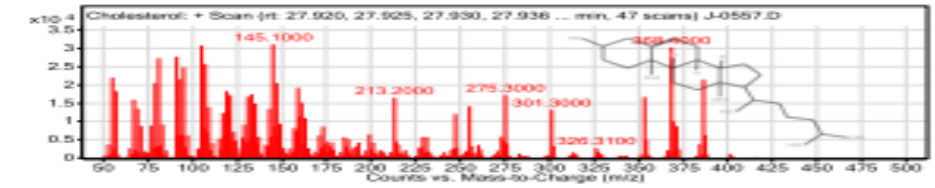
Peak	Start	RT	End	Height	Area	Area %
1	10.323	10.377	10.447	12960034.35	20741947.66	23.74
2	11.399	11.568	11.574	4932147.43	12703332.74	14.54
3	11.661	11.815	11.882	15229683.69	66012497.78	75.56
4	12.209	12.333	12.401	23296080.23	87358713.53	100

Qualitative Analysis Report



Peak List

m/z	Abund
55.1	11049.83
81.1	13907.8
91.1	13787.73
93.1	10605.19
95.1	12178.35
105.1	15269.48
107.1	12508.64
145.1	15429.96
147.11	10434.96
368.39	14722.18

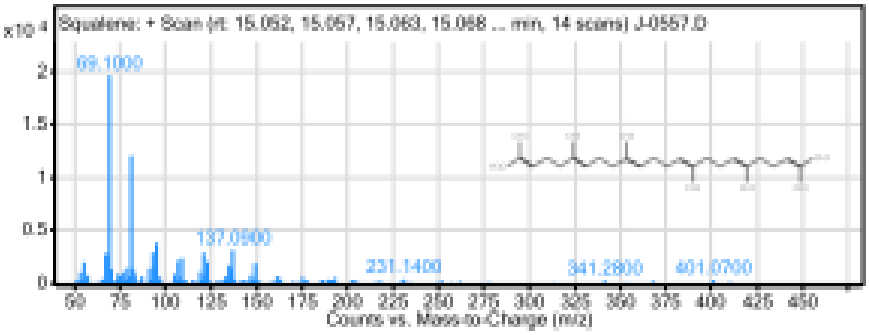


Peak List

m/z	Abund
55.1	22001.47
81.1	27361.19
91.1	27725.3
93.1	21645.15
95.1	24839.96
105.1	30818.04
107.1	25732.91
145.1	31157
368.4	30298.49
386.4	21474.74

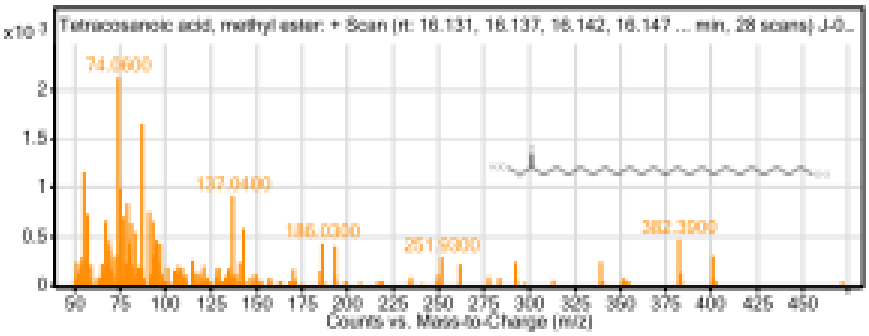
--- End Of Report ---

Qualitative Analysis Report



Peak List

m/z	Abund
67.09	2784.43
68.09	2744.21
69.1	19639.5
81.1	12070.43
93.1	2885.07
95.1	3827.43
107.09	2166
109.1	2391.14
121.1	2871.57
137.09	3144.29

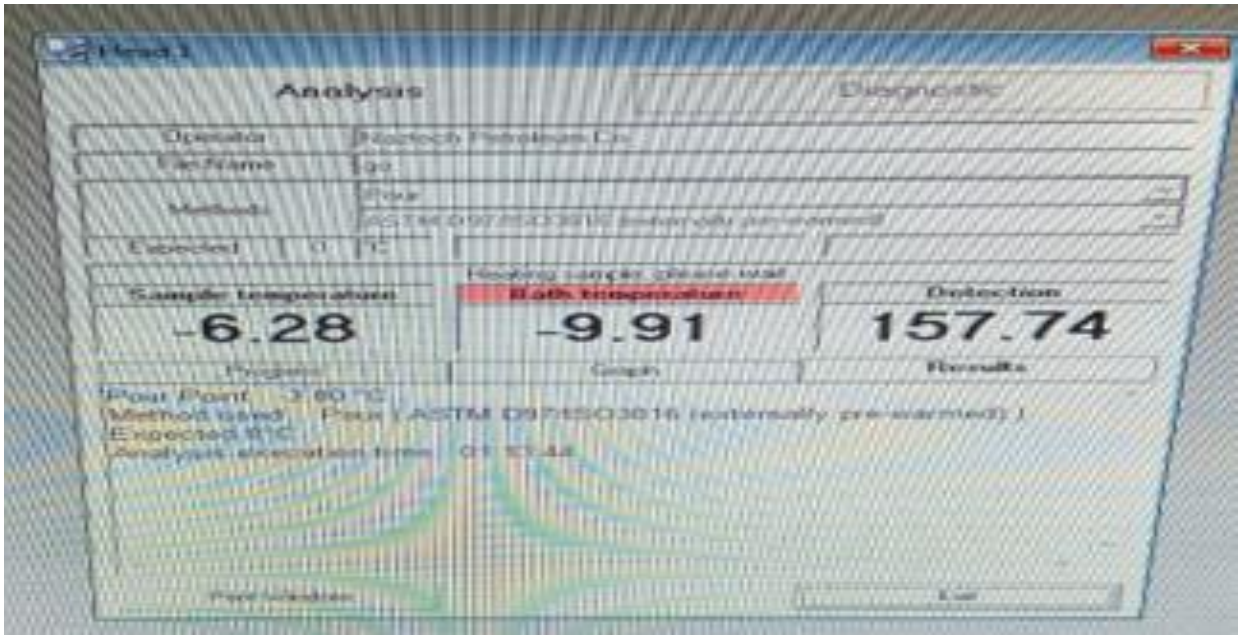


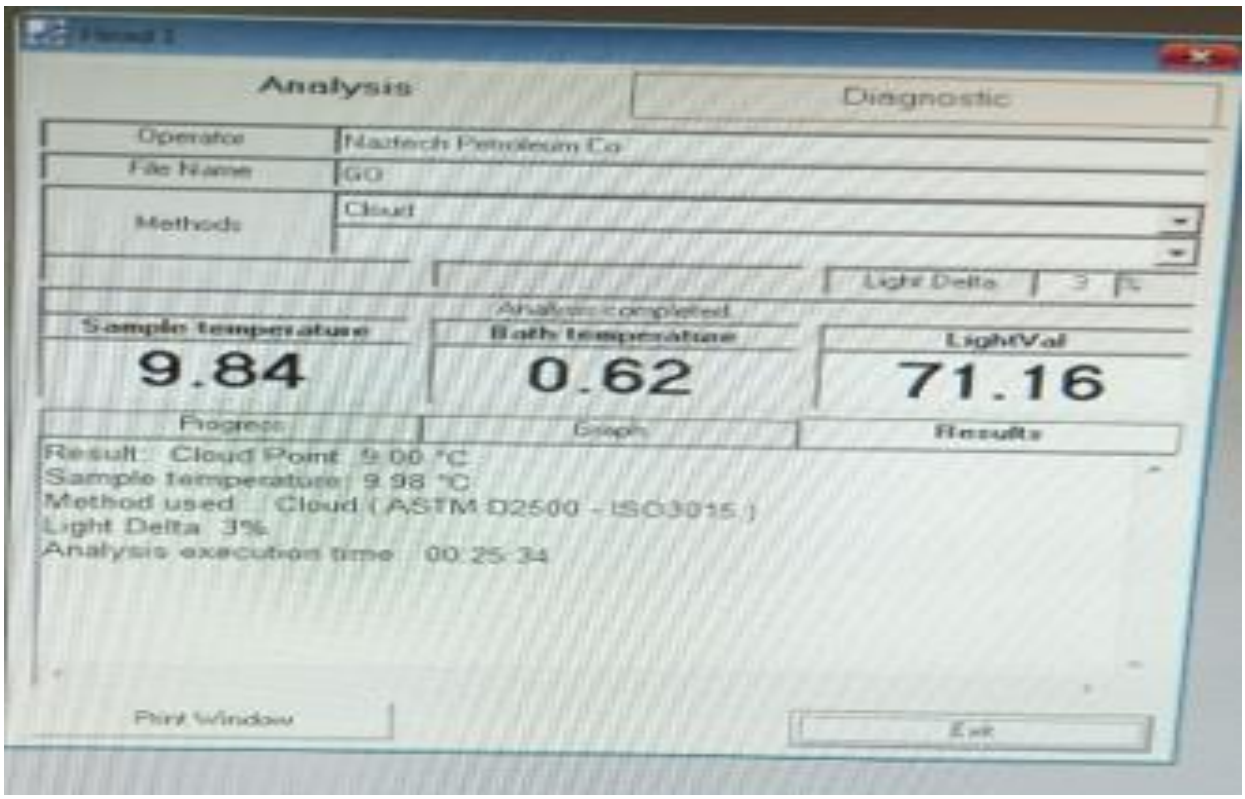
Peak List

m/z	Abund
55.07	1159.21
57.07	725.54
67.05	658.89
74.06	2124
75.06	989.61
77.05	696.36
79.05	838.29
87.1	1644.61
91.04	751.36
137.04	910.64

Appendix G: Pour point, and Cloud point of biodiesel and bio lubricant

I. For biodiesel

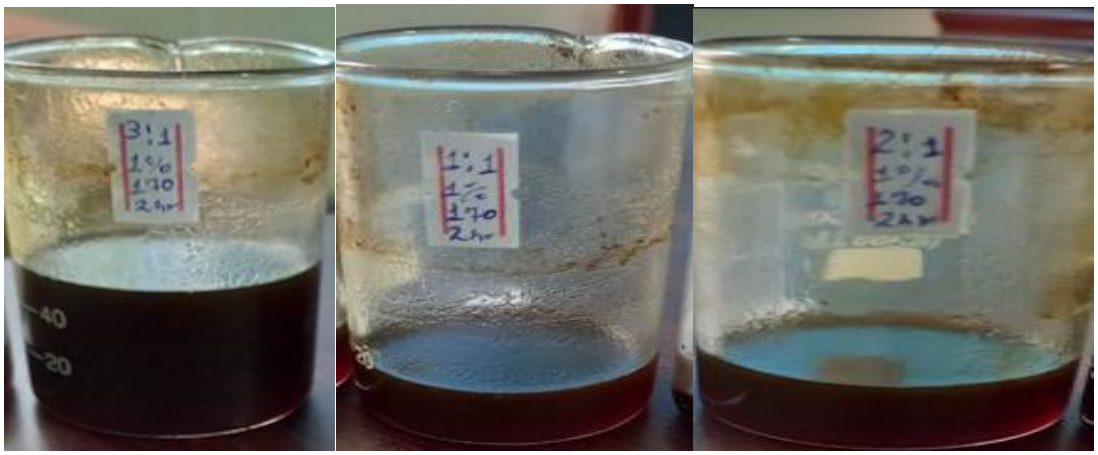




Appendix H: Effect of operating parameter on Bio-lubricant synthesis

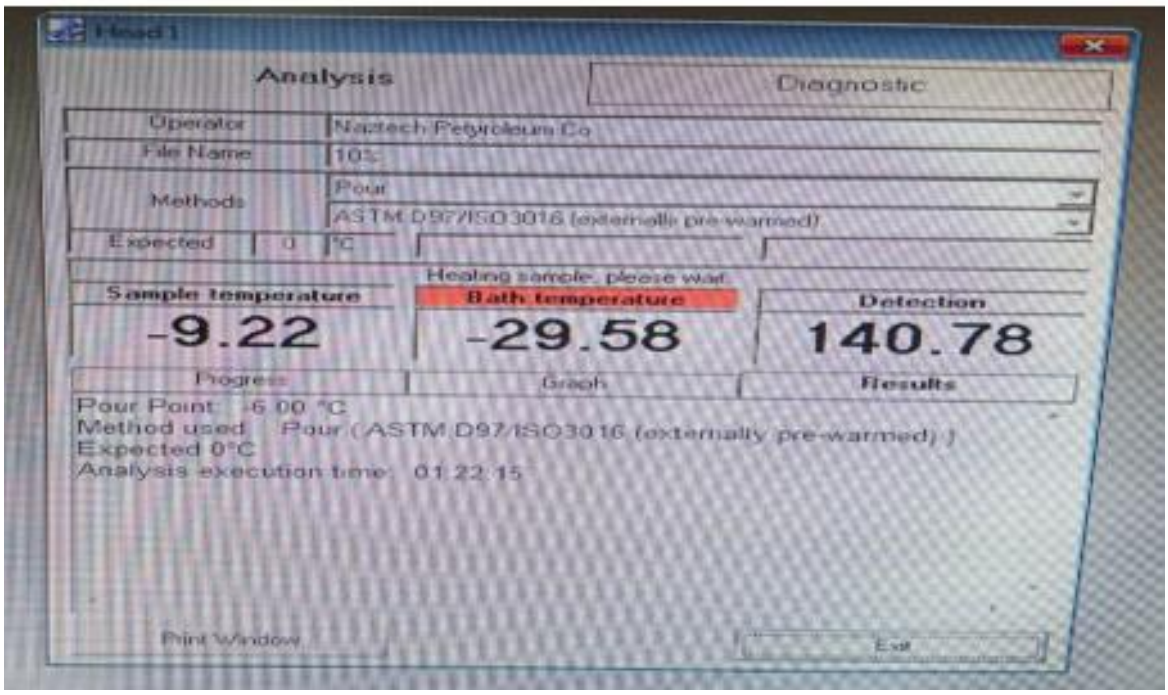
1. Effect of temperature

2. Effect of ethylene glycol to FAME molar ratio

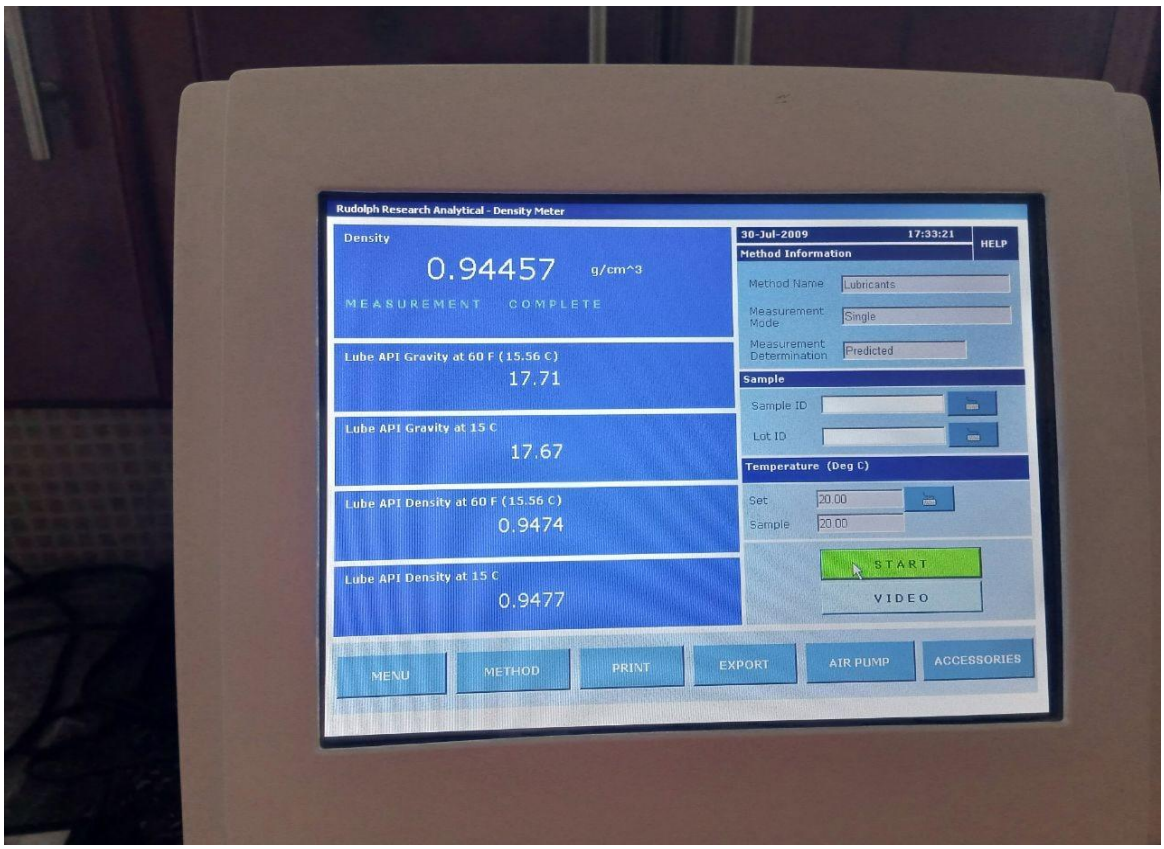


3. Effect of catalyst

II. Biolubricant

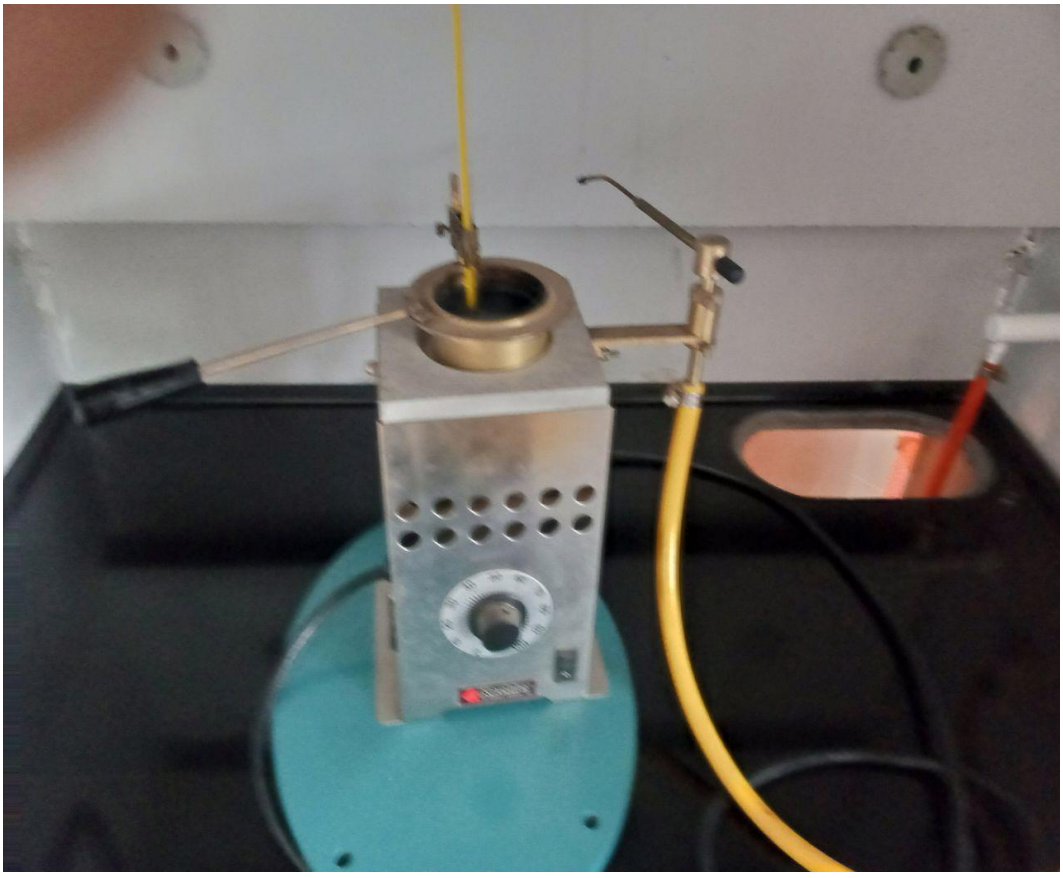


III. Density measurement for bio lubricant



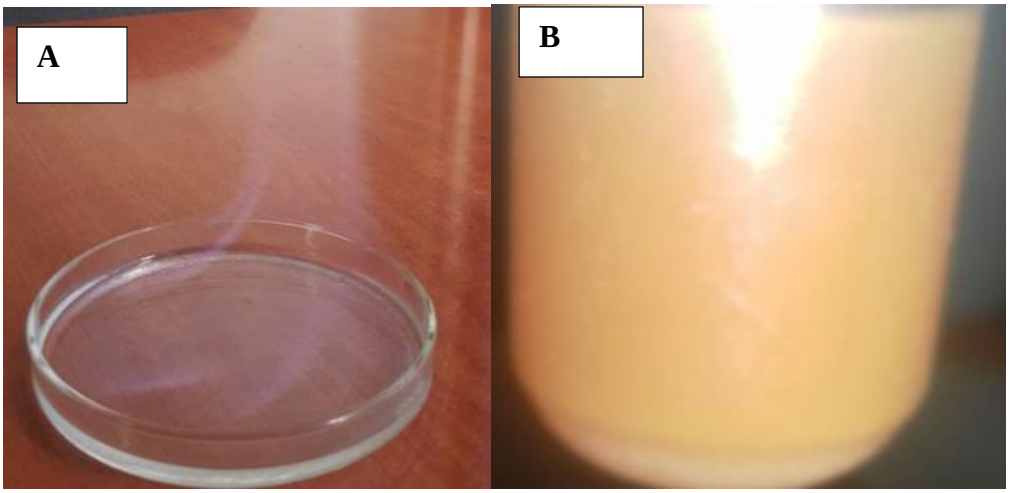
IV. Ostwald viscometer and Cleavanger

A. Calibrated viscometer at 40 ^{o}C B. Calibrated viscometer at 100 ^{o}C



B. Cleveland Flash point and Fire point tester

C. Methanol characterization (A. Testing burner, B. Iodoform test)



Appendix I: Standard of Viscosity grade

ISO VG viscosity grade	Midpoint viscosity cSt @ 40°C (104°F)	Kinematic viscosity limits cSt @ 40°C (104°F)	
10	10	9	11
15	15	13.5	16.5
22	22	19.8	24.2
32	32	28.8	35.2
46	46	41.4	50.6
68	68	61.2	74.8
100	100	90	110
150	150	135	165
220	220	198	242

ISO VG viscosity grade	Midpoint viscosity cSt @ 40°C (104°F)	Kinematic viscosity limits cSt @ 40°C (104°F)	
320	320	288	352
460	460	414	506
680	680	612	748
1000	1000	900	1100
1500	1500	1350	1650
2200	2200	1980	2420
3200	3200	2880	3520
4600	4600	4140	5060
6800	6800	6120	7480