PRODUCTION OF ENGINE BIOLUBRICANT OIL FROM NON-EDIBLE VEGETABLE OIL THROUGH CHEMICAL MODIFICATION AND FORMULATION

by

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PREFACE

The work presented in this dissertation was carried out in the analytical laboratory at the School of Engineering at the University of KwaZulu-Natal (Howard College Campus), Durban, from July 2020 to November 2021 under the supervision of Professor Amir H. Mohammadi.

This dissertation is submitted as the full requirement for the degree of Master of Science in Engineering (Chemical Engineering). All the work presented in this dissertation is original, unless otherwise stated. It has not (in whole or in part) been previously submitted to any tertiary institute as part of a degree.

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As the candidate's supervisor, I agree to the submission of this dissertation:

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a) their words have been re-written but the general information attributed to them has been referenced;

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(vi) this dissertation is primarily a collection of material, prepared by myself, published as journal articles or presented as a poster and oral presentations at conferences. In some cases, additional material has been included;

(vii) this dissertation does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the dissertation and in the References sections.

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Signed: Nhlamulo Khosa

Date: 08/12/2021

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ABSTRACT

Recently, the 26th Climate Change Conference (COP26) has pledged R130 billion to assist South Africa in transitioning to environmentally friendly energy sources. Some of the funds are being allocated to developing new sectors such as electric vehicles. This commitment highlights the urgency of developing environmentally friendly resources such as biolubricant to preserve the environment for the future generation. . In this study chemical modification of castor oil and waste cooking oil was carried out to produce environmentally friendly engine biolubricants. The chemical modification methods carried out in this study comprises of a two-stage base-catalysed transesterification method and ring-opening of the epoxidized vegetable oil.

The first stage transesterification was carried out using methanol in the presence of a sodium hydroxide catalyst producing Fatty Acid Methyl Esters (FAME). The FAME produced was then reacted with Trimethylolpropane (TMP) in the presence of a sodium methoxide catalyst producing TMP based esters (biolubricant). The transesterification of FAME was optimised in terms of TMP based triesters's yield. The actual optimum TMP based triesters's yield of 80.80 and 76.20% for waste cooking oil and castor oil, respectively were achieved. The optimised conditions to produce waste cooking oil TMP triesters were obtained at the temperature of 140°C, catalyst loading of 0.5wt%, the reaction time 3 hours of and WCOME to TMP ratio of 4.55:1 molar ratio. The optimised conditions to produce castor oil TMP triesters were obtained at the temperature of 140°C, catalyst loading of 0.52wt%, the reaction time of 3 hours, and the COME to TMP 5:1 molar ratio.

The second modification method was the epoxide ring-opening using 2-hexyldecanol. The reaction took place in two parts. The first part was the epoxidation of the vegetable oil which was carried out under the optimum conditions reported in the literature. The oxirane content of 5.6 and 5.2% were measured for the epoxidized castor and waste cooking oil, respectively. The second part of the reaction was the ring-opening of the epoxidized vegetable oil using 2-hexyldecanol alcohol. The reaction was optimised based on the hydroxy value measured at the end of reaction. The optimised conditions for the production of ring-opened epoxidized waste cooking oil using 2-hexyldecanol were obtained at the 120°C, 1.06wt% catalyst loading, 20 hours of reaction time and 2-hexyl decanol: epoxidized WCO molar ratio of 1:1. Whereas the optimum conditions for the ring-opening reaction for epoxidized castor oil were obtained at

the temperature of 140°C, catalyst loading of 2wt%, the reaction time of 20 hours and 2-hexyl decanol to eCO molar ratio of 1:1.

All the products were successfully confirmed through a and Gas Chromatography-Mass Spectrophotometer (GC-MS) and Fourier Transform Infra-Red (FI-TR) analysis. Four biolubricants were produced from the above-mentioned chemical methods, which are Waste Cooking Oil-based TMP esters (WCO-TMP), Castor Oil-based TMP esters (CO-TMP), Ring Opened epoxidized waste cooking (RO-eWCO) and Ring Opened Castor Oil (RO-CO). The produced biolubricants were subjected to various property tests to determine their suitability for engine oil application. The tests conducted included the Total Acid Number (TAN), Density, Viscosity, Viscosity index, Pour point, cloud point and thermal stability. In addition, tribological characteristics viz Coefficient of friction, was determined via a regressed correlation as the equipment was not available for measurements.

WCO-TMP showed very poor performance in terms of the pour point (+1°C), viscosity and thermal stability. Therefore, it was conclusive that its not suitable for use as an engine biolubricant. RO-eWCO, RO-eCO and CO-TMP biolubricants conformed to the requirements for engine oil application and were classified as SAE 20 viscosity grade lubricant. Thus, their properties were satisfactory for engine lubrication application.

Silicon dioxide (SiO_2) and Copper Oxide (CuO) were also added to the lubricants to improve the lubricity of the biolubricant. It was found that the nanoparticles increased both the density and viscosity of the biolubricant. Subsequently, affecting the COF based on the regressed correlation. The effect of nanoparticles on the thermal stability of the biolubricant could not be investigated due to the limited access to the hermogravimetric Analysis.

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Chapter 1 Introduction

1.1 Justification

According to researchers between 30 to 40 million tons of lubricants are used every year. Among this, about 20 million (Approximately 55%) finds itself back into the environment (Mang & Dresel, 2007). It is also estimated that 95% of the lubricants that end up in the environment are made of crude petroleum oil, which is very harmful to the environment (Schneider, 2006). The consumed oil returns into the environment through spillages, leakages, oil plant processes evaporation and deliberate lubricant disposal methods. This is a concerning matter as the mineral oil are toxic and non-biodegradable.

According to the American Petroleum Institute ‘s (API) predictions made in 1999, the world oil reserves would be depleted between 2062 and 2094. This was based on the assumption that the world remaining oil reserve was between 1,4 trillion and 2 trillion barrels and the daily consumption was 80 million. In 2004, API further predicted a shift in the depletion year from 2062 to 2057, owing to the increase in the consumption rate of fuel (UKEssays, 2018). It is now clear that an alternative and renewable oil is crucial to ensure sustainable energy sources. The oil prices have also been reported to increase due to the increased demand (Reeves, et al., 2015).

Various measures have been taken to minimize these threats, such as reclaiming and recycling mineral oil lubricants, preventing undesirable losses, and, most importantly, using lubricants (Bart, et al., 2013). Recently, researchers have called for a robust intervention in developing a more environmentally friendly lubricant. Vegetable-based oils have emerged as the potential alternative to mineral-based oil due to their high lubricity, high viscosity index, high flash point, high biodegradability and good resistance to shear (Soni & Agarwal, 2014; Syahir, et al., 2017). The vegetable oils can be extracted from seeds, nuts, cereal grains, and fruits (Hammond, 2003). The examples of oils that are used for the production of bio-lubricant oil include castor, soybean, rapeseed, rice bran, Karanja, sunflower oil, olive, sunflower, safflower, cottonseed, canola, coconut, and peanut oils (Dubai, et al., 2018; Tung & McMillan, 2004).

When selecting the suitable bio-lubricant, special attention should be given to the properties such as purity (particle count), pour point, oxidative stability homogeneity during long term storage, moisture content, acid number, viscosity, viscosity index, cloud point, volatility and some other properties based on the proposed application (Erhan & Asadauskas, 2000). These are the properties mainly influenced by the base oil component of the lubrication oil.

Although bio-lubricants present several advantages, some challenges exist within the industry, such as poor performance at elevated temperatures, lack of encouragement from the government, and low production scale. The performance challenges faced with the use of bio-lubricants include low oxidation stability, poor hydrolytic stability, high melting point,

substandard low-temperature characteristics, and low production rate (Salimon, et al., 2010; Syahir, et al., 2017; Woma, et al., 2019). According to the guidelines provided by Syahir *et al.* (2017) indicates that chemical modifications methods are required for applications where the lubricant is exposed to elevated temperatures and atmospheric oxygen.

Significant advancements have been made in improving bio-lubricants low oxidative stability and poor low-temperature limitations. Several methods have been implanted to combat these challenges, such as chemical modifications, emulsification, thermal modifications and the addition of additives (Syahir, et al., 2017). Chemical modification processes have received great interest from literature, namely esterification, transesterification and epoxidation. The results reported from the literature have shown that the use of chemical modification methods improves the vegetable's oil oxidative stability and low-temperature characteristics (Annisa & Widayat, 2018; Amit & Amit, 2012; Ghazi , et al., 2009; Li & Wang, 2015).

In the current study, biolubricants were produced through two modification methods and formulation.
Method A: The vegetable oils were reacted with methanol alcohol through a transesterification reaction. And in the second stage, the produced fatty acid methyl ester was transesterified using Trimethylolpropane (TMP) to produce the bio-lubricant base oil in the presence of sodium methoxide catalyst. The Silicon dioxide (SiO_2) and copper oxide (CuO)nanoparticles additives were added to the bio-lubricant base oil to enhance tribological properties.
Method B: The vegetable oils were first subjected to an epoxidation process followed by an oxirane ring-opening reaction using 2-hexyldecanol alcohol. The nanoparticles additives were added to the bio-lubricant base oil to enhance tribological properties.

The selection of vegetable oils was based on a number of factors, including accessibility, quality, cost and availability. Two different vegetable oils were selected: castor oil and waste cooking oil for investigation. Castor oil and waste cooking oil selection were mainly since they are edible oil and do not interfere with food security. As a result, it can easily be accessed as both the raw and the waste oil.

Several reports were published focusing on the use of vegetable oil as biodiesel; however, just a couple have revealed the use of vegetable oil-based oils as bio-lubricants. The main objective of the present study is to study the production of engine bio-lubricant oil using different chemical modification methods and the formation and comparison with the mineral-based engine oil.

1.2 Aim

The main aim of this research work was to investigate different chemical modification methods and formulation that can produce an engine biolubricant to replace the available commercial petroleum lubricants.

1.3 Objectives

- Conduct literature review on the chemical modification method for the production of biolubricants
- Characterisation of the raw vegetable oils
- Investigate the optimum conditions for the selected chemical modification methods
- Evaluate the physicochemical, rheological and tribological behaviours of the produced biolubricant oil
- Blend the produced biolubricants with additives to enhance rheological and tribological properties
- Determination of the synthesised biolubricants fitness for the application of the engine oil

1.4 Outline of dissertation structure

Chapter 1 Provides the background for the investigation. The problems and challenges currently facing the use of biolubricants are presented. The solutions proposed are outlined in terms of the aim and the objectives of the project

Chapter 2 Provides the details and status of different biolubricants, chemical modification methods, and feedstocks currently being utilised. The results from different methods are being discussed on both their advantages and disadvantages as well as the prospects.

Chapter 3 The methodology to produce biolubricants was outlined in terms of the operating conditions, apparatus and chemicals required. The optimisation strategy was also established.

Chapter 4 The optimisation results are discussed and validated. The results from the characterisation of waste cooking oil-based biolubricants are discussed. Based on the results obtained from the characterisation methods, it was then determined if the biolubricants was suitable to be used as engine biolubricants

Chapter 5 The optimisation results are discussed and validated. The results from the characterisation of castor oil based biolubricants are discussed. Based on the results obtained

from the characterisation methods it was then determined if the biolubricants was suitable to be used as an engine biolubricants

Chapter 6 The tribological study for the produced biolubricants was carried out using a regreased correlation for the coefficient of friction

Chapter 7 The main conclusion from the production and characterisation of the biolubricants are drawn

Chapter 2 Literature review

2.1 The purpose of lubrication oil

Since the first industrial revolution, humankind has always wanted to perform work with efficiency, meaning less mechanical breakdown and less energy input. However, this has always been met with challenges before the introduction of lubrication. The introduction of lubrication was aimed at improving the efficiency of machines through the protection of surfaces from corrosion, limitation of heat loss from surfaces in contact, reduction of wear from contacting surfaces, reduction of oxidation insulation in transformer applications, sealing agents to protect from water and dirt (Jamat, et al., 2010; Tirth, et al., 2017).

Lubricants are primarily used to reduce wear between two surfaces in shared contact by reducing friction. In order to ensure the safe and reliable operation of an automobile during operation, an effective lubricant is required. An effective lubricant allows moving parts to slide on each other smoothly hence reducing wear and friction (Syahir, et al., 2017). The reduction of friction subsequently results in a decrease in energy losses, mainly in the engine (Annisa & Widayat, 2018; Mobarak, et al., 2014). According to Inked et al. (2015), the standard specifications for an oil to be used as an engine oil are 4.1-6.6 cSt viscosity, >90 viscosity index,<-5°C pour point and >190°C flashpoint.

2.2 The discovery and development of lubricants

It is believed that humankind has known lubrication since the invention of the wheel (Honary & Richter, 2011). This is evident from the pictorial documents that depict the use of water, edible oils as lubricants by the Egyptian pyramid builders. The liquid was applied to reduce the friction when moving heavy and large pieces of rocks on wooden rollers (Honary & Richter, 2011). The Painting of the Egyptian pyramid builders is displayed in Figure 2-1 The painting of the Egyptian pyramid builders moving on colossal pyramid stones on the wetted sand (Honary & Richter, 2011) A man can be seen discharging what is believed to be water in front of the roller while the other men pull the roller.

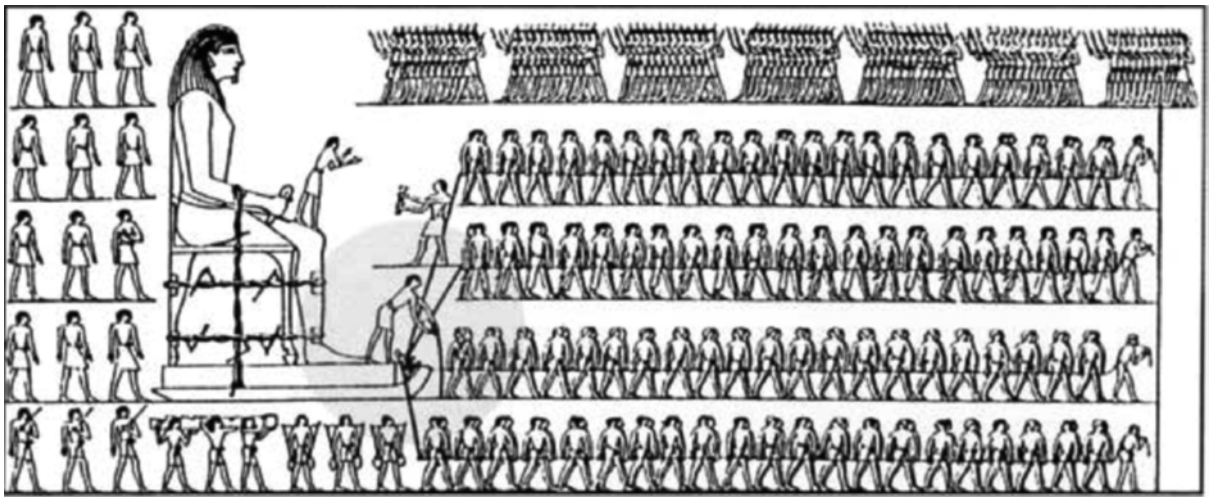

Figure 2-1 The painting of the Egyptian pyramid builders moving on colossal pyramid stones on the wetted sand (Honary & Richter, 2011)

According to Downson (1974), vegetable oil and animal fats were used extensively on mechanical machines such as pulleys from the first century AD. In around 1760, during the industrial revolution palm oil, groundnut oil and sperm whales were amongst the highly used bio-lubricants (Nie, 2012). This trend continued until the exploitation of the petroleum reserves in the 1859s (Honary & Richter, 2011). The use of petroleum oil sparked a record high due to its capabilities and low cost, which led to a decline in the use of bio-lubricants. During the first year, a company in the United States (US) called Spindletop produced over 3.59 million barrels of oil, followed by 17.4 million barrels in the second year (Honary & Richter, 2011). In 1877, chemists Charles Friedel and James Mason Crafts produced the first synthetic oil containing only hydrocarbon molecules. This led to the complete decimation of the bio-lubricants market as the US ramped up mass production of the automobile through the invention of mass production techniques by Eli Olds. However, it didn't last long before there were ranging concerns about the detrimental effect of petroleum products on the environment. The concerns were due to many factors such as global warming, decreasing petroleum reserves, Exxon Valdez Oil Spill in 1989, the explosion at the BP well of oil in Mexico year 2010 and many other disasters (Honary & Richter, 2011). These factors shifted the attention back to the use of bio-lubricant oil.

2.3 Different types of base lubricant oil

2.3.1 Mineral-based

The mineral-based lubricants are composed mainly of petroleum-based lubricants. The majority of Petroleum-based lubricants are produced from refined, and chemical modified crude oil (Honary & Richter, 2011). Crude oil contains complex mixtures of hydrocarbons such as gasoline, diesel fuel, heavy hydrocarbons and Light hydrocarbon gases. Moreover, crude oil contains a variety of unwanted components such as oxygen, sulphur waxes and nitrogen compounds (Madanhire & Mbohwa, 2016). The fractional distillation process is utilized to separate the mixtures within the crude oil based on their boiling points (Nie, 2012). Various processes such as hydrogenation, cracking is further used to optimize the properties of petroleum. The lubricants are extracted from the bottom of the main crude distillation unit with its constituents. The extracted crude lubricant oil can withstand temperatures as high as 650°C (Madanhire & Mbohwa, 2016). Various other processes such as vacuum distillation, de-asphalting, and extraction are used to remove some hydrocarbon with a similar boiling point, asphalt-related compound, and aromatic content. Such processes are necessary to remove all unwanted constituents before the lube base stock is ready for blending. Crude oil lubricant can have different properties depending on the processing technique used. At the final processing stage, the base oil is blended with additives to enhance its properties. The final lubricant oil contains 80-90% base oil and 10% additives (Mangas, et al., 2005).

The American Petroleum Institute (API) API 1509, Appendix E, has grouped the base oil into five groups according to their origin. Group, I, II and III base oils are derived from crude oil. Group IV includes all the synthetic base oil. Synthetic base oils are more costly than Group III base oils because of the severe extent of preparing expected to produce them. Group V includes all the other base oil not included in group I to IV. The criteria of the groups have been summarised in Table 2-1

Table 2-1 API base oil categorisation (API 1509, Appendix E (Simonovich , 2017))

Base oil groups	Saturates (%)	Sulphur (%)	SAE viscosity index range	Operating temperature range(°C)	Process
Group I	<90	>0.03	80-120	0 to 65°C	solvent-refined
Group II	>90	<0.03	80-120	-	hydrocracking
Group III	>90	<0.03	>120	-	Severe hydrocracking
Group IV	-	-	>120	-	-
Group V	The rest of the base oil excluded in group I-IV.				

2.3.2 Synthetic based lubricant oil

Synthetic lubricants are produced through the chemical modification of petroleum oil (Tucker, 1998). According to Rudnick (2013), the global market growth of synthetic lubricants is expected to grow by 12% before the end of the current decade. The increase can be attributed to advancing technology(machinery) to perform critical functions in extreme conditions. Synthetic lubricants' cost is higher than mineral lubricants due to their improved performance advantage and long-lasting effect (Bartz, 2013). The entire molecular structure of a synthetic lubricant is determined by tightly controlled chemical reactions to produce predictable properties (Lubrication Engineers, 2020). Unlike crude oil, there is no significant difference between carbon chain length, molecular size and branching in synthetically produced lubricants (Madanhire & Mbohwa, 2016). As a result, synthetic-based lubricants have more uniform characteristics.

The synthesised lubricants are produced through chemical reactions that do not occur naturally. The combination of synthetic esters, polyolefin and alkylated is often used to produce synthetic lubricant oil (Rudnick & Shubkin, 1999). Synthetic lubricants are characterized by high viscosity index, enhanced thermal stability, minor evaporation losses, enhanced oxidation resistance, a high viscosity index, enhanced low-temperature properties, reduced flammability and a wide operational temperature range (Lubrication Engineers, 2020). Hence, synthetic oils are preferred over refined petroleum oil in extreme operating conditions.

The comparison between synthetic and typical mineral oil in terms of their operating temperatures have been shown in Figure 2-2. It could be seen in Figure 2-2 that the synthesised lubricating oils have a more comprehensive operating range compared to the typical mineral oils. Some of the primary applications for synthetic lubricants include aircraft engines, mental stamping, refrigeration Lubes, marine industry and many other extreme applications (Pirro & Daschner, 2001).

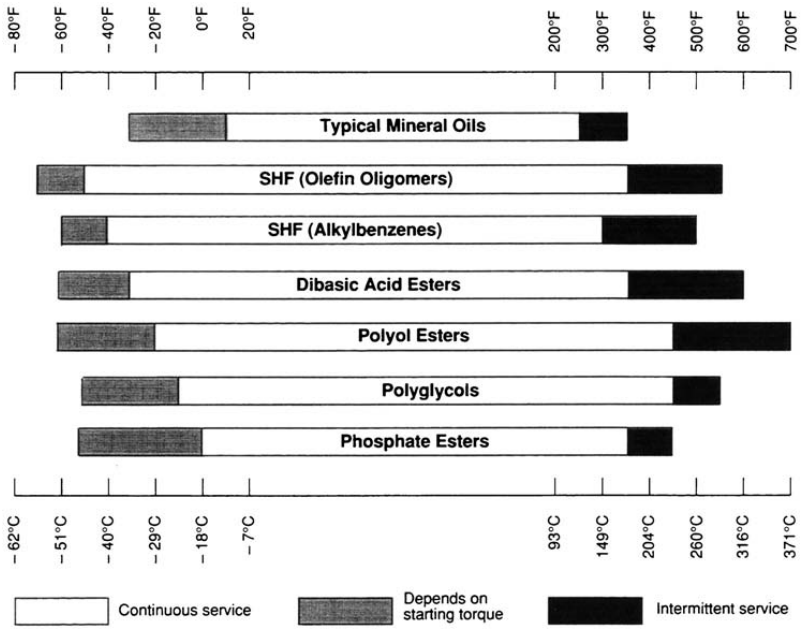

Figure 2-2 The temperature limits illustration of the typical mineral oil and synthetic lubricants (Pirro & Daschner, 2001)

2.3.3 Bio-based lubricants

The term bio-based lubricant or bio-lubricant concerns lubricants obtained from animal fats and vegetable oils, which are biodegradable, renewable, non-toxic and environmentally friendly (Annisa & Widayat, 2018; Syhir, et al., 2017). There has been an immense interest in the use of bio-lubricants nowadays due to the growing concern in protecting the environment, increasing petroleum prices and the depletion of crude reserves (Salimon, et al., 2010). Bio-lubricants are 95% biodegradable, whereas mineral oils are only 20 to 30% biodegradable (Owuna, et al., 2020; Jeevan & Jayaram, 2018)

In the past century(20th), vegetable oil has been shown to be more dominant than animal oil (Gunstone, 2011). During the same century, the animal oil contribution was reported to have declined from 50% to 20%, which decreased further to 16% in 2009 (Gunstone, 2011).

Vegetable oils are more effective than mineral oil of the same viscosity due to their high lubricity (Woma, et al., 2019; Huang, et al., 2003). The lubricity of vegetable oil enables the oil to adhere firmly to the surface.

The vegetable oil can be extracted from seeds, nuts, cereal grains, and fruits (Hammond, 2003). Vegetable oils have oily, liquid and fatty textures (Shahbandeh, 2020). According to the literature reports, there are over 350 oil-bearing crops; however, not all are suitable for producing bio-lubricants or biofuels. The eligible vegetable oil that can be used for the production of bio-lubricant and biofuel includes the castor, rapeseed, rice bran Karanja, sunflower oil, coconut, soybean, olive, safflower, cottonseed, canola and peanut oils (Dubai, et al., 2018; Tung & McMillan, 2004).

Other than lubrication, some vegetable oils can be used to manufacture soaps, skin products, candles, perfumes, cooling oils and other personal care and cosmetic products (Shahbandeh, 2020; Karak, 2012). The type of vegetable oils that can be consumed as food are referred to as edible vegetable oils, which includes olive, palm, soybean, canola, and sunflower oil (Negash, et al., 2019; Mobarak, et al., 2014). However, some vegetable oils are toxic; therefore, they cannot be consumed. Vegetable oils that cannot be consumed as food are non-edible oil and include Karanja oil, Rubber seed oil, Jatropha oil, Polanga (Foreign agricultural services, 2020; Islam, et al., 2018).

Vegetable-based lubricants can be used in various maintenance and industrial applications (Abdullah, et al., 2016; Jain & Suhane, 2013; Masood, et al., 2012). Industrial application of the vegetable oil includes compressor oil, metalworking oil, hydraulic oils; Automotive oil, such engine oils, gearbox oils and brake hydraulic fluids (Woma, et al., 2019). The main target of the bio-lubricants use has been on the application where oil spillages are invertible during application. This includes applications such as water treatment, sea transportation and the food industry (Gurram, et al., 2015).

Bio-lubricants derived from vegetable oil have the following advantages compared to mineral-derived lubricants (Salimon, et al., 2010; Silva, et al., 2013; Derawi & Salimon, 2013; Woma, et al., 2019):

- Better lubricity due to the reduced friction losses, which result in high power efficiency and lower fuel consumption

- Relatively higher viscosity indices compared to petroleum-based oil
- Highly biodegradable
- Higher shear stability
- Higher detergency hence disregarding the need for detergent additives
- Higher flash point
- Higher solvency for additives
- lower cost than synthetic oils

As per standards, the required properties of lubricants have been displayed in Table 2-2 alongside the unmodified vegetable oil properties. Biolubricants generally contain over 90% of the base stock and nearly pre-characterize lubricants properties. The main properties of bio-lubricants such as viscosities, oxidative stability, hydrostatic stability, deposit formation, solidification at low temperature is highly influenced by the base stock content (Woma, et al., 2019). Therefore, these properties must be considered first to select the most suitable lubricant for the intended application.

Additives can alter properties such as wear protection, lubricity foaming and many others. In addition to biodegradability, Woma et al.(2019) pointed out the following characteristics to be determined prior to the use of bio-lubricants: oxidative stability, viscosity, pour point, viscosity index (VI), Cloud point, pour point volatility, homogeneousness throughout long-term storage, Purity content of water, acidity and compatibility with mineral oil lubricants.

Table 2-2 Lubricant requirements and unmodified vegetable oil properties (McNutt & He, 2016)

Lubricant Requirement	**Viscosity 40°C (cSt)**	**Viscosity 100°C (cSt)**	**Viscosity Index (VI)**	**Pour Point (°C)**	**Flash point(°C)**	**Coefficient of friction**	**Wear Scar (mm)**	**Reference**
ISO VG46	>41.4	>4.1	>90	-6	220	-	-	(Wang, et al., 2014)
ISO VG32	>28.8	>4.1	>90	-6	204	-	-	(Wang, et al., 2014)
SAE 20W40	105	13.9	132	-21	200	0.117	0.549	(Rani, et al., 2015)
SAE 20W50	171[a]	18.9[a]	125[a]	-30[a]	206[a]	0.1121[c] 0.08	0.52355 [c] 0.36	a. (Castrol, 2019) c. (Woma, et al., 2019) d. (Jayadas, et al., 2007)
SAE 40	170.45	15.60	98	-12[d]	260[d]	-	-	(Tulashie & Kotoka, 2020)
Soybean	28.86	7.55	246	-9	325	-	-	(Siniawski, et al., 2011)
Sunflower	40.05	8.65	206	-12	252	-	-	(Siniawski, et al., 2011)
Castor	220.6	19.72	220	-27.00	250	-	-	(Salih, et al., 2011)
Jatropha	35.4	7.9	205	-6	186			(Sammaiah, et al., 2014)
Coconut	24.8	5.5	169	21	325	0.101	0.601	(Rani, et al., 2015)
Palm oil	52.4	10.2	186	-5	-	-	-	(Ghazi , et al., 2009)

2.4 The challenges faced with the use of vegetable-based lubricants

Though the use of vegetable oil in lubrication seems to be the best substitute for mineral oil, there are some challenges such as low oxidation stability, poor hydrolytic stability, high melting point, substandard low-temperature characteristics and low production rate (Salimon, et al., 2010; Syahir, et al., 2017; Woma, et al., 2019). The cloud point and pour point are referred to as the low-temperature properties, while high-temperature properties consider the volatility and flash point of the vegetable oil (Syahir, et al., 2017).

Oxidation and thermal instability are the most critical problems faced with vegetable oil (Erhan & Asadauskas, 2000). Oxidation stability refers to the measure of lubricant's resistance to react in the presence of oxygen (Woma, et al., 2019). In the occurrence of oxidation reaction, some of the lubrication properties such as density, anti-corrosive, wear protection diminishes as a result (Trajano & Moura, 2014). Therefore, oxidation should be avoided or prolonged to allow a more extended service. According to Machinery lubrication (2020), oxidation reduces a lubricants service life by half, as the temperature increases by 10°C above 60°C.

Thermal stability refers to the measure of resistance to molecular degradation at elevated temperature in the absence of oxygen (Menezes, et al., 2013). Vegetable oil containing multiple double bonds, such as polyunsaturated oil, exhibits low oxidative stability (Adhvaryu & Erhan, 2002). The presence of high linoleic/linolenic acid content and the CH group from glycerine also contribute to the thermal and oxidative instabilities of vegetable lubricants oil (Ajithkumar, 2009). The oxidation of bio-lubricants is responsible for the formation of corrosive by-products in grease, engine oil and the formation of sludges and deposits (Heikal, et al., 2017). Another concern with bio-lubricants is the high pour point due to the high number of double bonds present in some vegetable oil structures (Salih & Yousif, 2013; Annisa & Widayat, 2018).

One of the challenges several countries face in developing bio-lubricants is the lack of encouragement from the authorities. The insecurity of raw material availability of vegetable oil is also a challenge in developing bio-lubricant technology (Petran, et al., 2008). The production of bio-lubricants oil from edible oil has also been faced with much criticism from the food industry. Some developing countries do not even produce enough edible oil to consume as food (Islam, et al., 2018). Due to the lack of efficient oil extraction methods, the final bio-lubricants tend to cost somewhere between 30–40% more than the conventional lubricant (Woma, et al.,

2019; Hsien, 2015). As a result, the market for bio-lubricant oil has been growing at a plodding pace.

According to the report presented by Statista in 2019/20, the global production of vegetable oil has reached 203.91 million metric tons. Figure 2-3 shows the worldwide consumption of vegetable oil by oil type from 2013 to 2019. Palm oil constitutes the largest consumed vegetable oil worldwide. However, about 90% of palm oil is used for food production, while only 10% is used in cosmetic products, fuel,nd diesel (Shahbandeh, 2020).

According to Salimon *et al*. (2010), Europe, America and Asia consume about one-third of the worldwide lubricants while Africa only consumes 5%. The actual worldwide consumption of bio-lubricant in percentage is displayed in Figure 2-4. Mordor intelligence (2019) data shows that the African lubricants market is expected to register a compound annual growth rate (CAGR) of 2.64% from 2019 to 2024. The report also indicated that the development of synthetic and bio-based lubricants would result in a growth opportunity in the market.

In South Africa, the demand for lubricants is expected to continue increasing due to the growth in the industrial and transportation sector, with engine oil projected to be the largest product type (MarketsandMarkets Research Private Ltd, 2020). The world market growth of lubricants is expected to reach USD 203million by 2020 (Hussan, et al., 2016). Moreover, Tung and McMillan (2004) predicted a bleak prospect of mineral oil as bio-lubricants for the automobile. Hence vegetable-based oils are perceived as the potential alternative for mineral-based oil (Tung & McMillan, 2004; Owuna, et al., 2020).

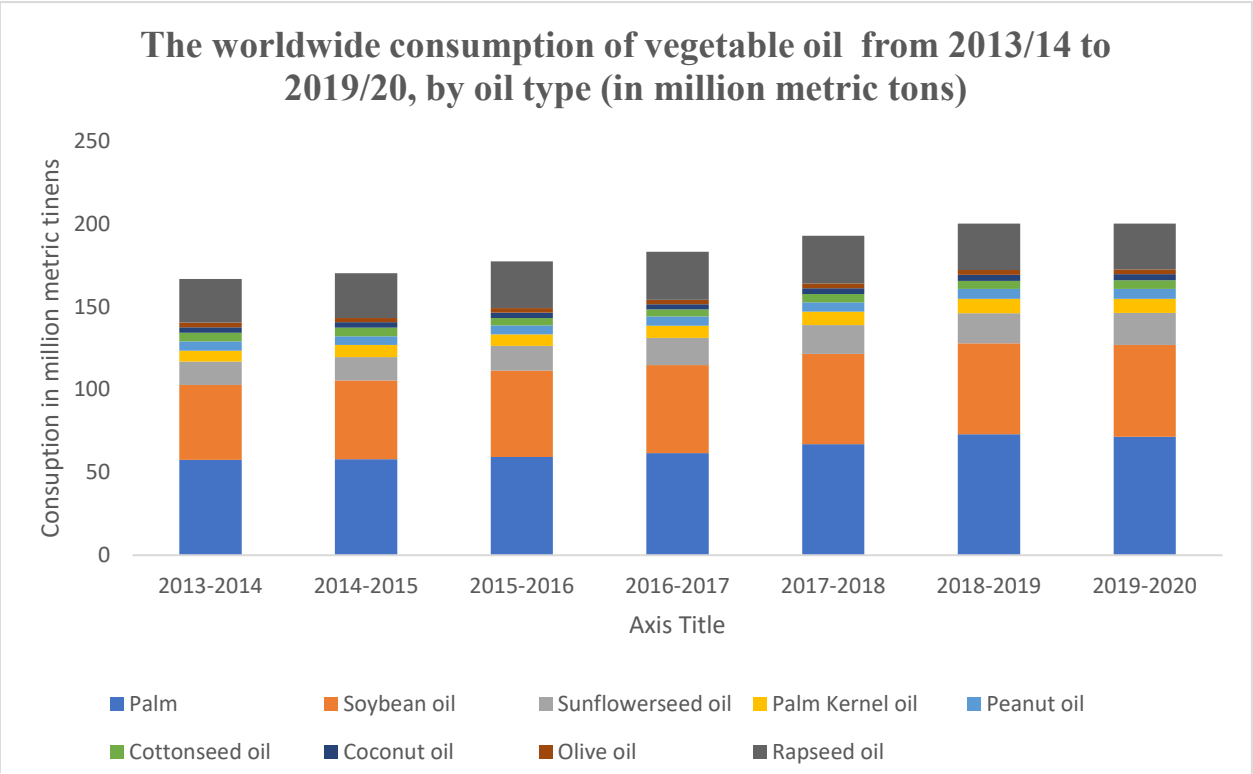

Figure 2-3 Worldwide consumption of vegetable oils from 2013/14 to 2019/20 (Statita, 2020)

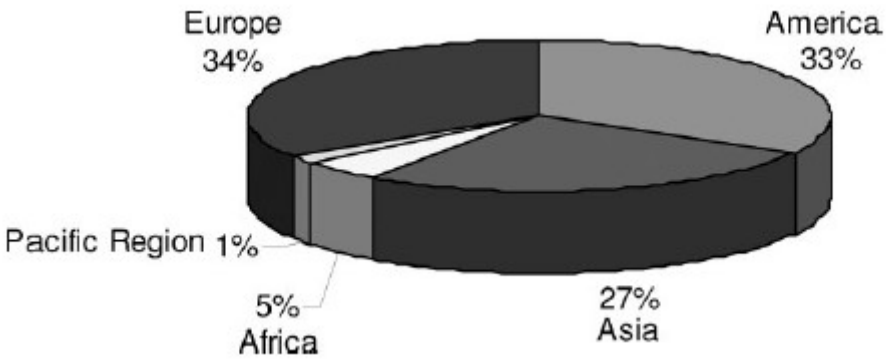

Figure 2-4 The worldwide bio-lubricant production chart

2.5 The structure and properties of vegetable oil

When discussing the physicochemical properties and performance of bio-lubricants, it is crucial to consider the influence of each component of the molecular structure. Vegetable oils are mainly made up of triglyceride molecules (Syahir, et al., 2017). Other components may be

Phospholipids, triterpene alcohols, hydrocarbons tocols (tocopherols and tocotrienols), free sterols, and fat-soluble vitamins found in small quantities (Karak, 2012).

Triglyceride molecules are produced through the polycondensation of one of the molecules of glycerol and three molecules of fatty acid (Syahir, et al., 2017; Woma, et al., 2019; Lawal, et al., 2012) . The generic diagram of the triglyceride molecule is displayed in Figure 2-5. The Glycerine component consists of three linked hydroxyl groups and is identical to all vegetable oil (Lawal, et al., 2012).

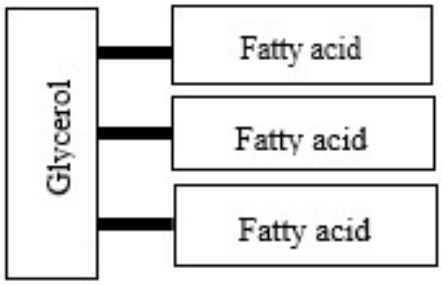

Figure 2-5 generic diagram of the triglyceride molecule

Fatty acids (FA) are made up of (C_4-C_{36}) long hydrocarbon chains attached to each hydroxyl group (Syahir, et al., 2017). Vegetable oils have different fatty acids depending on the type of oil (Karak, 2012). The variation in the fatty acid may be due to the chain length or the degree of saturation (the number of double bonds) (Woma, et al., 2019). Table 2-3 shows some of the common fatty acids found in vegetable oils. The contribution of fatty acid content is between 94% to 96% of the triglyceride molecule's total weight (Karak, 2012). Fatty acids can be found in three different types: saturated, monounsaturated and polyunsaturated fatty acids (Syahir, et al., 2017). Unsaturated fatty acid contains double bonds, while saturated fatty acids contain no double bonds. The unsaturated part of the fatty acid acts as the reactive centre since it is highly reactive compared to the other part of the molecule. The double bond found in the unsaturated fatty acid can be isolated or conjugated (Song, et al., 2015). Isolated double bonds are separated by either two or more single bonds, whereas conjugated FA refers to alternating single or double bonds.

An iodine number is used to measure the degree of unsaturation of vegetable oil (Knothe, 2002; Sanders, 2003) (Barrera-Arellano, et al., 2019). The vegetable oils with a high saturated fatty

acid content have low iodine number, while the unsaturated fatty acid high content vegetable oils have a high iodine number (Gupta & Kanwar, 1994; Negash, et al., 2019). As a result, the iodine number can express the vulnerability of the vegetable oil to oxidise during operations. The iodine number can also be used to characterise oil as either drying, semi-drying, or non-drying type of oil (Malshe & Sikchi, 2004). The iodine value of over 150 represents drying oils. The semi-drying oil has an iodine value of between 100 and 150, including soybeans, watermelon, and sunflower. The iodine value below 100 represents non-drying oils, including castor, cottonseed, coconut, rice bran, rapeseed, olive, and groundnut.

According to Karak (2012), the five critical points listed below should be considered on the structure of the vegetable oil as they predefine the properties of the resulting vegetable oil. The points have been listed below in no order.

i. The length of a Fatty acid chain
ii. The presence of unsaturation in the chain
iii. The double bond's position.
iv. The presence of other components such as -OH, chlorides and triple bonds

Table 2-3 shows the physical properties and chemical structures (Condensed) of vegetable oils' most common fatty acid. The physicochemical properties of the vegetable oil are strongly dependent on the fatty acid distribution and degree of saturation (Syahir, et al., 2017). Generally, a longer carbon chain of fatty acids results in higher viscosity and melting point. In contrast, the fatty acids containing double bonds have low melting points, viscosity, and thermo-oxidative stability.

Mono-saturated fatty acids are widely preferred as they exhibit more desirable properties such as low melting point, good thermo-oxidative stability and viscosity (Garcés, et al., 2011; Nagendramma & Kaul, 2012; Hoelderich, 2001). This is evident in the chemical structures shown in Table 2-3. Moreover, factors such as plant growth season, soil conditions, and the seeds' maturity may also affect the vegetable oil properties. Table 2-4 shows the physical properties and composition of some of the commonly used vegetable oils.

One of such beneficial properties is high lubricity caused by the oxygen present in the ester molecule, making the molecules create a monolayer over the metal surfaces (Silva, et al., 2013). Due to the chemical arrangement and orientation, the attachment between the oil and the

surface is not easily eroded by water, mechanical and or thermal stresses (Ajithkumar, 2009; Bongfa, et al., 2015). The vegetable oil with a high number of double bonds exhibits a better pour point(low) but low oxygen stability (Syahir, et al., 2017).

Table 2-3 The physical properties and chemical structures of some of the common fatty acids present in vegetable oils

Fatty acid	Condensed chemical structure	Density	Melting point(°C)	Boiling point(°C)
Palmitic		0.85	63-64	351
Stearic		0.94	66-70	365-370
Oleic		0.89	13-14	360
Linoleic		0.90	-5	229
Linolenic		0.91	-11	230-232

Table 2-4 Physical properties and composition of common vegetable oils (Karak, 2012)

Common name	Botanical name	Composition if different fatty acid (%)							Iodine value	Saponification value
		Oil content (%)	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other acids		
Canola	*Brassica Juncea*	25	3.5	1.5	60.1	20.1	9.6	Erucic (2)	110-120	188-198
Castor oil	*Ricinus communis L*	40-55	1	1	3	3-4	<0.2	Ricinoleic (89) around 90% (Silva et al., 2013),	82-88	195-187
Coconut	*Cocos nucifera L*	35.3	8	3.8	5	2.5	-	Lauric (48.2)	81.4	250-264
Linseed	*Linum usitatissimum*	35–45	9–10	7–8	10–21	13–15	50–61	-	170–204	189–196
Palm	*Elaies guinensis*	40–45	44	4	40	10	10	Trace	Other	51.5-57
Rapeseed	*Brassica napus L*	36	3-4	1-2	9-16	11-16	7-12	Eicosenoic (10), Erucic (42)	94-120	168-187
Soybean	*Glycine max*	16-22	10.5	3.2	22.3	54.5	8.3	Eicosanoic (0.9), Arachidic (0.2)	130	189-195

2.6 Chemical modification

The vegetable oils main limitations are the poor thermal stability and low oxidation stability at extreme loads (Sadiq, et al., 2018; Salih, et al., 2013; Erhan, et al., 2006; Cortes & Ortega, 2019). Researchers have developed different methods to try and overcome these limitations. The methods developed include chemical modification, emulsification, epoxidation and addition of additives. Within these methods, chemical modification and addition of additives have received great attention due to their proven record of imparting new properties to a base oil and enhancing desired properties (Syahir, et al., 2017; Kleinaite, et al., 2014). The use of additives is to be discussed in detail in later sections.

The chemical modification is aimed at the double bond within the unsaturated fatty acid in the triglyceride molecule. The double bond makes the vegetable oil very susceptible to oxidation in the presence of atmospheric oxygen (Buist, 2010). Researchers have reported improved lubricating properties after carrying out various vegetable oil chemical modification methods. (Jeevan & Jayaram, 2018; Amit & Amit, 2012; Jamat, et al., 2010; McNutt & He, 2016; Salih, et al., 2011). Chemical modifications are necessary for the production of bio-lubricants to operate in extreme conditions (Syahir, et al., 2017).

Chemical modification methods include esterification/transesterification, epoxidation, estolide formation, selective hydrogenation, (McNutt & He, 2016). The general pathways of the reactions mentioned have been displayed in Figure 2-6. Due to the poor low-temperature characteristics of the epoxidized vegetable oil, further chemical modifications are required. Such chemical modification can include ring-opening, esterification and acetylation reaction, as shown in Figure 2-6. Furthermore, Table 2-6 summarises some of the pros and cons of some chemical modification methods. The use of chemical modification methods to improve the vegetable oil ‘s performance has been reported in the literature (Li & Wang, 2015; Salimon, et al., 2010; Salih, et al., 2011; Sharma, et al., 2015; Madankar, et al., 2013; Ahn, et al., 2012; Gorla, et al., 2014).

2.6.1 Esterification/Transesterification

The production of bio-lubricants through esterification or transesterification involves multiple steps with different sequences. The vegetable oil is first evaluated to determine the water

content and the free fatty acid. According to Leung et al. (2010), if the free fatty acid is above 2.5wt%, a pre-treatment step is required to avoid forming the unwanted product. The free fatty acid can be reduced through an acid catalysed reaction (Leung, et al., 2010). When the free fatty acid has reached an acceptable level (<2.5wt%), the oil is then taken to the first step of the biolubricant production. The first step involves the reaction of unmodified triglyceride with alcohol to produce fatty acid methyl ester (FAME) in the presence of an acidic catalyst. Alongside FAME, Glycerol is produced as the by-product. In the second step, the resulting methyl ester reacts with various types of alcohol to produce triesters in the presence of a basic catalyst.

Researchers have reported using one and two-step base-catalysed transesterification process, while others reported using the esterification reaction first, followed by a transesterification reaction. However, the two-step transesterification is the most popular method in the literature and the basis for the current study. The bio-lubricants produced by two-step transesterification can have varying properties due to the wide range of reactants used (McNutt & He, 2016). The current study focuses on using two-step transesterification using methanol and TMP, respectively. Tulashie & Kotoka (2020) carried out experiments to produce bio-lubricants via transesterification, followed by the addition of special additives. The method is preferred as it does not use toxic alcohols such as ethyl glycerol and polyols. Therefore, the method reported by Tulashie & Kotoka (2020) is deemed safer for human usage compared to the other method (Tulashie & Kotoka, 2020).

Esterification and transesterification reactions involve modifying a carboxylic group in the fatty acid. Esterification is the chemical reaction used to produce an ester (FAME) through the reaction of alcohol and acid (Heikal, et al., 2017). Short-chain alcohols such as methanol are often used as a reactant to react with the unmodified triglyceride in the presence of an acidic catalyst (McNutt & He, 2016; Owuna, et al., 2020; Annisa & Widayat, 2018). The catalyst used can either be homogeneous or heterogeneous (Fattah , et al., 2020).

Homogeneous catalysts are highly reactive and require mild reaction conditions to produce low free fatty acid biodiesel (FAME) (Romero, et al., 2011). However, the use of homogenous catalysts has some drawbacks, such as the formation of soap, slow reaction rate, corrosive nature and challenges in separating the catalyst from the product, subsequently driving the cost

of production up (Fattah , et al., 2020). On the other hand, heterogeneous catalyst possesses several advantages such as high-water adaptability, recyclability, reusability, and can be easily recovered from the produced biodiesel (Romero, et al., 2011).

Transesterification is the process that is used to convert an ester (FAME) into the triesters (bio-lubricant) through the addition of an alcohol reactant in the presence of an alkaline catalyst (McNutt & He, 2016). According to literature, the transesterification of methyl ester results in the enhanced thermo-oxidative stability and reduced pour point while maintaining the other beneficial properties such as viscosity and lubricity (Kamalakar, et al., 2013; Gryglewicz, et al., 2013; McNutt & He, 2016; Ghazi , et al., 2009).

The use of polyols to replace the glycerol molecule after the first reaction (Transesterification) is a commonly used route in producing bio-lubricant (McNutt & He, 2016). Glycerol is not desirable in the triglyceride structure due to the hydrogen linked to the carbon atom in the β-position of ester groups. The presence of the carbon atom in the β-position of the ester group results in the degradation of the ester molecule (Owuna, et al., 2020). Polyol alcohols are highly biodegradable (>70%) (Tung & McMillan, 2004). In the transesterification reaction, the polyols are reacted with the fatty acid methyl ester in an alkaline base catalyst to produce the bio-lubricant (Polyol ester). According to the results reported by Ghazi et al.(2009) and Muhktar et al. (2014), the use of sodium methoxide as a catalyst result in improved oxidative stability and degradation temperature of over 325°C. The produced bio-lubricants poses an improved physicochemical property and enhanced thermo-oxidative stability (Owuna, et al., 2020).

The Polyhydric alcohols that may be used for the production of bio-lubricants include the neopentylpolyols, pentaerythritol (PE), trimethylolpropane (TMP), neopentyl glycol (NPG) (Nie, 2012). TMP (2-ethyl-2-(hydroxymethyl)-1,3-propanediol) is the commonly used polyhydric alcohol in the production of bio-lubricants oil (Arbain & Salimon, 2009; Schneider, 2006). When TMP is utilized as the reactant, three products could be formed: monoesters, diesters, and triesters due to the presence of the three hydroxyl groups in the TMP structure. Amongst these products, triesters are the most dominant product type and have superior temperature behaviour compared to the rest of the product (Yunus, et al., 2002; Annisa & Widayat, 2018).

The use of TMP in the transesterification reaction of the vegetable oil has been extensively studied and was reported to improve the oxidation stability, flash point, fire point, lubricity and anti-corrosion characteristics (Salimon, et al., 2010; Silva, et al., 2013; Salimon, et al., 2014). Researchers have found different factors that affect the production of bio-lubricants through esterification and transesterification reactions. These factors include reaction temperature, type of alcohol, the water content in alcohol, reaction time, stirrer speed, the molar ratio of alcohol to oil, concentration and nature of catalyst (Dibal, et al., 2017; Annisa & Widayat, 2018).

Hussein *et al.* (2021) carried out a two-step transesterification process of waste cooking oil using potassium hydroxide and calcium oxide catalyst, respectively. Hussein's study focused more on the second transesterification reaction instead of waste cooking oil methyl ester production. The second reaction conditions were optimised to obtain the highest conversion. The optimum conditions were obtained at the temperature of 130 °C, WCOME: Ethylene glycol ratio of 3.5: 1, the reaction time of 1.5 h and 1.2% (w/w) catalyst loading. The produced biolubricant were found to conform to the ISO VG68 viscosity grade requirements with much improved low temperature properties (Hussein, et al., 2021). Bahadi et al., (2021) also synthesised the trimethylolpropane tetraester-based biolubricant using Elaeis guineensis kernel oil via homogeneous acid-catalyzed transesterification. The optimum yield of 79% and 91% selectivity was of tetraesters was obtained (Bahadi, et al., 2021). The produced biolubricants exhibited favourable properties for lubrication applications. The biolubricants conformed to the ISO VG 100 lubricant grade used as a food-grade hydraulic fluid (Bahadi, et al., 2021).

Similarly, Kamarudin *et al.* (2020) conducted a two-step transesterification process to produce TMP esters from waste cooking oil and rubber seed oil. The results showed a better conversion of waste cooking oil to TMP triester compared to rubber seed oil within a similar operating condition. The reaction conditions were optimised based on the TMP conversion to TMP triesters. The resulting biolubricant's viscosity met the requirements for standard lubrication ISO VG46 (Kamarudin, et al., 2020). Heikal *et al.* (2017) prepared and characterised the TMP ester synthesised from palm oil and Jatropha oil through a two-stage transesterification method. Potassium hydroxide and sodium methoxide were used as catalysts for the first and second transesterification, respectively. The 97.8 and 98.2% yields were obtained for palm oil-based biolubricants and Jatropha oil-based biolubricants, respectively. The results showed that the jatropha oil based biolubricants exhibited improved pour point temperature of -3°C, high

viscosity of 140 and conformed to the ISO VG46 grade oil requirements. On the other hand, palm oil based biolubricant had a high pour point temperature of 5°C while the other properties were comparable to the commercial oil, such as ISO VG32 and VG46 (Heikal, et al., 2017). A detailed summary of physical properties and the chemical conditions of the various chemical modification methods have been displayed in Table 2-3.

2.6.2 Epoxidation, Ring Opening and Acetylation

Epoxidation reaction involves the conversion of the double bond between two carbon atoms into an oxirane ring by using generated in situ performic acid and hydrogen peroxide in the presence of strong mineral acids such as sulphuric acid (Trajano & Moura, 2014; Derawi & Salimon, 2013). An oxirane ring comprises of one oxygen atom and two carbon atoms. The process requires very moderate to low temperatures compared to the other chemical modification methods (Madanhire & Mbohwa, 2016). The epoxidation of vegetable oil has been reported to result in an improved bio-lubricants lubricity, increased oxidation stability, better acid value, increased viscosity, higher pour point in the lubricant oil (McNutt & He, 2016; Castro, et al., 2006; Silva, et al., 2015; Salih, et al., 2011).

Epoxidized vegetable oil still faces some challenges due to the poor low-temperature properties, such as increased pour point and decreased viscosity index (McNutt & He, 2016). In order to improve these properties, further chemical modification is required. Oxirane ring-opening, esterification/transesterification and acetylation are the modification methods that may be used to further enhance the epoxidized vegetable oils (Li & Wang, 2015; Hwang & Erhan, 2006). The ring-opening method can be achieved through water hydrolysis or alcoholysis in the presence of an acid catalyst such as sulfuric acid (Derawi & Salimon, 2013).

After the oxirane ring-opening, the epoxidized vegetable oil is reacted with oleic acid to produce an ester through an esterification reaction. Hwang & Erhan (2001) carried out a study to produce bio-lubricants from the epoxidized soybean oil and Guerbet alcohols. The epoxidised soybeans were ring-opened through alcoholysis, followed by the resultant hydroxyl esterification to attach a side branch alkyl group. Their result showed a significant improvement in oxidation stability and low-temperature characteristics. The acetylated 100% transesterified products with Jarcol I-16 and Jarcol I-18T Guerbet alcohol showed the lowest pour points of −42°C. Gast *et al.* (1954) also reported an improvement in the low-temperature

characteristics for several epoxidised vegetable oils that were subjected to ring-opening and esterification

An acetylation reaction may also be used to enhance vegetable oil properties further. The hydroxyl group in the vegetable oil is converted into acetate during the acetylation reaction (McNutt & He, 2016). It is noteworthy to mention that not all epoxidized vegetable oils are subjected to the reaction sequence mentioned above. Some epoxidized vegetable oil can be converted to FAME first and then transesterified with more complex alcohols (Li & Wang, 2015). For instance, Li and Wang (2015) reacted the epoxidized waste cooking oil with methanol followed by branched alcohols (iso-octanol, iso-tridecanol and iso-octadecanol) to produce biolubricants. The results showed a significant improvement in the low-temperature properties and oxidative stability (Li & Wang, 2015). The improved performance was attributed to the addition of branched chains into the epoxidized waste cooking oil and the elimination of the double bond between carbon and carbon.

Bashiri *et al.* (2021) also performed the epoxidation of sunflower waste cooking oil to improve the lubricating properties. The optimum yield of 82.9% was obtained after 4.1 hours of reaction time, 30.1 g of hydrogen peroxide and 53.7 g of acetic acid. The product obtained from the epoxidation reaction was further chemically modified to produce sunflower waste cooking oil triesters. The resultant product possessed physical properties that were in agreement with the ISO VG10 requirements (Bashiri, et al., 2021).

Researchers in the past have focused on using different chemical modification routes to obtain biolubricants with desirable properties. For instance, Rios *et al.* (2020) carried out a study to produce castor oil-based biolubricants using esterification first, followed by epoxidation, then finally, the ring-opening reaction. The ring opening reaction was carried out using two nucleophilic agents, namely 1-butanol and water. The results showed that the less polar biolubricant (ring opened with1-butanol) showed superior pour point temperature and oxidation stability than polar biolubricant(ring opened with water) (Rios, et al., 2020). Similarly, Parente *et al.* (2021) carried out the same study using soybean oil and investigated the feasibility of integrating biolubricant production into the existing biodiesel plant. The study found that the integration of the two processes was feasible and could improve the economic competitiveness of the biodiesel industry (Parente, et al., 2021).

Kamairudin *et al.* (2021) studied the production of the bio-polyol from the ring opening of the epoxidised palm oil derivative(Methyl oleate). The ring-opening reaction was optimised to maximise the hydroxyl value using response surface methodology (RSM) with a combination of central composite rotatable design (CCRD) with three variables at five levels. The optimum hydroxyl value of 306.190 mg KOH/g was obtained during the optimisation. The FTIR and NMR were used to confirm the structure of the products (Kamairudin, et al., 2021). Unfortunately, this study did not measure critical properties such as pour point and oxidation stability. A detailed summary of physical properties and the chemical conditions of the various chemical modification methods have been displayed in Table 2-3.

Recently the attention has been set on improving the product properties and improving the efficiency of the epoxidation of vegetable oil, ring-opening reaction, esterification and acetylation (McNutt & He, 2016). This is done by developing new catalysts, cheaper feedstocks and improving the existing process. Several breakthroughs have been reported in the literature on the use of a different catalyst that accelerated the epoxidation of vegetable oil such as H_2SO_4,sulfated-SnO_2, Catalyst Amberlite IR - 120H, sulfated Ti-SBA-15, Amberlyst-15, IRA-200 and IRA-400 (Hwang & Erhan, 2006; Sammaiah, et al., 2014; Kulkarni, et al., 2013; Salimon, et al., 2011; Sharma, et al., 2015; Somidi, et al., 2014; Sharma & Dalai, 2013).

Several studies are currently being carried out to develop chemical modification methods with the ultimate goal to speed up the large-scale industrial production of bio-lubricants (McNutt & He, 2016). The majority of research on chemical modification generally focuses on lowering the cost of production and improving the yield rate (Kleinaite, et al., 2014). This is necessary as economic benefits motivate industrial partners to switch from the use of mineral lubricants to bio-lubricants. Thorough testing of the vegetable oil in mineral oil applications is still required to increase awareness of the vegetable ‘s advantages (Bongfa, et al., 2015)

Table 2-5 The summary of physical properties and the chemical conditions of the various chemical modification methods

Reactant	Products	Catalyst	Reaction conditions	Viscosity 40°C (cSt)	Viscosity 100°C (cSt)	Viscosity Index (VI)	Pour point	Oxidative thermal stability	Yield (%)	Ref
Jatropha and Trimethylolpropane	Trimethylolpropane triesters	CH_3NaO	150°C, 10mbar, 3h	43.90	8.71	180	-6	-	>80	(Ghazi , et al., 2009)
Castor biodiesel and Trimethylolpropane	Trimethylolpropane triesters	CH_3NaO	120°C, 0.01 bar	11.28	3.100	141	-	-	-	(Silva, et al., 2013)
Jatropha ME and Trimethylolpropane	Trimethylolpropane triesters	CH_3NaO	150°C, 55 min	42.57	9.37	183	-6	325°C Degradation on temp	-	(Resul, et al., 2012)
Palm ME and Trimethylolpropane	Trimethylolpropane triesters	Ca $(OCH_3)_2$	180°C, 50 mbar, 8h	-	-	-	-	-	92.38	(Masood, et al., 2012)saf
Castor biodiesel and Trimethylolpropane	Trimethylolpropane triesters	Dibutyltin dilaurate	170° 0.01 bar	287.2	26.13	119	-27	-	89.7	(Silva, et al., 2013)
Castor biodiesel and Trimethylolpropane	Trimethylolpropane triesters	Amberlyst 15 ionic exchange resin	120°C, 0.01 bar	20.94	4.467	127	-	-	-	(Silva, et al., 2013)
Epoxidation										
Oleic acid, formic acid, and H_2O_2	Epoxidized oleic acid		4°C, 2h	-	-	45.44	0	FP:113.11°C	-	(Salih, et al., 2011)
Epoxidized canola oil and n-butanol	Ring opened product	Amberlyst-15	100°C, 15h	190.5	-	-	-8	Thermal stability: 361°C	-	(Madankar, et al., 2013)
Epoxidized fatty acid waste cooking oil methyl esters, methanol, and isooctanol	Epoxidized branched ester	CaO	90 TO 140°C	15.9	3.4	157	-15	RPVOT: 127.4 min PDSC: 79.2 min	-	(Li & Wang, 2015)
Ring opened epoxidized soybean oil (2) and acetic anhydride	Acetylated, ring-opened product	Pyridine	80°C, 2h, Nitrogen atmosphere	74.3 – 103.4	11.7 – 14.6	136 – 152	(-27) – (-33)	-	-	(Erhan & Hwang , 2006)

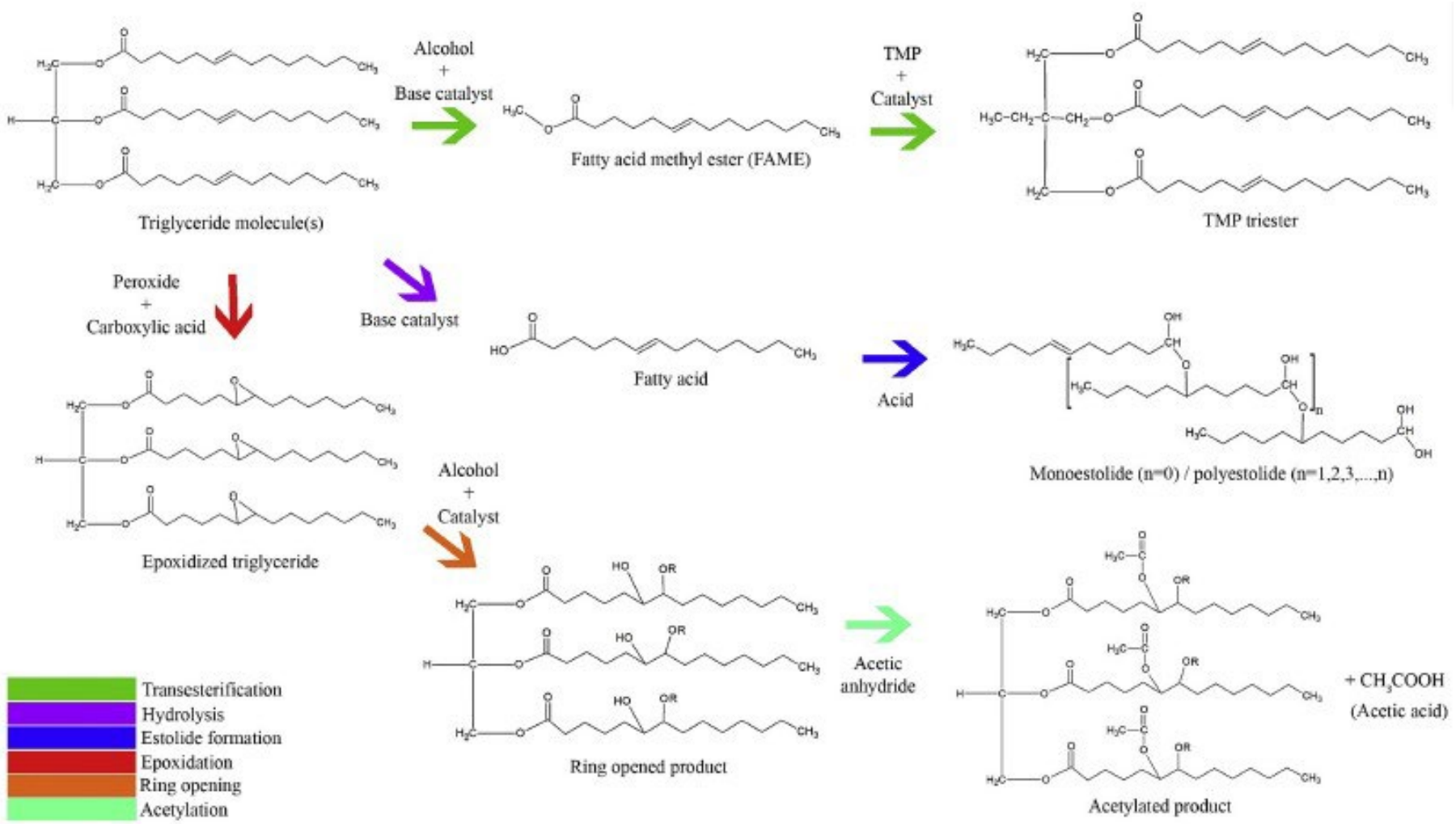

Figure 2-6 Various modified chemical reactions for transesterification, epoxidation, estolide arrangement, ensuing ring opening and acetylation forms alongside the intermediate reactions (Syahir, et al., 2017) .

Table 2-6 The summary bio-lubricants production methods.

Method	Description	Advantage	Disadvantage
Esterification/ transesterification	• Transformation of ester into another ester through an interchange of alkoxy moiety	• Improves oxidative stability and low-temperature characteristics	• Requires high temperature for the reaction • High oleic acid content required
Estolide formation	• The oligomerization or expanding of various FA through ester linkage of one FA particle to the alkyl spine of another FA (Borugadda & Dalai, 2018)	• The improvement of oxidative stability and low-temperature characteristics. • The low temperature required for the reaction • Applicable to various vegetable oil	• The capping agent for FA needed for initial reaction are expensive
Selective hydrogenation	• The rection that occurs between hydrogen and other compounds or element. Various unsaturated FAs transforms into single FA (Wagner , et al., 2001)	• The oxidative stability is increased • Reduce the iodine number	• Requires high temperature for the reaction
Epoxidation	• The conversion of the carbon-carbon double bond into oxiranes (peroxides). utilizing an assortment of reagents including air oxidation, hypochlorous corrosive, hydrogen peroxide, and natural peracid (Fettes, 1964)	• The low temperature required for the reaction • Performance Improvement in terms of lubricity and oxidative stability	• Pour point value increases • Viscosity index decreases
Oxirane ring opening, acetylation	• Ring-opening: Introduction of a hydroxyl group from the cleavage of carbon-oxygen bonds. • Acetylation: The acetate production from the hydroxyl group present in the vegetable oil.	• Products with desirable properties	• High manufacturing cost

2.7 Additives for vegetable-based oil

In light of the current developments in human lifestyle and technology, it has become difficult to satisfy lubrication requirements nowadays without using additives. In most parts, additives are chemical substances manufactured (synthetic), which are utilized in lubrication oil to change a wide range of properties by upgrading what is required and smothering what is undesirable (Madanhire & Mbohwa, 2016). Numerous additives are multifunctional items that may show synergistic or antagonistic when combined. As a general guideline, additives do not add. This makes adjusting and optimization of additives relatively challenging to perform. Generally, additives make up about 10%, while base oil makes up the balance of lubricating oil content (Berlamen & Sunil, 2018; Ajithkumar, 2009).

Different additives may be used based on the performance and operating condition requirements. The most common additives include extreme pressure (EP), oxidation inhibitors, anti-wear additives, improver, corrosion inhibitors/Rust inhibitor, Friction modifiers, anti-foaming agents, dispersants and viscosity index improvers (Madanhire & Mbohwa, 2016; Woma, et al., 2019; Rizvi, 1999; Stachowiak & Batchelor, 1993).

Bio-lubricants' thermo-physical and lubricating propertie can be enhanced by including nanoparticle additives into the base oil (Cortes & Ortega, 2019; Sadiq, et al., 2018). Nanoparticles are extremely small particles made up of different chemical elements such as Silicon, carbon, titanium and oxygen (Trajano & Moura, 2014; Sadiq, et al., 2018). Due to the particle size being extremely small has allowed nanoparticles to act as the rolling bearing in the interface of the contacting surfaces (Lee, et al., 2009). According to Xue et al.(1997) and Dong *et al.* (1999), nanoparticles at a low concentration such as 1 wt.% is capable of improving adhesion characteristics and tribological properties of the bio-based lubricant properties. Tribological properties are improved through minimising friction which subsequently reduces wear.

Researchers have been studying the effect of nanoparticles on the rheological and tribological properties of vegetable-based bio-lubricant (Berlamen & Sunil, 2018; Kedzierski, 2012). Some of the conditions currently being investigated include particle sizes, the concentration of nanoparticles, and the chemical compatibility of the nanoparticles to the base oil (Cortes & Ortega, 2019; Trajano & Moura, 2014). Although nanoparticles are expected to enhance

lubrication properties in some cases, they may have a detrimental effect on the base lubricant (Chiñas-Castillo & Spikes, 2000).

Some reports from literature reveal that kinetic viscosity and density increase as the concentration of the nanoparticles increase but decrease as the temperature increases (Berlamen & Sunil, 2018; Maheswaran & Sunil, 2018; Redhwan, et al., 2017; Sadiq, et al., 2018). However, the experimental study carried out by Cortes and Ortega (2019); Trajano and Moura (2014) on oxide nanoparticles found the opposite effect. For instance, Cortes and Ortega (2019) experiment's results showed that the increase in the concentration of CuO decreased the viscosity of the nano-Lubricants, while other studies done by Berlamen and Sunil (2018) showed otherwise. Trajano and Moura (2014) also reported that bio-lubricants with ZnO and CuO nanoparticles performed poorly in their tribological effectiveness compared to pure bio-lubricants (without additives).

Moreover, Rende et al. (2010) also used some rare earth nanoparticles as additives to enhance the tribological performance of the lubricant. The analytical results showed that the utilisation of nanoparticles (less than 30 nm) improved anti-wear, load-bearing and friction reduction capabilities. When using nanoparticles as additives, it is essential to pay close attention to the amount and size of the nanoparticle additives added, as this could have a detrimental effect on the tribological properties. Sadiq *et al.* (2018) experimentally studied the effect of Silicon carbide (SiC) nanoparticles on the tribological properties of vegetable oil. The results showed no improvement on the tribological properties of nano-lubricant with SiC weight fraction up to 1.05wt%. The size of the 130 nm nanoparticles used was considered the reason for the deterioration of tribological properties. The revelation from this study agrees with the previous observation made by Padmini et al.(2016) on the deterioration of properties due to the use of larger nanoparticles.

Cortes and Ortega (2019) demonstrated the rolling and polishing effect by using SiC and CuO nanoparticle's inclusion in the coconut oil. Using a Scanning Electron Microscope (SEM) and profilometry for surface analysis has confirmed the polishing effect introduced by nanoparticles (Cortes & Ortega, 2019; Thottackkad, et al., 2012; Lee, et al., 2009).

The main challenge with nanoparticles is identifying the nanoparticle that will be compatible with the base oil. Some nanoparticles used in the nano-lubricant have been reported to produce

sediments and deterioration tribological properties over a long period (Che Sidik & Alawi, 2014).

Recently there has been an interest in using small quantities of vegetable oil as additives to mineral-based oil. The vegetable-based oils are preferred as additives due to their superior "oiliness" property than mineral-based oil (Ajithkumar, 2009). This has led to the massive production of organic and polymer additives on mineral-based oil for better performance in extrema applications. Bahari et al. (2018) carried out a study to determine the effect of blending Soybeans and palm oils in commercial mineral oil SAE 15W40. The results showed the wear improvement of 25% and 27% of Palm oil blend (50%) and soybean oil blend (50%) from their raw oil state, respectively. However, the blends were unsuitable for the engine lubrication oil as they performed below the commercial oil. Shahabuddin, et al.(2013) reported an improvement in the lubricant's performance after blending jatropha oil with the commercial mineral-based oil SAE-40.

2.8 Engine oil

An engine is a mechanical machine used to convert one form of energy into mechanical energy (Colwell, 2019). Engine lubricants are a vital component of the engine as they ensure that an engine runs longer and efficiently. According to Rudnick (2013), the typical life span of an automotive gasoline engine is approximately 3000 to 4000 hours and will use up to 200 litres during the operating time. At the same time, heavy-duty diesel engines have a life span of approximately 15000 hours and consume about 200 litres of lubricating oil during operation (Rudnick, 2013).

Engine oils are required in an engine to reduce friction and wear in surfaces in contact, inhabits corrosion, lower the engine temperature, improve sealing and removal of foreign particles into the engine system (Klamann, et al., 1984). Factors such as thermal stability, high-pressure tolerance and ability to operate at acid exposure must be considered when developing a bio-lubricant oil for engine application (Cecilia, et al., 2020). Researchers are still hard at work in trying to find new production methods and alternative feedstocks to be used to produce bio-lubricants. However, little focus has been given to testing bio-lubricants in an actual automobile engine setup. Singh (2011) and Masjuki *et al.* (2019) have tested castor oil and palm oil, respectively, as the two-stroke engine oil and found the vegetable oil to perform better than the

traditional mineral oil. Cecilia et al. (2020) reported that coconut and palm oil engine tests initially showed promising results. However, their properties deteriorated after prolonged use due to the absence of additives and poor thermo-oxidative stability. Cottonseed Trimethylolpropane (TMP) ester was also tested as an engine biolubricant (Siraskar, et al., 2020). It was found that the Cottonseed based biolubricant displayed similar results to the mineral based lubricant.

2.8.1 Castor oil

Castor oil is a non-edible vegetable oil harvested from drought-resistant castor plant seeds (Woma, et al., 2019). Castor oil is perceived as the potential source for the production of bio-lubricants as it does not impact food security. Castor oil contains about 90% of ricinoleic acid, which is responsible for the high viscosity and makes it suitable for use as engine oil (Silva, et al., 2013). Generally, castor oil is relatively cheaper and has a good shelf life than other vegetable oils (Udoh, et al., 2016). Bongfa, et al. (2015) carried out a study comparing the unrefined castor oil with the 20W-50 high-quality crank oil. The results have shown that castor oil has much better load-bearing and superior friction reduction capabilities than the 20W-50 engine oil. The study also recommended using an anti-wear agent on the castor oil to improve the wear protection, as it performed poorly compared to the commercial oil (20W-50).

2.8.2 Palm oil

Palm oil is an edible vegetable oil harvested from the fruits of the palm trees known as mesocarp (Basiron, 2007). Palm oil has received great attention as a bio-lubricant due to its outstanding lubrication properties such as high viscosity index, high flash point and low volatility (Legarand & D¨urr, 1998). The effect of chemical modification on palm oil's rheological and tribological properties has been reported (Zulkifli, et al., 2013; Inkerd, et al., 2015; Hussan, et al., 2016; Tulashie & Kotoka, 2020).

2.8.3 Coconut oil

Coconut oil is an edible, on-drying oil harvested from the white meat of the coconut tree, known as copra. Coconut oil generally contains a high content of saturated fatty acids (approximately 91%); hence it does not oxidize easily (Berlamen & Sunil, 2018). Lauric acid makes up a considerable proportion of the fatty acid in coconut oil (Cortes & Ortega, 2019). The coconut tree is grown in different parts of the world, including Africa, America, Sri Lanka, Indonesia, Thailand and the Philippines (Karak, 2012; Gunstone, 2011). In India, coconut oil has been

extensively utilised as a two-stroke engine lubricating oil in autorickshaws and bikes countries (Berlamen & Sunil, 2018). The coconut lubricants users have reported on the wide range of advantages offered by the coconut oil, such as improved mileage, less smoke, smoother engine operation and improved pick up (acceleration) (Jayadas, et al., 2007).

2.8.4 Waste Cooking Oil

Waste cooking oil is the type of oil that remains after food processing or cooking. The oil may be collected from food industries such as restaurants and cafes. In most small towns in South Africa, the waste cooking oil generated by households and street fast-food sellers is simply dumped into the environment. This results in serious social, environmental, economic and health challenges to the community. The recycling of waste cooking oil could solve today's environmental, waste management, and economic issues (Degfie, 2019). The waste cooking oil can be used to manufacture cosmetics, soaps, animal food and bio-lubricants (Dabai, et al., 2018). Hassan et al., n.d. reported that about 15 litres of cooking oil are used from households and restaurants per day. Other sources have reported that over 18 million tons of waste cooking oil is produced worldwide from restaurants, eating establishments, and food industries (Li & Wang, 2015). If these oils are not properly disposed of, they can cause sewage blockages, damage and contamination to the groundwater. Subsequently kills the plants and animals due to oxygen suffocation.

Waste cooking oils are less costly, inexhaustible and non-poisonous. This makes waste cooking oil a favourable and promising feedstock for manufacturing biolubricants. (Weimin & Xiaobo, 2015; Jagadeesh, et al., 2018; Gobinda, et al., 2017; Panadare & Rathod, 2015). According to McNutt and He (2016), about 70 to 60% of the biolubricants production cost is due to the high-cost feedstock. Suppose such cost can be eliminated by using the waste cooking oil. In that case, it will result in production processes that are affordable and easy to implement even in disadvantaged communities. Several researchers have reported on the production of bio-lubricants from modified waste cooking oil with promising results (Li & Wang, 2015; Owuna, et al., 2020; Dabai, et al., 2018).

2.9 Rheological properties

2.9.1 Viscosity and viscosity index (VI)

Viscosity is one of the essential properties when considering lubrication oil (Trajano & Moura, 2014). Viscosity can be defined as a quantity expressing resistance of fluid or semi-fluid from flowing (Diaz, et al., 1996; Berlamen & Sunil, 2018). Generally, vegetable oils have a viscosity range of between 30 to 50 mm^2/s (Syahir, et al., 2017). The viscosity is dependent on the pressure, temperature and film formation (Tung & McMillan, 2004). As per ASTM D-445 (1999), viscosity is measured at the temperature of 40°C and 100°C. Most vegetable oils generally possess high viscosity index compared to mineral-based lubricants (Woma, et al., 2019). Due to this advantage, the vegetable oils have a wider comprehensive operating range.

Ideally, for lubrication application, the temperature is required to have a minimal effect on the viscosity (Inkerd, et al., 2015). In order to measure the effect of change in temperature on the viscosity, an arbitrary number known as viscosity index is utilised. A low viscosity index indicates a significant change in kinematic viscosity with temperature. The viscosity index is calculated by using kinematic viscosity at 40°C and 100°C as per ASTM D-2270. Some vegetable oils have a high viscosity index of23, while the viscosity index of 90 to 100 is common for most mineral oils (Tung & McMillan, 2004).

2.9.2 Acid number

The acid number indicates the amount of base (mass of KOH) required to neutralise the lubricant. The acceptable standard range of acid number is between 0.20 to 50.00 mg KOH g^{-1} for engine oil (Danjuma & Dandago, 2009; Muhktar, et al., 2014). A high concentration of acid compound could result in the corrosion of the machine and clogging of oil filters due to the formation of sludge and varnish (Owuna, et al., 2020). Hence, biolubricants with a high acid number are undesirable for engine applications.

2.9.3 Total Base Number (TBN)

The calculation of the alkaline reserve of a lubricant is known as the Total Base Number (TBN) (Tulashie & Kotoka, 2020). This parameter is crucial as it determines the potential of lubricants to neutralise acidic combustion products. As a result, TBN can be used for routine tests to monitor a lubricant oil condition (Yaylayan, 2001). The acceptable TBN range for the engine is between 7-10 mg KOH/g while for a diesel engine is 10-14 mg KOH/g. (Asadauskas, et al., 1997; Petroleum Quality Institute of America, 2010).

2.9.4 Pour point

Pour point is defined as the lowest temperature at which the fluid flows or pours (Soufi, et al., 2018). According to Annisa and Widayat (2018), the vegetable oil with a higher number of double bonds has a lower pour point. This can be attributed to the bent configuration of the fatty acid, which prevents close packing (Syahir, et al., 2017; Jayadas & Nair, 2006). The pour point can be measured by following the ASTM D-97 method (Tulashie & Kotoka, 2020).

2.9.5 Flash point

The Flash point is the lowest temperature at which the fluid's vapours start to ignite, provided there is an ignition source such as air (Syahir, et al., 2017). Another property closely related to the flash point is the fire point. Fire point refers to the temperature at which the combustion of bio-lubricants can be maintained for at least 5 minutes after removing the ignition source (Owuna, et al., 2020). These properties determine the lubricant volatility and fire resistance capabilities. Knowledge of the flash point temperature becomes very crucial during the transportation and storage of the oil. The higher the flash point, the more suitable the ester can be used to produce bio-lubricants. Generally, bio-lubricants have higher flash points than mineral-based oil (Woma, et al., 2019). The high flash point demonstrates the non-volatile nature of the vegetable oil and can be attributed to the fatty acid within the vegetable oil (Lowenstein & Vollertsen, 1915). The flash point temperature of bio-lubricants can be as high as 326°C, while most mineral-based oil is around 200°C (Tung & McMillan, 2004).

2.9.6 Cloud point

Cloud point is the lowest temperature at which the oil begins to solidify and forms crystals (become immiscible) on cooling and consequently displays cloudiness. The operation temperature must be kept above the cloud point temperature to avoid clogging the filter. (Babu & Anand, 2019). This subsequently increases lubricants viscosity (Owuna, et al., 2020). The pour point can be determined by following ASTM D-2500 (Sarin, et al., 2009).

2.10 Tribological properties

2.10.1 Coefficient of friction and wear scar diameter

The tribological properties that are of great interest in lubrication are friction and wear) (Bahari, 2017). These properties may be measured using four-ball tribometers, pin-on-disk tribometers or linear reciprocating friction testers. However, a four-ball tribometer is widely used to

measure wear scar diameter and coefficient of friction. The measurements are done in accordance with ASTM D4172 (Kiu, et al., 2017).

Previously researchers have studied the relationship between different physicochemical properties and tribological parameters (Thapliyal & Thakre, 2017; Abdo, 2008; Trzos, et al., 2013). Various mathematical and statistical strategies have been used to try to establish empirical relationships between physicochemical parameters. Thapliyal & Thakre (2017) developed a correlation for mineral and synthetic oil to calculate the coefficient of friction. The developed correlation was found to be fairly accurate with the deviation percentage of less than 20%.

2.11 Evaluation methods of lubricants

Different standard methods are currently being used to determine different properties of the lubricants. The results of these properties enable the characterisation of a bio-lubricant oil and assessment of the suitability of the lubricants for a specific application (Mang & Dresel, 2007). One popular and widely used method is the American Standard Testing Mechanical (ASTM). Below is the table that indicates the common ASTM test methods and their intended property measurement.

Table 2-7 Summary of the ASTM test method and their associated properties

ASTM test method	Property (Units)
D-97	Pour point (°C)
D-93	Flash point (°C)
D-445	Viscosity (cSt)
D-1298	Density (kg/m^3)
D-2270	Viscosity index
D-2500	Cloud point (°C)
D-2896-11	Total base number
D-4172	The friction coefficient and wear scar diameter

Chapter 3 Methodology

3.1 A two-step base-catalysed transesterification reaction.

3.1.1 Chemicals

The Waste Cooking oil was collected from different restaurants in Durban, South Africa. Castor oil was obtained from Lichro chemical and laboratory supplies (Durban). The Methanol (≥99.8%), Sodium hydroxide(pallets Analytical Reagent), Sodium methoxide (reagent grade,95% powder), Trimethylolpropane (TMP) (≥98%), Magnesium sulfate (≥99.5%) were obtained from Sigma-Aldrich.

3.1.2 Transesterification of raw vegetable oil (WCO/CO)

The method used for the transesterification of vegetable oil was reported by Ghazi et al.(2009). The same method was applied for both vegetable oils.

A mass of 100 g vegetable oil was weighed and added in the three-neck flask. The required amount of methanol was added using the molar ratio of 6:1 methanol to Castor oil/Waste cooking oil. The methanol was then mixed with the vegetable oil in the three-neck flask. A 1 wt.% of sodium hydroxide (NaOH) was added to the flask. The reaction temperature was set between 60-65°C. A magnetic stirrer was used to ensure thorough mixing of the chemicals. After 3 hours, the reaction was stopped. The reaction mixture was placed in the separating funnel. The mixture was left overnight to settle in the funnel. The glycerol rich phase(bottom) was decanted. The top layer (fatty methyl ester) was washed with water to remove impurities and dried over magnesium sulfate. A sample was obtained from the top layer for GCMS and FTIR for product characterization. The yield was then calculated using equation 3-1 below:

$$Yield\% = \frac{Mass\ of\ the\ produced\ fatty\ acid\ methyl\ ester\ (Biodiesel)}{mass\ of\ oil} \ldots (3-1)$$

3.1.3 Experimental Design for the transesterification of WCOME/COME with TMP

The Box-Behnken design of experiments was utilized for transesterification of the fatty acid methyl esters with TMP. The Box-Behnken design is one of the surface response designs which requires three levels of each factor. The Box-Behnken design approach was conducted in Minitab® 21.1 (64-bit). A total of 27 experiments with 3 replicas were suggested by the Box-Behnken design. The four varied conditions included reaction temperature, reaction time, catalyst loading and FAME: TMP. Table 3-1 shows the 27 experiments with the conditions at which they were conducted. Each of the experiments was run twice to increase the reproducibility.

Table 3-1 The reaction conditions for the waste cooking oil transesterification with TMP

Run Order	Temperature (°C)	Catalyst loading (wt%)	Time (h)	Molar ratio WCOME:TMP
1	110	0.5	4	3
2	140	0.8	4	5
3	110	1	4	5
4	140	1	4	4
5	140	0.5	4	4
6	140	0.8	4	3
7	80	0.5	4	4
8	140	0.8	3	4
9	110	0.8	4	4
10	110	0.8	4	4
11	110	0.5	5	4
12	110	1	4	3
13	110	0.8	4	4
14	110	0.8	5	5
15	80	1	4	4
16	110	0.8	3	3
17	110	0.8	3	5
18	110	0.8	5	3
19	80	0.8	4	3
20	80	0.8	5	4
21	110	0.5	4	5
22	110	0.5	3	4
23	110	1	5	4
24	80	0.8	3	4
25	140	0.8	5	4
26	110	1	3	4
27	80	0.8	4	5

Table 3-2 The reaction conditions for the castor oil transesterification with TMP

Run order	Temperature (°C)	Catalyst loading (%wt.)	Time (h)	Molar ratio COME:TMP
1	140	0.8	4	3
2	110	0.8	4	4
3	110	0.8	5	3
4	80	0.8	5	4
5	110	0.5	4	5
6	140	1	4	4
7	110	0.5	3	4
8	110	1	4	3
9	110	1	3	4
10	110	0.8	4	4
11	80	1	4	4
12	110	0.8	5	5
13	80	0.8	3	4
14	140	0.8	5	4
15	80	0.8	4	3
16	140	0.8	4	5
17	80	0.8	4	5
18	110	0.5	5	4
19	110	0.8	3	5
20	110	1	4	5
21	110	0.8	3	3
22	110	1	5	4
23	110	0.5	4	3
24	80	0.5	4	4
25	140	0.8	3	4
26	110	0.8	4	4
27	140	0.5	4	4

3.1.4 Transesterification of biolubricant from fatty acid methyl ester

A 500 mL two-necked round bottom flask was used for the experiment. One neck was connected to a vacuum pump, while the other had a thermometer connected.

The flask was placed on a heating mantle with a temperature and stirrer controller. Firstly the measured mass of TMP was heated to 60°C melting point. The required mass of

WCOME/COME was added based on the WCOME/COME to TMP molar ratio. The required amount of sodium methoxide catalyst was added. The reaction temperature was set to the required temperature. Once the reaction time had been reached, the reaction was stopped, and the mixture was allowed to cool. The product mixture was then filtered under vacuum pressure to remove the soup. The samples were then taken for GCMS and FTIR for product characterization. The GC-MS results were then used to calculate the TMP conversion, product selectivity, and yield using equations 3-2,3-3, and 3-4, respectively. The product mixture was subjected to the rotary evaporator to remove the methyl ester and methanol.

$$\%\, TMP\ Coversion = \frac{initial\ mass\ of\ TMP - final\ mass\ of\ TMP}{Inital\ mass\ of\ TMP} \ldots (3-2)$$

$$product\ selectivity = \frac{mass\ of\ the\ desired\ product}{mass\ of\ all\ the\ products\ produced} \ldots (3-3)$$

$$\%\, yield = \frac{product\ selectivity\ \times\ \%\, TMP\ Coversion}{100} \ldots\ (3-4)$$

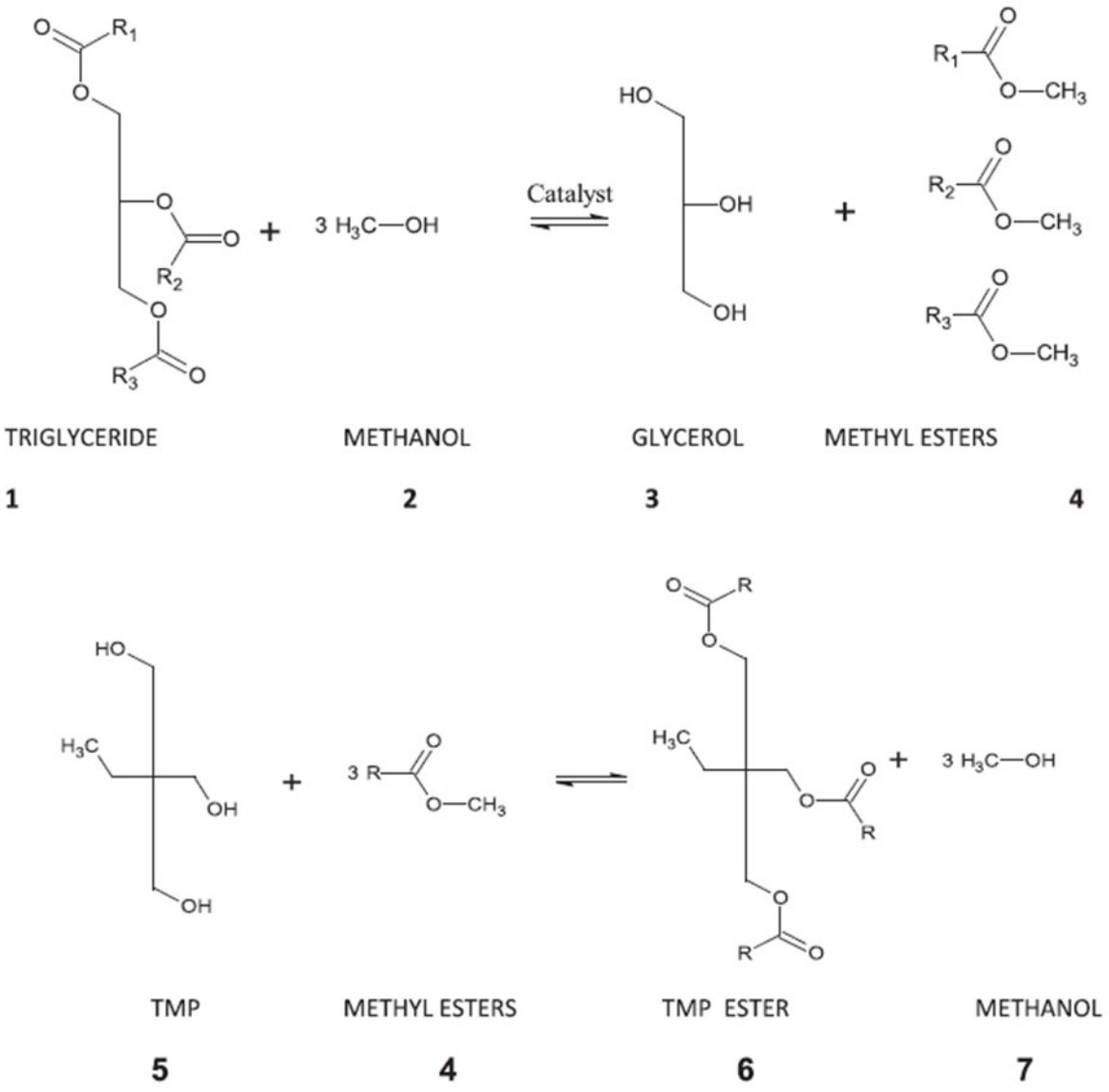

Figure 3-1 The production of the TMP based ester

3.2 The epoxidation of vegetable oil and ring-opening of the epoxidised vegetable oil using 2-Ethylhexanol alcohol

3.2.1 Chemicals

The Waste Cooking oil was collected from different restaurants in Durban, South Africa. Castor oil was obtained from Lichro chemical and laboratory supplies (Durban). Acetic acid (99.8%), Hydrogen peroxide (35 AR), Amberlyst 15(hydrogen form), Diethyl ether (≥98.0%), Sulfuric acid (), Sodium bicarbonate(Analytical Reagent),Acetic anhydride (Acetic anhydride ReagentPlus®, ≥99%),2-Ethyhexanol (99.0%) were obtained from Sigma-Aldrich

3.2.2 The production of epoxidized vegetable oil

The epoxidation reaction was based on the work of Li & Wang (2015). A 500 mL three-necked round bottom flask was used for the experiment. The middle neck was used to fit a reflux condenser connected to the water bath. The reaction contents were introduced through one of the side necks while the other side neck had a thermometer connected. The flask was fitted on a heating mantle with a temperature and stirrer controller. The picture of the setup is shown in Figure 3-2.

The epoxidation reaction was carried out based on the condition described by Li and Wang (2015). A sample of 100 g WCO/CO, 20 g (20 wt% of the feedstock) Amberlite 15 and acetic acid was added into the reaction flask. The temperature of the reaction mixture was increased to 65 ℃. This was followed by the addition of 75 g aqueous hydrogen peroxide. The reaction mixture was maintained at 65°C for 10 hours with rapid stirring. The product was separated through a vacuum pump filter. The reaction product was then vacuum filtered to remove the catalyst. Then, the diethyl ether was added to a separating funnel to extract the product. The mixture was then separated into two polar layers. The bottom layer was decanted off, while the top layer was treated with a solution of sodium bicarbonate (5g of NaHCO3 in 100g water. The sodium bicarbonate was added to neutralize the free acid (PH=7). After adding the sodium bicarbonate, the top layer was washed with water and dried over anhydrous sodium. The removal of the solvent was carried using a rotary evaporator under a vacuum at 90°C for 1 hour. The oxirane oxygen content was then calculated using equation 3-5, and the products were given an e- prefix.

$$The\ oxirane\ oxygen\ content(Epoxide\ value) = \frac{1.60 * N * Volume\ of\ Hbr}{mass\ of\ a\ sample\ (g)} \ldots . (3-5)$$

3.2.3 Experimental Design for the ring-opening reaction of the epoxidized vegetable oil using 2-hexyl decanol

The Box-Behnken design of experiments was utilized for transesterification of the fatty acid methyl esters with TMP. The Box-Behnken design is one of the surface response designs requiring three levels of each factor. The Box-Behnken design approach was conducted in Minitab® 21.1 (64-bit). A total of 27 experiments with 3 replicas were suggested by the Box-Behnken design. The four varied conditions included reaction temperature, reaction time, catalyst loading and 2-hexyldecanol alcohol to epoxidized vegetable oil. Table 3-3 shows the 27 experiments with the conditions at which they were conducted. Each of the experiments was run twice to increase the reproducibility.

Table 3-3 The reaction conditions for the ring-opening reaction of the epoxidized waste cooking oil/castor oil using 2-hexyl decanol alcohol

Run Order	Reaction temperature (°C)	Reaction time (h)	Catalyst loading (wt%)	Molar ratio 2-hexyl decanol: WCO
1	120	11.5	2	1
2	140	11.5	1.25	10
3	120	3	2	5.5
4	100	11,5	1,25	10
5	120	11,5	1,25	5,5
6	120	11,5	0,5	10
7	120	20	0,5	5,5
8	140	11,5	0,5	5,5
9	120	3	1,25	10
10	140	11,5	2	5,5
11	140	3	1,25	5,5
12	140	11,5	1,25	1
13	100	11.5	1.25	1
14	120	11.5	1.25	5.5
15	100	11.5	0.5	5.5
16	120	20	1.25	10
17	120	20	2	5.5
18	100	11.5	2	5.5
19	140	11.5	0.5	1
20	120	20	1.25	1
21	140	20	1.25	5.5

22	100	20	1.25	5.5
23	100	3	1.25	5.5
24	120	11.5	2	10
25	120	3	0.5	5.5
26	120	3	1.25	1
27	120	11.5	1.25	5.5

3.2.4 Ring-opening of the epoxidized ring-opening reaction of the epoxidized vegetable oil using 2-hexyl decanol

The same experimental set-up used for the epoxidation reaction was used for the ring-opening reaction. The resultant epoxidized waste cooking oil /castor oil and the calculated (based on the molar ratio) mass of 2-Ethylhexanol was added into the 500ml three-necked flask. The mixture was preheated to the desired temperature. The required amount of the Amberlyst 15 catalyst was added to the reaction mixture. The reaction was thoroughly stirred for a specified reaction time (3-20 hours) and temperature(100-140°C). The oxirane content was monitored throughout the reaction by withdrawing the sample hourly. After 15 hours, the reaction temperature was cooled down to 25°C. The mixture was then filtered to remove the catalyst. The final product was sampled for FT-IR analysis and hydroxyl value determination. Equation 6 below was used to determine the hydroxyl value (HV).

$$HV\left(\frac{mgKOH}{g}\right) = \frac{[(blank\ volume(ml) - sample\ volume(ml)\ ]) * Normality * 56.1}{sample\ mass(g)} + acid\ number \ldots\ldots (3-6)$$

Figure 3-2 The reaction set up for epoxidation and ring opening reaction

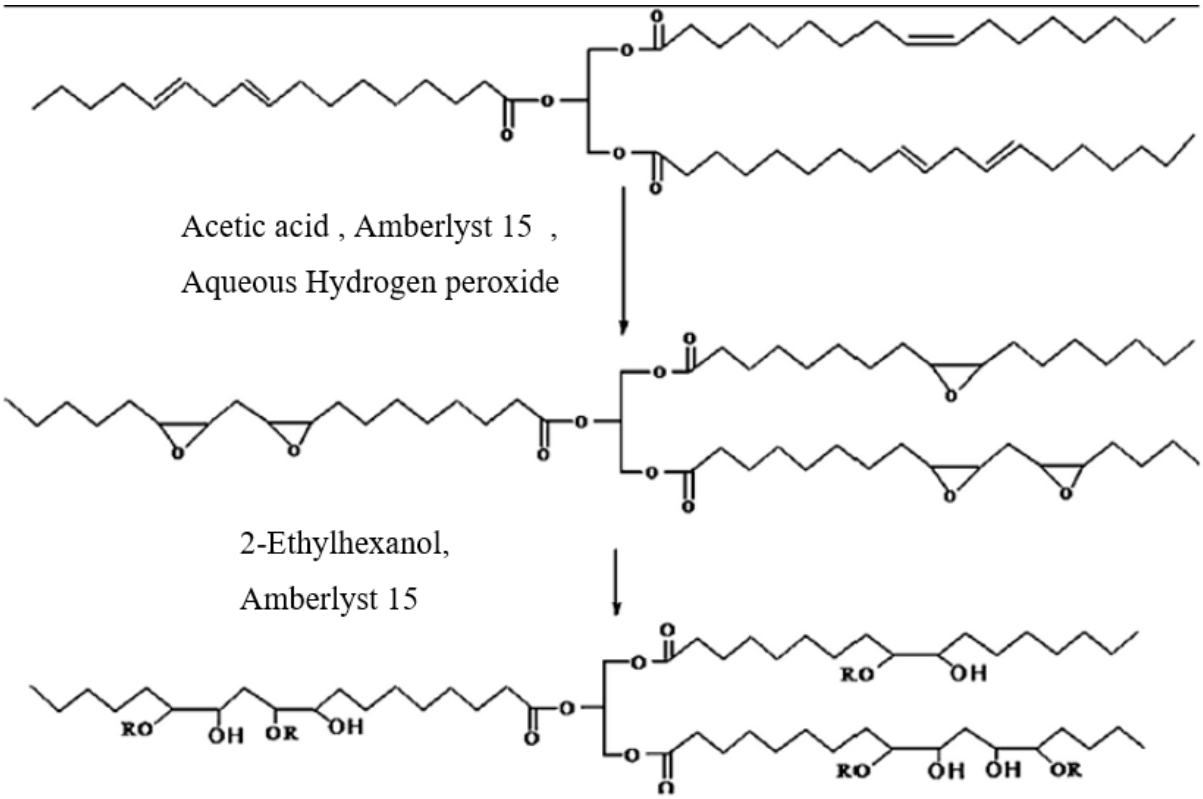

Figure 3-3 Two step synthesis of biolubricant from vegetable oil

3.3 Addition of nanoparticles on the vegetable oil

The Silicon dioxide (SiO_2) and copper oxide (CuO) nanoparticles of size 20–30 nm were obtained from Sigma-Aldrich.

The required nanoparticle was weighed and added to the synthesised biolubricant at an elevated temperature. The mixture was then heated to at least 80°C followed by stirring for 200 minutes to ensure a steady suspension of nanoparticles in the oil. This was followed by ultra-sonification for 5 minutes with a 120-Watt sonic dismembrator. The frequency was set at 20 kHz to ensure uniform dispersion and good suspension stability. Once the nano-biolubricant had been cooled, various tests were conducted.

Chapter 4 Results and discussion: Waste Cooking Oil

4.1 The collection and pre-treatment of the Waste Cooking Oil

Waste Cooking Oil (WCO) was collected from different restaurants around Durban, South Africa. The oil was first filtered to remove any solid particles and then placed in a separating funnel for water washing. The WCO was heated to 110°C for 60 minutes to remove moisture content. Figure 4-1 presents pictures of the pre-treatment of the Waste Cooking Oil.

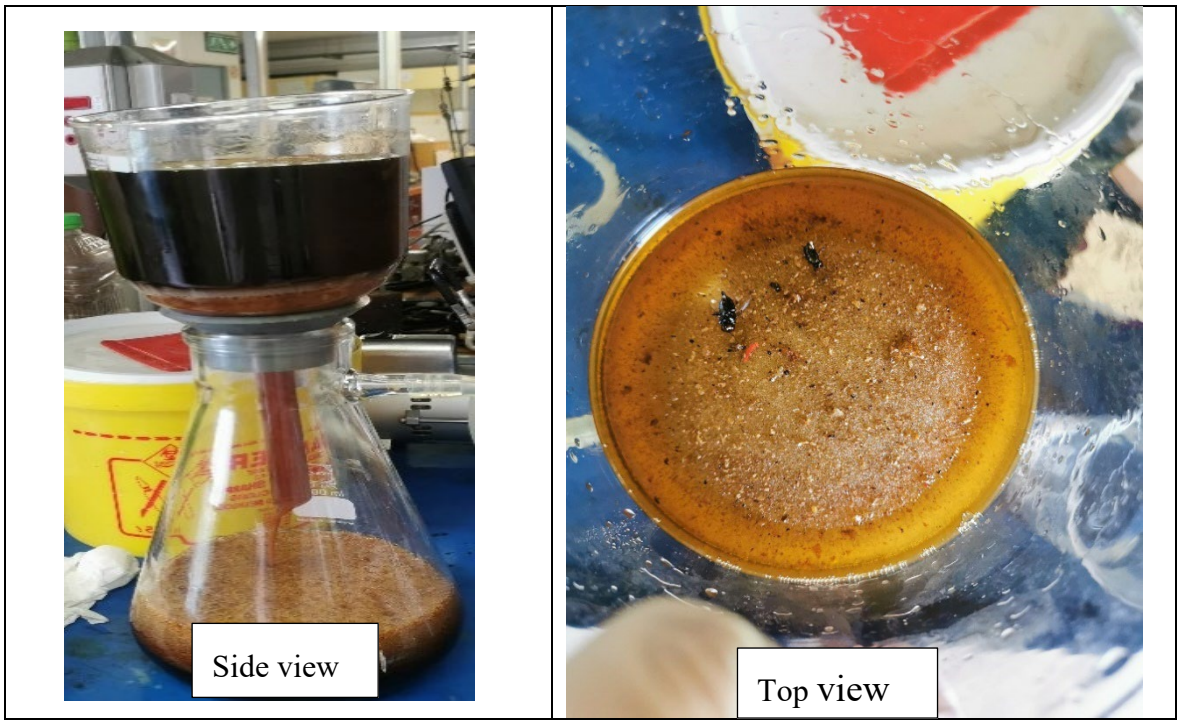

Figure 4-1 The Images of the pre-treatment of the Waste Cooking Oil

4.2 The transesterification of the waste cooking oil

The Waste Cooking Oil Methyl Esters (FAME) were produced under the specified literature conditions (Ghazi , et al., 2009). A yield of 70% was achieved. The yield obtained was relatively low compared to some of the values reported in the literature (McNutt & He, 2016). This was not much of a concern to the current study as the primary aim of the first transesterification was to produce WCOME for the second transesterification. The WCOME obtained was then prepared for transesterification with TMP.

4.3 The optimisation of the waste cooking oil methyl ester transesterification reaction condition

In order to produce a TMP based ester with superior properties, the yield of triesters must be significantly high compared to the monoester and diesters (Yunus et al., 2002; Annisa & Widayat, 2018). Therefore, it is required that the production of triester is optimised to ensure that the produced biolubricant has desirable properties. The optimisation of the triesters was carried out using the Box-Behnken design of experiments. The yield of the triester was calculated using the peak areas obtained from the GC-MS analysis. The chromatograph such as the ones shown in Figure 4-2 was used to calculate the yield through equations 3-2 to 3-4.

The Box-Behnken design was applied using Minitab® 21.1 (64-bit).). A total of 27 experiments with 3 replicas were suggested by the Box-Behnken design. The Box-Behnken design of experiments provides a high order response with fewer experiments. The parameters of interest in the study included the dependent variable, yield of triesters and independent variables; reaction temperature, reaction time, catalyst loading and WCOME: TMP molar ratio.

The reaction temperature, reaction time, catalyst loading and WCOME: TMP molar ratio was varied from 80 to 140°C, 3 to 5 hours, 0.5 to 1wt% and 3:1 to 5:1, respectively. These experimental conditions were selected based on optimum conditions reported in the literature (Sripada, et al., 2013; Musa, et al., 2015; McNutt & He, 2016; Woma, et al., 2019). The conditions set for the experiments with the measured and predicted triesters yield are shown in Table 4-1. Each of the experiments was run twice to increase the reproducibility.

The Minitab software was used to regress the experimental data to obtain the model that will best describe the results. TMP triester yield was set as the response variable while the reaction temperature, reaction time, catalyst loading and WCOME: TMP molar ratio was set as the independent variables.

A Linear, linear+square, Linear+interaction and quadratic regression models were accessed for the regression of the experimental data. The coefficient of determination (R^2) for Linear, Linear+square, Linear+interaction and quadratic regression models were 0.7789,0.8323,0.8791 and 0.9325, respectively. Among the four regression models examined for the experimental data, the quadratic model had the highest R^2 value. The R^2 value of 0.9325 means that the independent variable could best describe 93% of the yield response variation.

The model could not describe only 7% of the variation. Therefore, the quadratic model was selected as the best model to predict the behaviour of the experimental data.

Table 4-1 The conditions of the experiments with the measured and predicted waste cooking oil based TMP triesters yield

Run order	Temperature	Catalyst	Time(h)	WCOME: TMP	Actual yield	Predicted Yield
1	110	0,5	4	3	68,30	68,10
2	140	0,8	4	5	68,21	74,37
3	110	1	4	5	58,13	58,72
4	140	1	4	4	58,58	59,12
5	140	0,5	4	4	73,24	73,80
6	140	0,8	4	3	63,50	61,18
7	80	0,5	4	4	48,47	46,18
8	140	0,8	3	4	72,25	69,78
9	110	0,8	4	4	58,13	59,24
10	110	0,8	4	4	61,20	59,24
11	110	0,5	5	4	63,42	66,64
12	110	1	4	3	41,10	46,59
13	110	0,8	4	4	58,23	59,24
14	110	0,8	5	5	73,12	69,67
15	80	1	4	4	38,16	35,19
16	110	0,8	3	3	55,10	56,99
17	110	0,8	3	5	58,20	56,17
18	110	0,8	5	3	58,00	58,48
19	80	0,8	4	3	49,32	43,78
20	80	0,8	5	4	48,16	51,87
21	110	0,5	4	5	66,47	62,89
22	110	0,5	3	4	62,36	63,86
23	110	1	5	4	58,44	57,72
24	80	0,8	3	4	28,17	32,38
25	140	0,8	5	4	68,14	65,28
26	110	1	3	4	50,41	47,09
27	80	0,8	4	5	38,31	40,97

$$Yield = 31 + 1{,}950\,A - 64{,}9\,B + 4{,}4\,C - 42{,}8\,D - 0{,}00529\,A*A - 33{,}0\,B*B + 0{,}40\,C*C + 0{,}65\,D*D - 0{,}103\,A*B - 0{,}2008\,A*C + 0{,}1310\,A*D + 7{,}80\,B*C + 17{,}17\,B*D + 3{,}01\,C*D$$

A→Reaction temperature (°C)

B→ Catalyst loading

C→Reaction time

D→WCOME: TMP

According to Kamairudin et al. (2021), the positive sign in the regressed model represents an antagonistic effect while the negative showed a synergistic effect.

An analysis of the variance (ANOVA) for the selected model was carried out to determine the model's fitness further. The primary function of the ANOVA analysis is to check the significance of the developed model. The ANOVA results are displayed in Table 4-2 below.

Table 4-2 Analysis of variance for the transesterification reaction optimization

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	3173,43	226,673	11,60	0,000
Linear	4	400,13	100,032	5,12	0,012
A	1	166,41	166,410	8,51	0,013
B	1	14,29	14,292	0,73	0,409
C	1	0,87	0,871	0,04	0,836
D	1	83,82	83,815	4,29	0,061
Square	4	173,77	43,443	2,22	0,128
A*A	1	120,90	120,904	6,19	0,029
B*B	1	20,56	20,557	1,05	0,325
C*C	1	0,84	0,837	0,04	0,839
D*D	1	2,22	2,219	0,11	0,742
2-Way Interaction	6	336,81	56,136	2,87	0,057
A*B	1	2,44	2,441	0,12	0,730
A*C	1	145,20	145,202	7,43	0,018
A*D	1	61,78	61,780	3,16	0,101
B*C	1	15,60	15,603	0,80	0,389
B*D	1	75,67	75,669	3,87	0,073
C*D	1	36,12	36,120	1,85	0,199
Error	12	234,56	19,546		

Lack-of-Fit	10	228,47	22,847	7,51	0,123
Pure Error	2	6,09	3,043		
Total	26	3407,98			

As can see in Table 4-2, the p-value of the developed model was determined to be extremely small (P<00000.1). According to Martín et al. (2020) a p-value, less than 0.05 indicate statistical significance; therefore, the developed model is statistically significant. This implies that the developed model is suitable for determining the relationship between the significant and response variables. The lack of fit was determined to be insignificance (F-value =7.45), implying that the quadratic model can represent the entire experimental data. The large F-value for the lack of fit can be attributed to the experimental noise (Azman, et al., 2020).

The independent variables' significance was also determined based on the p-value and the F-value. A small P-value and a large F value imply that the variable is significant. As a result, it can broadly impact the response variable when varied (Roselan, et al., 2020). From Table 4-5, B(catalyst loading), C (reaction time) and A^2, D^2 and C^2 are insignificant since the p-value is far greater than 0.05. Whereas A (reaction temperature), D (WCOME: TMP molar ratio) and B^2 are significant. The developed model did not show any significance for any of the two-way interaction's variables, implying there is no mutual interaction between any of the variables. Although these insignificance terms contribute to a small error, they were not eliminated from the final model.

The developed quadratic model was then used to determine the optimum conditions for the transesterification reaction. The results for the optimum conditions have been displayed in Table 4-3

Table 4-3 The optimum condition for the waste cooking oil methyl ester transesterification reaction

Reaction temperature (°C)	Reaction time (h)	Catalyst loading (wt%)	Molar ratio WCOME: TMP	Predicted Yield (%)	Actual yield (%)
140	3	0.5	3	81.23	80.80

The predicted and actual yields were determined to be 81.23 and 80.80 %, respectively. The error was calculated to be 0.53%. This proves that the developed correlation can accurately predict the TMP triesters yield. Sripada et al.(2013) reported the optimum condition at 110°C,

0.5% sodium method catalyst after 5 hours for the transesterification of methyl oleate and canola biodiesel.

4.4 Characterization of the waste cooking oil based TMP esters biolubricant

FITR and GCMS analysis were conducted to characterise the biolubricants produced from the two chemical modification methods. The GCMS-QP2010 SE Gas Chromatograph Mass spectrometer Shimadzu was used to determine the composition of the biolubricant. Both the intermediate and final products were analysed during the analysis. The GC chromatogram for the products has been displayed in Figure 4-2. The GC analysis was performed using the capillary column SH-Rxi-5MS, 30 m × 0.25 mm, thickness. 0.25 μm. The oven temperature was initially set at 90ºC, held for 0 min, then increased at the rate of 10ºC/min to 230ºC and held for another 1 min. The temperature is then increased to 300°C at the rate of 8 ºC/min and held for 5 minutes. The injector and detector temperatures were at 200 and 260ºC, respectively. Helium was used as the carrier gas at 55.5 mL/min flow rate. The split ratio was set at 50.0, and 1.0 μL of the sample was injected into the GC system. The GCMS solution to be analysed was prepared using the Dichloromethane as a solvent.

Figure 4-2 contains the chromatographs for the fatty acid methyl and TMP-based esters produced through Method A for WCO. As anticipated, the WCO product displayed multiple picks at various retention times. This can be attributed to the different cooking oil samples collected from various suppliers. Pick 1-10 shown in Figure 4-2 shows the waste cooling methyl esters (WCOME) produced from the transesterification of WCO. The appearance of these picks confirms the formation of the intermediate product WCO biodiesel. Various sources have reported the formation of fatty acid methyl ester picks after the transesterification of the different vegetable oils (Sripada, et al., 2013; Kamarudin, et al., 2020).

The main constituent of WCOME is the saturate content: n-Hexadecanoic acid methyl ester (22.78%), Methyl stearate (10.96%) and unsaturated content:9-Octadecenoic acid methyl ester (2.07%), 9-Octadecenoic acid 12-hydroxy-methyl ester (59.92%). According to Heikal et al. (2017), unsaturated content in biolubricants contributes to poor oxidative-thermal stability.

Figure 4-2 (b) shows the chromatogram of the WCO-TMP based esters. The WCO-TMP based monoester, diesters and triesters are denoted by peak 7 to 14 in the chromatogram. The

unreacted methyl esters are indicated by peak 2 to 5, while peak 1 indicates the unreacted TMP. The conversion of TMP was calculated to be 96.7 %. The large presence of unreacted methyl esters in the product can be attributed to the excess molar ratio of WCOME to TMP that was added. A rotary evaporator was used to remove unreacted methyl ester from the product.

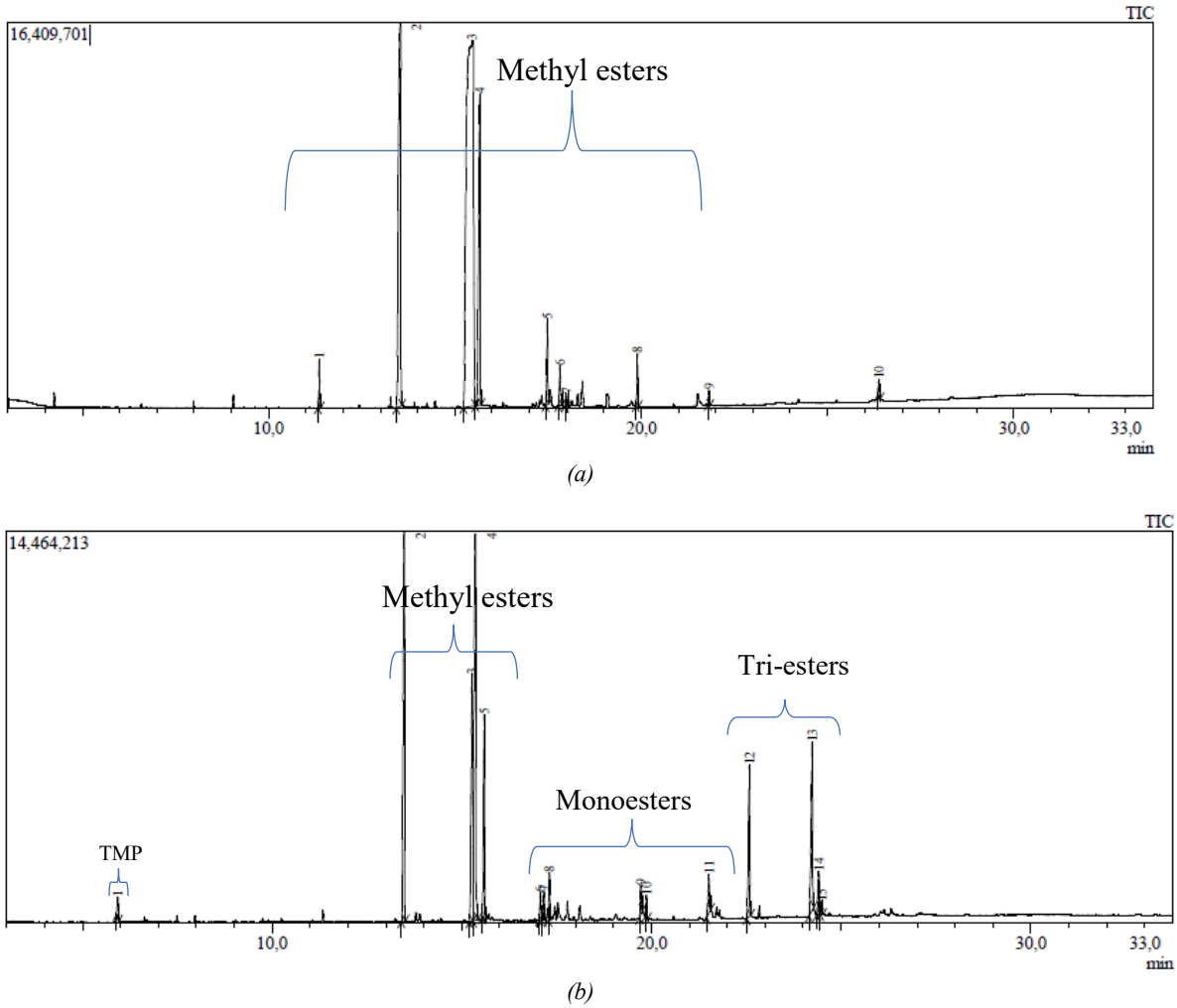

Figure 4-2 (a) Waste Cooking Oil methyl ester and (b) TMP-based ester Chromatograph produced through Method A.

The product's characterisation was also carried out using a QATR™-S single-reflection ATR accessory with a diamond Crystal for Fourier transform infrared (FTIR) analysis. The analysis was done to identify the functional groups present within the product. The FTIR spectrum for the WCO based TMP esters has been displayed in Figure 4-3 together with the TMP and pure WCO for reference. The pick at 1170 cm^{-1} denotes the presence of the C-O stretch from the ester functional group. A distinct pick can also be observed at 1460 $cm^{1,}$ indicating the presence of the alkane functional group. The C=O stretching vibration was also observed at 1720 cm^{1}, further supporting the presence of the ester functional group. The peak at 2860 and 2820 cm^{-1} indicates the presence of C-H and CH_2 stretching vibrations in the carboxylic acid. The

appearance of the peak at 3400 cm^{-1} indicated the presence of water and phenols. The TMP spectra has a distinctive peak at 3307 cm [1,] indicating the presence of a hydroxide group in the compound. However, the peak appears to diminish in the WCO based TMP (biolubricant) spectra. This implies that the transesterification of the WCOME was considerably close to completion.

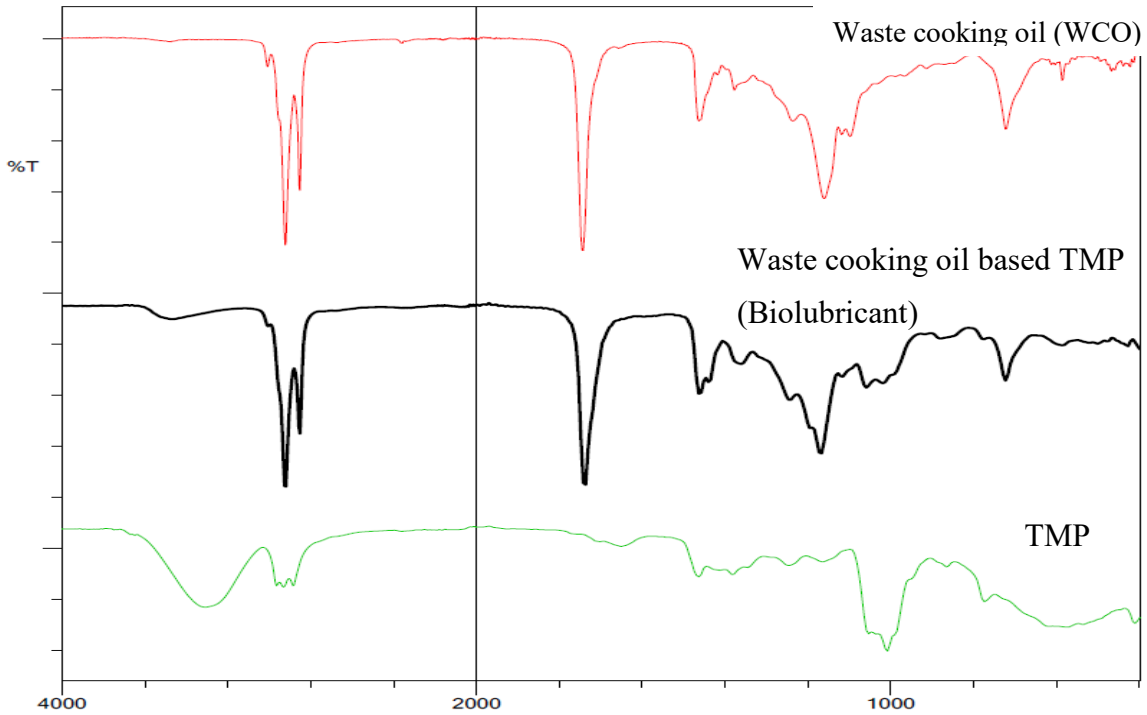

Figure 4-3 The FTIR spectra of Waste Cooking Oil, Waste cooking oil based TMP esters and TMP

4.5 The epoxidation of waste cooking oil

The optimum conditions applied for the epoxidation reaction were obtained from the work of Li &Wang (2015). The oxirane content for the current study was calculated to be 5.2%, translating to 81% conversion. AOCS Cd 9-57 method was used to determine the oxirane ring content. Malankara et al.(2012) reported an oxirane content of 5.6% for the epoxidized canola oil. Similarly, Li and Wang (2015) obtained a value of 5.4% for the oxirane content.

4.6 The optimisation of the ring-opening reaction conditions for epoxidized waste cooking oil

The hydroxyl value was used to measure the extent or performance of the epoxide ring-opening reaction. The hydroxyl value is defined as the measure of free hydroxyl content in a chemical substance (Kamairudin, et al., 2021). The procedure outlined in DIN EN ISO 4692-2 with the equation 3-6 were used to measure the hydroxyl value at the end of the reaction. Since the opening of the epoxide ring give rise to the (OH) hydroxyl function group, as can be seen in Figure 3-3. The Hydroxy value is expected to increase as the epoxidized vegetable oil reacts with the 2-hexyldecanol.

The Box-Behnken design of experiments was used to find the optimum conditions for the ring-opening reaction of epoxidized waste cooking oil. The Box-Behnken design was applied using Minitab® 21.1 (64-bit).). A total of 27 experiments with 3 replicas were suggested by the Box-Behnken design. The Box-Behnken design of experiments provides a high order response with fewer experiments. The parameters of interest in the study included the dependent variable, hydroxyl value and independent variables viz, reaction temperature, reaction time, catalyst loading and 2-hexyldecanol to eWCO molar ratio.

The reaction temperature, reaction time, catalyst loading and 2-hexyldecanol to eWCO molar ratio were varied from 100 to 140°C, 3 to 20 hours, 0.5 to 2wt% and 1:1 to 10:1 were considered based on literature reported optimum conditions for the epoxide ring-opening reaction (Kamairudin, et al., 2021; Madankar, et al., 2012; Wai, et al., 2019; McNutt & He, 2016). Table 4-4 shows the measured and predicted hydroxyl value at different experiment conditions. Each of the experiment was run twice to increase reproducibility.

The Minitab software was used to regress the experimental data. This was done to obtain the model that will best describe the results. The hydroxyl value was selected as the response variable, while the reaction temperature, reaction time, catalyst loading and 2-hexyl decanol to eWCO ratio were set as the independent variables. Linear, linear+square, Linear+interaction and quadratic regression models were accessed for the regression of the experimental data. The coefficient of determination (R^2) for Linear, Linear+square, Linear+interaction and quadratic regression models was determined to be 0.7178, 0.7761, 0.7789,0.8592, respectively. Among the four regression models examined for the experimental data, the quadratic model had the

highest R^2 value. The R^2 value of 0.8592 implies that the independent variable could best describe 86% of the hydroxyl value (HV) response variation. The model could not describe only 14% of the variation. Therefore, the quadratic model was selected as the best model to predict the behaviour of the experimental data.

Table 4-4 The conditions of the experiment with the measured and predicted ring-opened epoxidized waste cooking oil hydroxyl value

Run Order	Reaction temperature (°C)	Reaction time (h)	Catalyst loading (%wt.)	Molar ratio 2-hexyldecanol: eWCO	Actual Hydroxyl value	Predicted Hydroxyl value
1	120	11,5	2	1	160,20	155,52
2	140	11,5	1,25	10	132,30	131,70
3	120	3	2	5,5	130,24	140,42
4	100	11,5	1,25	10	130,43	135,16
5	120	11,5	1,25	5,5	150,46	155,02
6	120	11,5	0,5	10	120.00	122,41
7	120	20	0,5	5,5	164,23	154,08
8	140	11,5	0,5	5,5	124.0	132,89
9	120	3	1,25	10	135,23	126,98
10	140	11,5	2	5,5	155,30	150,54
11	140	3	1,25	5,5	120,13	121,96
12	140	11,5	1,25	1	154,07	151,96
13	100	11,5	1,25	1	152.00	151,78
14	120	11,5	1,25	5,5	166,31	155,02
15	100	11,5	0,5	5,5	132,24	137,51
16	120	20	1,25	10	150,16	150,71
17	120	20	2	5,5	167,12	170,14
18	100	11,5	2	5,5	154,14	149,20
19	140	11,5	0,5	1	153.00	149,56
20	120	20	1,25	1	164,12	173,75
21	140	20	1,25	5,5	160,14	160,33
22	100	20	1,25	5,5	155,16	151,92
23	100	3	1,25	5,5	135,24	133,64
24	120	11,5	2	10	155,24	156,41
25	120	3	0,5	5,5	130,13	127,15
26	120	3	1,25	1	140.00	140,82
27	120	11,5	1,25	5,5	150.00	155,07

$$Hydroxyl\ value = -147 + 5{,}09\,A - 0{,}49\,B - 4{,}3\,C - 2{,}15\,D - 0{,}02304\,A*A - 0{,}0522\,B*B - 5{,}69\,C*C - 0{,}152\,D*D + 0{,}0294\,A*B + 0{,}093\,A*C - 0{,}0095\,A*D + 0{,}118\,B*C - 0{,}059\,B*D + 2{,}86\,C*\mathrm{D}$$

A→Reaction temperature (°C)

B→Reaction time (hr)

C→Catalyst loading

D→2-hexyl decanol to eWCO

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An analysis of the variance (ANOVA) for the selected model was carried out to further determine the model's fitness. The primary function of the ANOVA analysis is to check the significance of the quadratic model. The ANOVA results have been displayed in Table 5-5 below.

Table 4-5 Analysis of variance for epoxy ring-opening reaction optimization

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	4864,31	347,451	5,25	0,003
Linear	4	433,84	108,460	1,64	0,228
A	1	354,78	354,777	5,36	0,039
B	1	1,48	1,482	0,02	0,884
C	1	0,80	0,797	0,01	0,914
D	1	7,49	7,486	0,11	0,742
Square	4	457,00	114,251	1,73	0,209
A*A	1	449,77	449,769	6,80	0,023
B*B	1	74,22	74,221	1,12	0,310
C*C	1	56,07	56,070	0,85	0,375
D*D	1	51,77	51,773	0,78	0,394
2-Way Interaction	6	473,04	78,839	1,19	0,373
A*B	1	100,00	100,000	1,51	0,242
A*C	1	8,51	8,511	0,13	0,726
A*D	1	3,18	3,185	0,05	0,830
B*C	1	2,25	2,250	0,03	0,857
B*D	1	20,25	20,250	0,31	0,590

C*D	1	321,65	321,651	4,86	0,048
Error	12	793,76	66,147		
Lack-of-Fit	10	623,09	62,309	0,73	0,702
Pure Error	2	170,67	85,333		
Total	26	5658,07			

As can see in Table 4-5, the p-value of the developed model was determined to be extremely small (P<00000.1). According to Martín et al. (2020) a p-value, less than 0.05 indicate statistical significance; therefore, the developed model is statistically significant. This implies that the developed model is suitable for determining the relationship between the significant and response variables. The lack of fit was determined to be insignificance (F-value =0.73), implying that the quadratic model can represent the entire experimental data. The large F-value for the lack of fit can be attributed to the experimental noise (Azman, et al., 2020).

The significance of the independent variables was also determined based on the P-value and the F-value. A small P-value and a large F value imply that the variable is significant. As a result, it can broadly impact the response variable when varied (Roselan, et al., 2020). From Table 4-5, B(Reaction time), C (Reaction time0 and D (2-hexyl decanol to eWCO) are insignificant since the p-value is far greater than 0.05. Whereas C (catalyst loading), A^2 and CD are significant. The developed model did not show any significance for any of the two-way interaction's variables, implying no interaction between any of the variables. Although these insignificance terms contribute to the error, they were not eliminated for this study.

The developed quadratic model was then used to determine the optimum conditions for the epoxide ring-opening reaction. The results for the optimum conditions have been displayed in Table 4-6

Table 4-6 The optimum conditions for the production of ring-opened epoxidized waste cooking oil

Reaction temperature (°C)	Reaction time (h)	Catalyst loading (wt.%)	Molar ratio 2-hexyl decanol: eWCO	Predicted Hydroxyl value (mg KOH/g)	Experimental Hydroxyl value (mg KOH/g)
120	20	1.06	1	174.45	168.50

The experimental hydroxyl value was 168.50 mg KOH/g at optimum condition, while the predicted was 174.45(mg KOH/g). This yielded an error of 3.76%. Since the error is less than 5%, this proves that the developed correlation fairly predicts the actual hydroxyl value.

4.7 The Ring-opened epoxidized waste cooking product confirmation

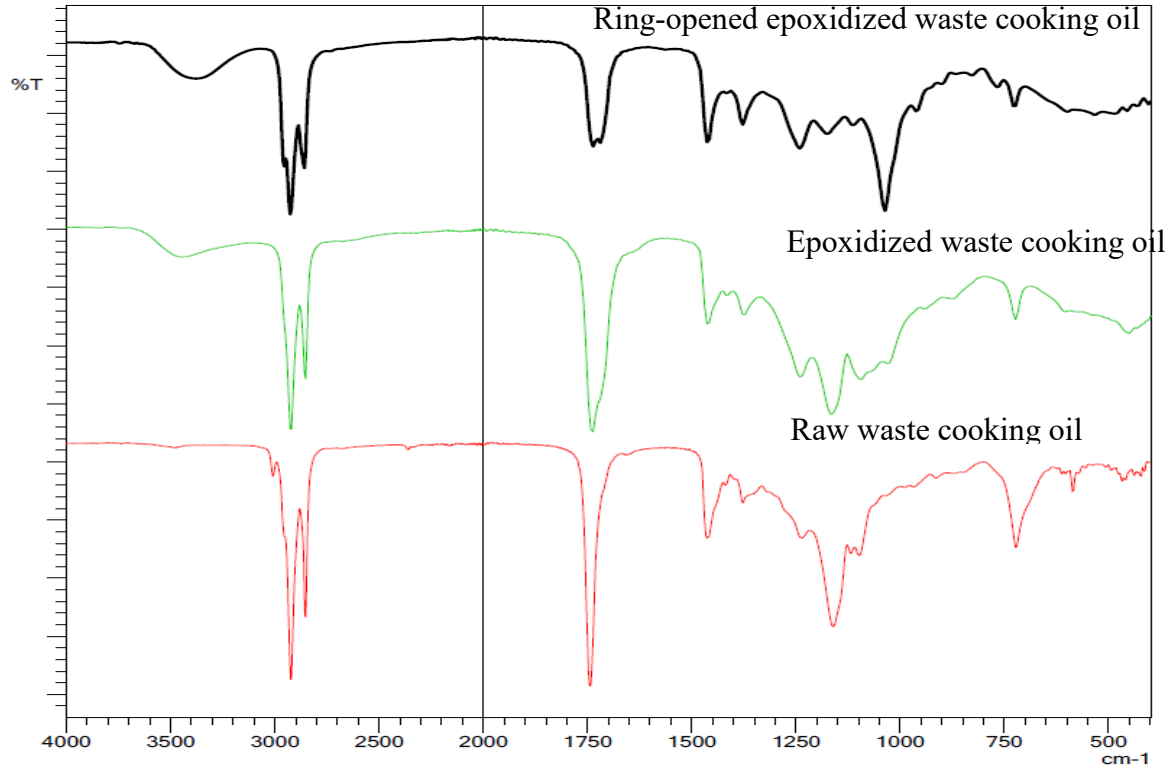


Figure 4-4 FTIR spectra of the raw waste cooking oil, epoxidized waste oil and the ring-opened epoxidized waste cooking oil

Figure 4-4 shows the FTIR spectra of the raw waste cooking oil, epoxidized waste oil and the ring-opened epoxidized waste cooking oil. The peaks at 3009 and 720 cm^{-1} of RO-eWCO indicate the vibration stretching and bending of C-H in C=C-H. The peak at 3000cm^{-1} disappears from the eWCO and RO-eWCO IR spectra, while the peak at 720cm^{-1} declines significantly. This implies that a large part of the raw castor oil's alkene (-C=C-) bonds has taken part in the reaction. A new peak is observed at 830 cm^{-1} for the epoxidized castor oil, denoting the presence of the epoxy-functional group. The peak at 3400 cm^{-1} for the ring-opened waste cooking oil can be attributed to the extent of O-H bond stretching present in the ring-opened epoxidized waste cooking oil. Rayung et al. (2019) identified the epoxide ring peak around 820 to 830cm^{-1} bandwidth. The presence of the hydroxyl O-H group in the ring-opened product further confirms the opening of the oxirane ring from the epoxidized product.

4.8 Physicochemical properties

4.8.1 Total acid number

The acid number of biolubricants was determined by the ASTM D 974 method. A sample of 0.3 g was dissolved in a solution of toluene and isopropanol with a small quantity of water. A prepared potassium hydroxide (KOH) solution of 0.05 M was added to the burette. Two drops of a phenolphthalein indicator were added to the sample for endpoint indication. A blank sample was prepared to determine the amount of reactive substance in the prepared solvent. In order to ensure repeatability, a total of three measurements were taken for each sample.

The acid number indicates the amount of base (mass of KOH) required to neutralise the lubricant. It is crucial to know the acid number of the biolubricants as a high acidy lubricant can result in oxidation (Cortes & Ortega, 2019). Once the oxidation has occurred, this can accelerate wear and rust formation in the engine.

Table 4-7 shows the results obtained for the acid number for the waste cooking oil biolubricant and raw oil. The WCO-TMP based ester had the lowest acid number than the RO-eWCO and Raw WCO. According to Owuna et al. (2020), biolubricants with a low acid number are mostly preferred for automobile engine application as they are less prone to the formation of sludges and clogging of oil filters. Heikal et al. (2017) reported a decrease in the acid number of Jatropha oil after a two-stage transesterification. The RO-eWCO had the highest acid number than the raw WCO and WCO-TMP. The high acid number can be attributed to the use of acid catalysts during epoxidation. However, the acid number is still within the acceptable range of 0.20 to 50.00 mg KOH/g for engine oil, as stated by Danjuma and Dandago (2009) and Muhktar et al. (2014). The uncertainty value was estimated to be ±0.002 $mgKOH/g$

Table 4-7 The total acid number measurement for the Waste Cooking Oil biolubricants

Sample	Test1 ($mgKOH/g$)	Test 2 ($mgKOH/g$)	Test 3 ($mgKOH/g$)	Average
Raw Waste Cooking Oil (WCO)	4.57	4.24	4.94	4.59
Waste Cooking Oil TMP esters (WCO-TMP)	0.82	0.84	1	0.88
Ring Opened epoxidized Waste Cooking Oil (RO-eWCO)	13.44	14.85	14.49	14.26

4.8.2 Density

The density was measured using an Anton Paar 800 equipment viscometer. The temperature range of 15°C to 60°C was considered for density measurements. The measure of density is essential when considering lubrication. According to Fitch (2021), the density can tell if the lubricant will flow or sink when mixed with water. The density value can also be used in some viscosity calculations; hence, it requires a great deal of attention when manufacturing biolubricants.

Figure 4-5 shows the density of Waste Cooking Oil Biolubriants at different temperatures. The WCO based TMP ester had the lowest density across all temperatures of consideration compared to Raw WCO and Ring opened eWCO. This could be attributed to the monoesters present in the WCO-TMP biolubricant. Monoesters have lower molecular masses compared to triesters hence the low density. In contrast, the triglyceride structure (raw WCO) did not significantly change in terms of the molar mass during the epoxidation and ring-opening reaction hence the higher density.

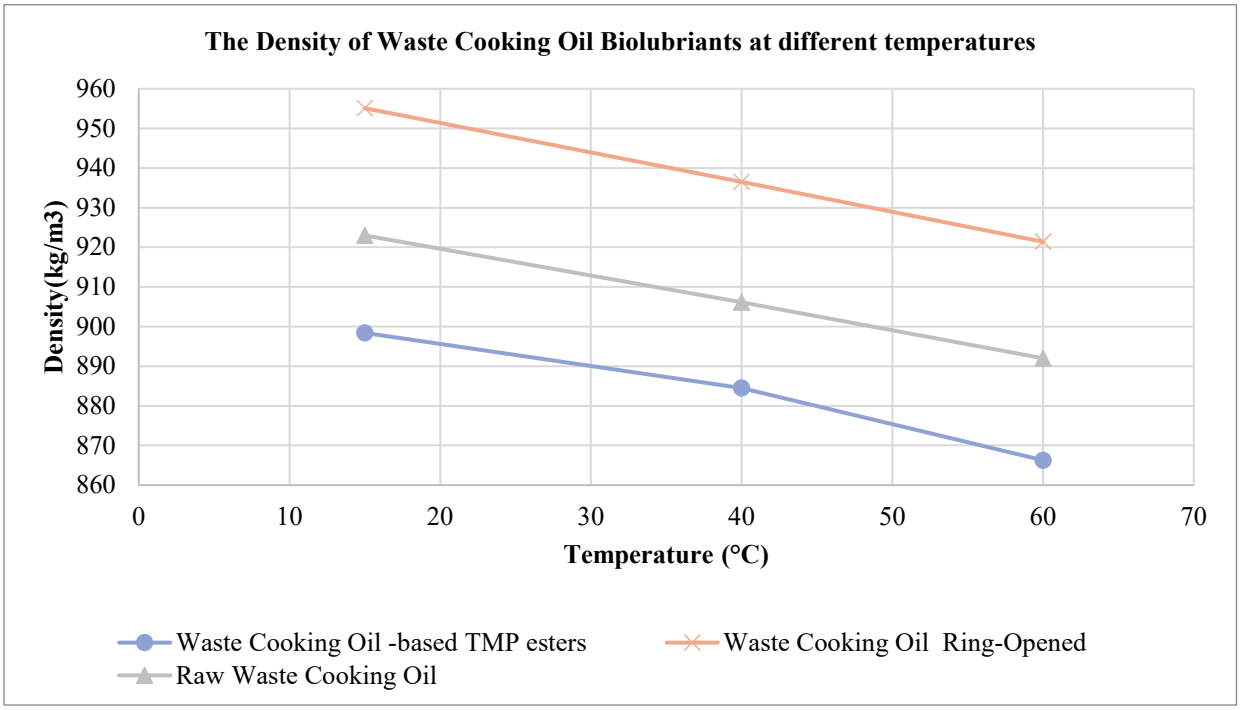


Figure 4-5 The density of Waste Cooking Oil Biolubriants at different temperatures

In order to improve the lubricity of the biolubricants, additives such as nanoparticles are added to the base oil (Cortes & Ortega, 2019) . In the current study, Silicon dioxide (SiO_2) and copper oxide (CuO) were added to the synthesised biolubricant. Therefore, it is essential to understand how such formation would impact some physicochemical properties such as density. Figure 4-6 shows nanoparticles' effect on the waste cooking oil-based biolubricants.

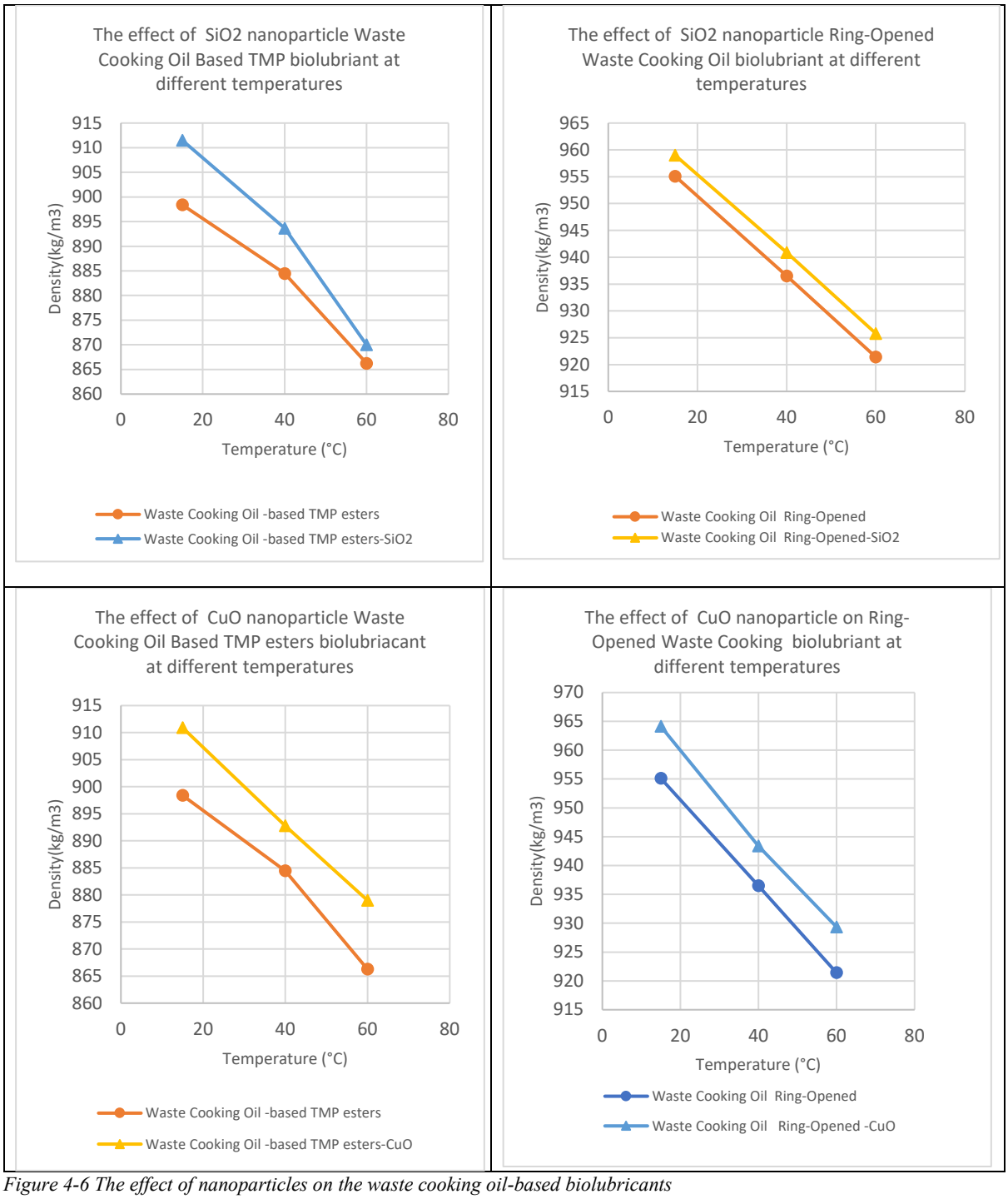


Figure 4-6 The effect of nanoparticles on the waste cooking oil-based biolubricants

The addition of nanoparticles on the base oil increased the density of the nano-biolubricant. The effect of both SiO_2 and CuO were the same irrespective of the biolubricant. However, CuO particles of the same amount as SiO2 increased the density by around 5% more than SiO_2. This can be attributed to CuO's greater molar mass than SiO_2.

4.8.3 Kinematic Viscosity and viscosity index

Kinematic viscosity is one of the essential properties of lubricants. Viscosity is defined as the measure of resistance for the fluid to flow. The kinematic viscosity for lubricants is generally determined at 40 and 100°C as per the ASTM standard. The RVDV-II+ Pro Brookfield Viscometer was used to measure the dynamic viscosity of the produced biolubricants. The uncertainty of the viscometer was estimated to be ±0.02 mm^2/s. Due to the small quantity of samples available, small adapters were utilized. Approximately 8mL of the sample was placed in a chamber fitted with the S21 spindle size to measure the dynamic viscosity. In order to ensure repeatability, a total of three measurements were taken for each sample. The recorded dynamic viscosity (Cp) was converted to kinematic (mm^2/s) using the equation below:

$$Kinematic\ viscosity(\frac{mm^2}{s}) = \frac{Dynamic\ viscosity(cP)}{Density\ (\frac{g}{cm^3})}$$

The viscosity index shows how the viscosity changes with respect to temperature. A high viscosity index implies that there is minimal change in viscosity as the temperature changes. The viscosity index is determined based on the ASTM D-2270 method. According to Inkerd et al. (2015), The viscosity index should be greater than 90 and 95 for engine oil and two-stroke engine oil, respectively.

Figure 4-7 shows the kinematic viscosity of the raw waste cooking oil (raw WCO), waste cooking oil-based TMP esters (WCO-TMP) and ring-opened epoxidized waste cooking oil (RO-eWCO). As expected from the literature, the viscosity of the produced biolubricants decreased as the temperature increased from 40 to 100°C (Syahir, et al., 2017).

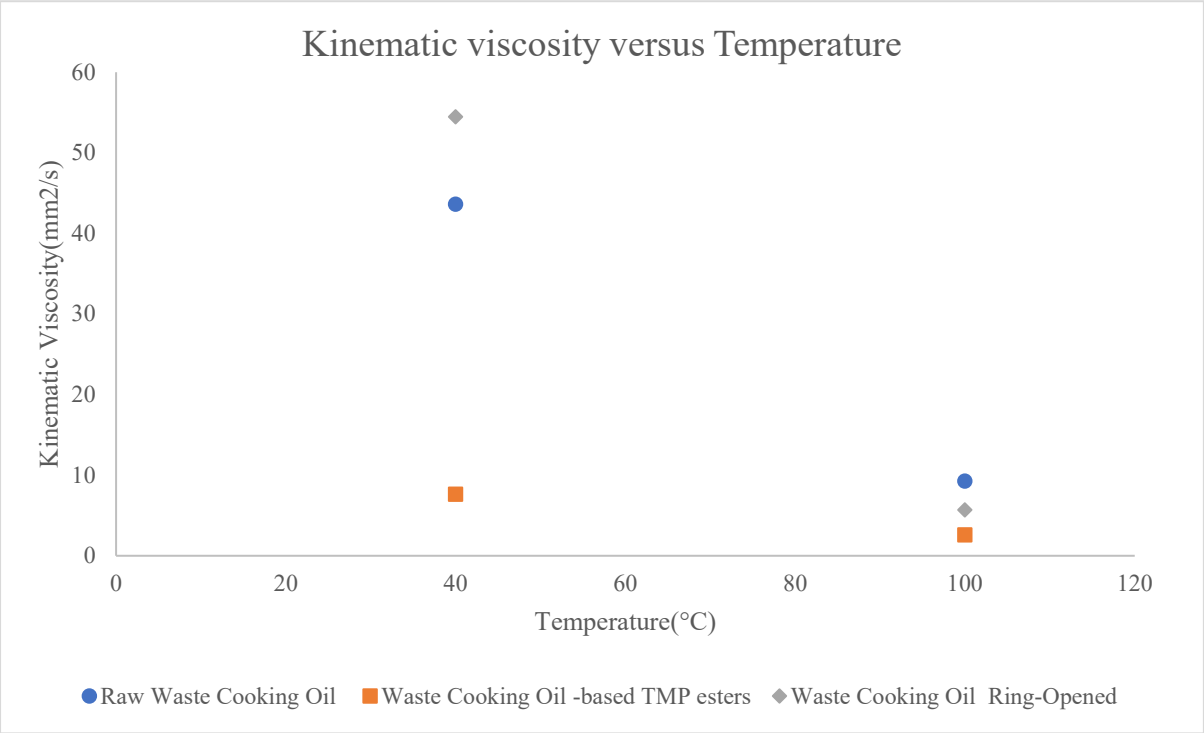


Figure 4-7 The waste cooking oil biolubricant's kinematic viscosity at 40 and 100°C.

The kinematic viscosity of the raw WCO was determined to be 43.59 and 9.52 mm^2/s at 40 and 100°C, respectively. Li and Wang (2015) reported a value of 36.7 and 8.5 mm^2/s at 40 and 100°C, respectively. The raw WCO had a viscosity index of 209. This result further agrees with the findings reported by Li and Wang (2015). The raw WCO kinematic viscosity is displayed in Figure 4-7 to help understand the effect of different chemical modifications. Based on Automotive Lubricant Viscosity Grades: Engine Oils – SAE J 300, Dec. 1999, the raw WCO conforms to the SAE 30 viscosity grade.

The kinematic viscosity of WCO-TMP was determined to be 7.63 and 2.60 mm^2/s at 40 and 100°C, respectively. As seen in Figure 4-7, the WCO-TMP biolubricant had the lowest kinematic viscosity across both temperatures (40 and 100°C). According to the SAE (2015), the WCO TMP biolubricant does not meet any SAE viscosity grades specified in SAE J300_201501. The lowest acceptable kinematic viscosity for engine oil at 100°C is 5.6 mm^2/s (SAE , 2015). The lowest acceptable kinematic viscosity for an engine oil based on SAE J 300 is 5.6 mm^2/s. The kinematic viscosity measured for the WCO-TMP biolubricant was too low to be considered for engine oil. However, the WCO-TMP can still be used for other industrial applications, such as electrical and hydraulic lubrication.

An excessively low kinematic viscosity implies that the oil forms a very thin film when applied to metal surfaces. The challenge with low viscosity fluids that have thinner oil films is that it is more difficult for the oil to keep the loaded contact surfaces in the engine adequately apart. The probability of contact between the two sliding engine metals is significantly increased as the fluid film becomes thin. This can result in faster wear rates and possibly greater friction locally (Galvão, et al., 2017). According to Galvão et al. (2017), there is a shift from fluid lubrication to elastohydrodynamic lubrication when the viscosity is too low such as the above kinematic viscosity of WCO at 100°C. Another issue with the low viscosity is the increase in the oil evaporation ratio due to low viscosity. This results in the oil level reduction, viscosity increase and turbocharges efficiency reduction (Galvão, et al., 2017).

Numerous studies have shown that epoxidized vegetable oils often have poor low-temperature properties; hence, it is necessary to carry out further processes to improve the lubricity of the biolubricant (McNutt & He, 2016; Syahir, et al., 2017). Although the epoxidized product is not required as the final product in the current study, the viscosity was measured to determine the effect of the oxirane ring-opening reaction. The kinematic viscosity of the epoxidized WCO biolubricant was determined to be 142 and 18mm^2/s at 40 and 100°C, respectively. There was a significant increase in the kinematic viscosity from the raw WCO. This can be attributed to the decrease in the degree of unsaturation(C=C) as the raw castor oil goes through the epoxidation reaction. Similar results were reported by Somidi et al. (2014).

The kinematic viscosity of the RO-eWCO was determined to be 35.23 and 5.96 mm^2/s at 40 and 100°C, respectively. The RO-eWCO had the highest kinematic viscosity at 40°C and 100°C compared to the WCO-TMP biolubricant. The RO-eWCO kinematic viscosity satisfied the SAE20 engine oil viscosity grade as stated in Automotive Lubricant Viscosity Grades: Engine Oils – SAE J 300, Dec. 1999. The viscosity index of 94.45 was calculated for the RO-eWCO. Based on the standard specifications for lubricating oil reported by Inkerd et al.(2015), the RO-eWCO is well within the engine oil range.

1.1.1.1 *The effects of nanoparticle additives on kinematic viscosity of the waste cooking oil-based biolubricants*

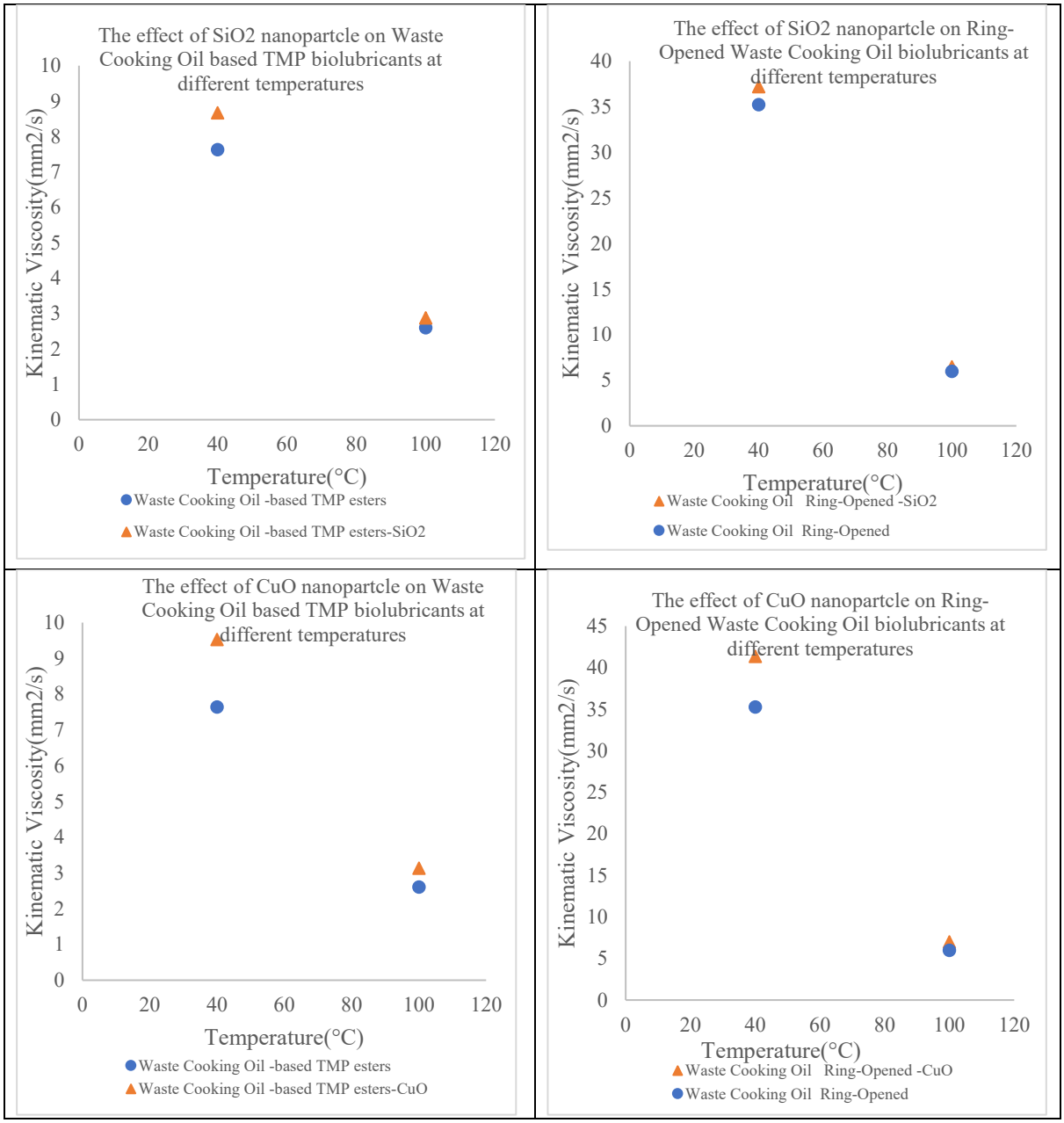


Figure 4-8 The effect of silicon dioxide and copper oxide nanoparticles on the waste cooking oil produced biolubricants

The silicon dioxide (SiO_2) and Copper oxide (CuO) nanoparticles were added to the waste cooking oil-based lubricants (base oil). A 1wt% fraction of the nanoparticle additive was added to the base oil. The same apparatus and procedure used to measure the kinematic viscosity for the base lubricants were used again for the biolubricant with the nanoparticles.

Figure 4-8 below shows the effect of nanoparticles on the kinematic viscosity of the synthesised biolubricant. Based on Figure 4-8, the kinematic viscosity is observed to increase due to the addition of SiO_2 and CuO nanoparticles. However, the SiO_2 is observed to have a superior

effect on the base lubricant, while the CuO had a minimal effect on the baser oil. The effect of both nanoparticles is observed to be minimal at higher temperatures. Similar results were observed by Cortes and Ortega (2019) after adding the nanoparticles into the sunflower oil flower oil.

4.8.4 The pour point and cloud point

Pour point is one of the crucial low-temperature properties of the lubricant. This property can be used to tell if the oil will be able to flow in between two sliding metals at low temperatures. In regions where the temperature gets very low, it is required that the lubricant has the lowest possible pour point. This is done to ensure that the engine is well lubricated.

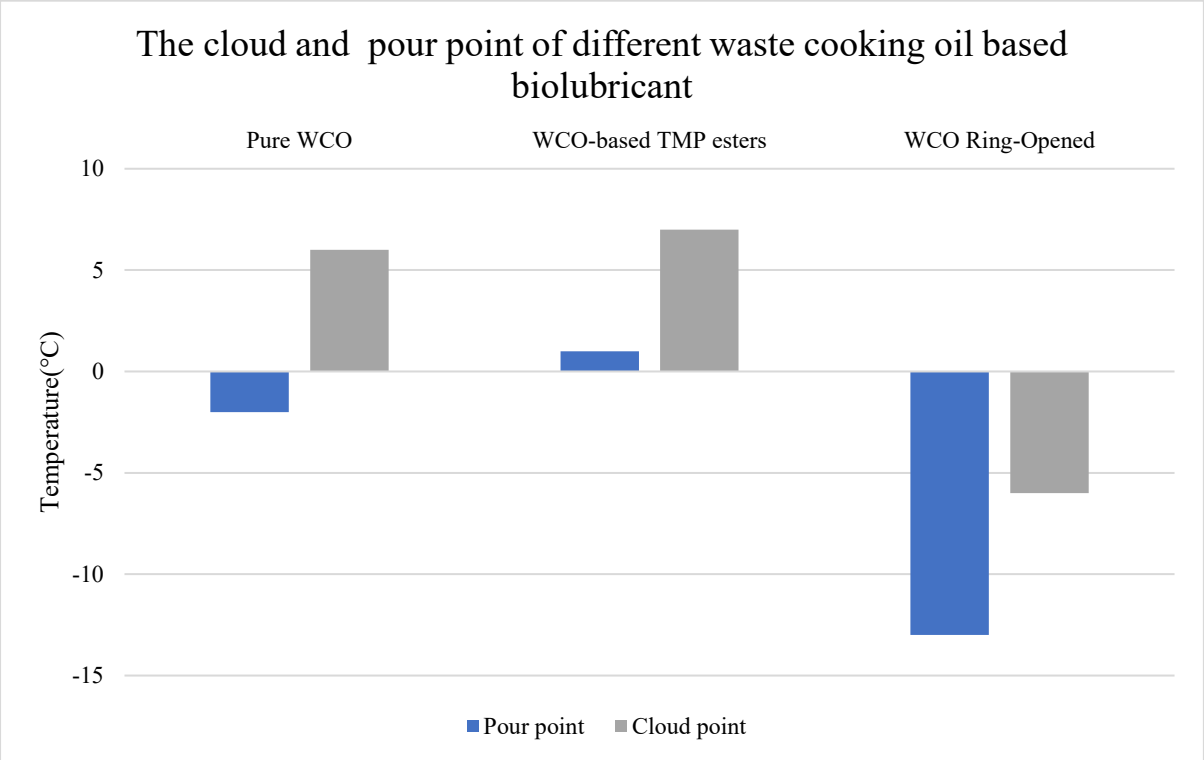


Figure 4-9 The cloud and pour point of Waste Cooking oil-based biolubricants

Figure 4-9 presents the pour point temperature of the raw Waste Cooking Oil (Raw WCO), Waste Cooking Oil-based TMP esters (WCO-TMP) and Ring-Opened epoxidized Waste Cooking Oil (RO-eWCO). The cloud and pour point of the raw WCO was found to be 6°C and -2°C, respectively. Li & Wang (2015) also reported the pour point of -2°C from the raw waste cooking oil. According to Inkerd et al. (2015), the engine biolubricant should have a maximum pour point of -5°C to ensure that the engine is well lubricated at low temperature operating

conditions or cold start. For this reason, the measured -2°C pour point for the raw WCO was too high for the oil to be used as the engine biolubricant.

The cloud and pour point of the WCO-TMP was found to be 1 and 7°C, respectively. The pour point of the WCO-TMP biolubricant had increased after the two-stage transesterification of the raw waste cooking oil. Kamarudin et al. (2020) reported the value of 8°C for waste cooking oil-based biolubricant with 48% of unsaturated content. While in the current study, the WCOME biolubricant had 62% of the unsaturated content with a lower pour point 1°C. This result agrees with the observation made by Jayadas & Nair (2006) and Syahir et al. (2017). According to the aforementioned authors, the vegetable oil with a higher quantity of unsaturated fatty acid content results in a lower pour point.

Although the pour point is less than some of the values reported in the literature, the recorded 1°C of the WCO-TMP pour point is still not in the engine oil biolubricant standard range. Therefore the WCO-TMP biolubricant cannot be used as the engine biolubricant. However, the pour point modifiers can be added to improve the pour point.

As seen in Figure 4-9, RO-eWCO had the lowest cloud point and pour point of -7°C and -13°C, respectively, making it the most suitable biolubricant to be used at low operating temperatures compared to WCO-TMP. The decrease in the pour point from -2°C of the raw waste cooking oil could be due to the increase in the chain length of the ring-opened product. According to Madanhire & Mbohwa (2016), molecular crystallization is inhibited by the presence of a large branching point which creates a steric barrier around the individual molecule. This results in the decrease of cloud and pour point.

1.1.1.2 The effects of nanoparticle additives on cloud and pour point of the waste cooking oil-based biolubricants

The silicon dioxide and copper oxide nanoparticles were added to the waste cooking oil-based lubricants (base oil). A 1wt% fraction of the additive was added to the based oil. There was no effect on both the cloud and pour point of the biolubricant observed.

4.8.5 Thermogravimetric (TGA) Analysis

The thermal stability study of the produced biolubricant was carried out using TGA/ DCS thermogravimetric analyser. An amount of approximately 26 mg of the sample was placed in an alumina cup at a constant nitrogen gas flow of 20 ml/s. The temperature was initially set at 50ºC, held for 5 minutes, then increased at the rate of 30ºC/minute to 600ºC and held for another 5 minutes. Figure 4-10 shows the percentage weight of the Raw Waste cooking Oil (Raw WCO), Waste Cooking oil-based TMP esters (WCO-TMP) and Ring-Opened epoxidized Waste Cooking Oil (RO-eWCO) as the temperature increases. The oil thermal stability was determined by observing the temperature at which there was a loss of 5% mass from the sample.

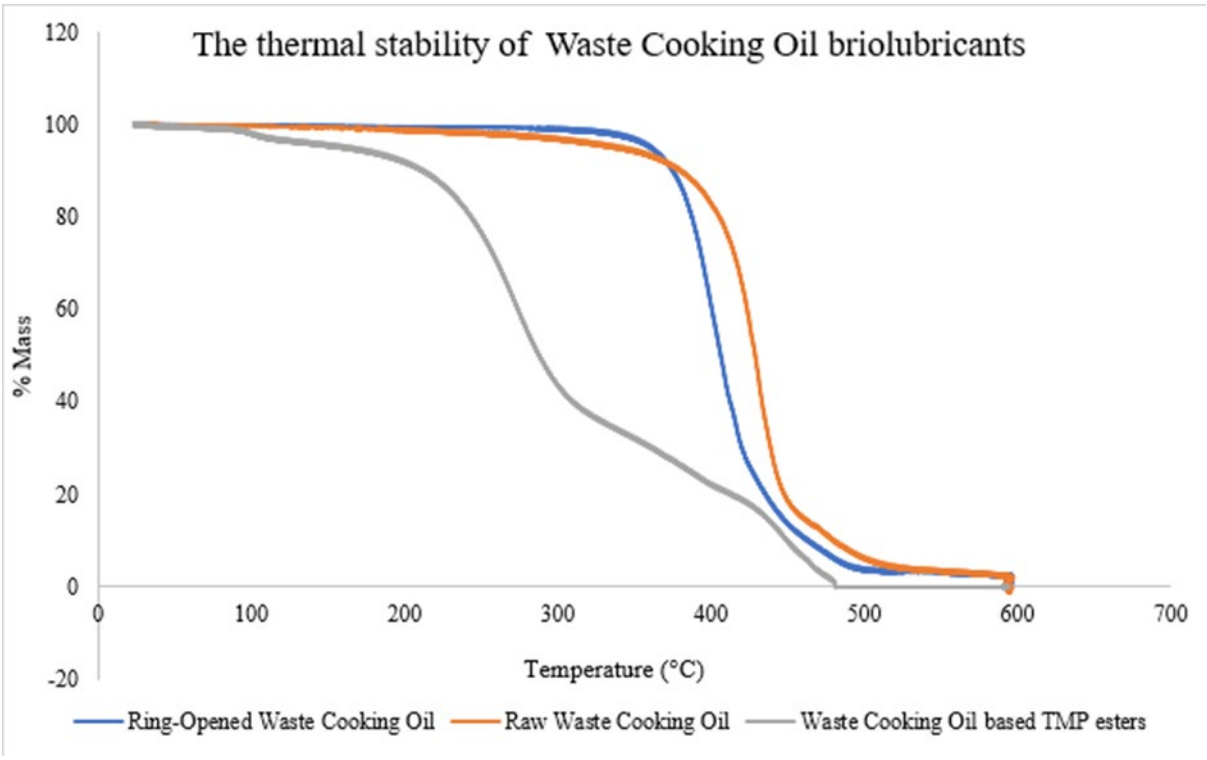


Figure 4-10 The thermograms of the Waste Cooking Oil biolubricants

According to Figure 4-10, the raw WCO, WCO-TMP and RO-eWCO were found to be thermally stable below 339, 190 and 360°C, respectively. The thermal stability of the WCO oil had improved due to the epoxidation and subsequence ring-opening reaction. The thermal stability had improved by 21°C from 339 to 360°C. These results show appreciable consistency with the results reported by Madankar et al. (2013) for the Ring opened product. The 95% mass loss was observed at 511, 470 and 488°C for the raw WCO, WCO-TMP and RO-eWCO, respectively.

It is clear from the curve that the WCO-TMP biolubricant was the worst-performing biolubricant compared to the RO-eWCO. The low thermal stability could be due to the high unsaturation content present in the WCO-TMP. Based on the GCMS analysis of the WCOME in Figure 4-2, there is approximately 62% of unsaturated content present in the raw waste cooking oil. Since the transesterification reaction doesn't aim at the double bond but the β-hydrogen instead, the double bond remains unmodified. This means that the WCO-TMP still has a higher degree of unsaturation. In addition to the unsaturation, there was a low yield of TMP triesters meaning that some molecules could still have the β-hydrogen; hence the WCO-TMP resulted in low thermal stability.

The WCO-TMP also showed a different mass degradation trajectory compared to the other oils under investigation. A multi-stage weight loss of the WCO-TMP was observed, with the last stage ending around 490°C. The first stage is up to 7% of mass loss. Previously researchers have reported that the first mass degradation, as observed in Figure 4-10, could be caused by moisture absorption and evaporation of volatiles (Halim & Chan, 2016; Wang, et al., 2015). The second stage of mass degradation starts from 200 to 300°C with about 55% mass loss. This can be attributed to the actual degradation of WCO-TMP biolubricant.

According to Figure 4-10, it can be concluded that the produced RO-eWCO biolubricant is suitable for higher temperature applications compared to the WCO-TMP.

Chapter 5 Results and discussion: Castor oil

5.1 The esterification of Castor oil

Generally, vegetable oils should have free fatty acid of less than 2.5 wt.% to avoid soap formation during the transesterification reaction (Leung, et al., 2010). The percentage of free fatty acid content is directly calculated by dividing the acid number by two. The ASTM D-664 method was used to determine the acid number of the oil. The acid number and %free fatty acid were determined to be 5.09 and 2.54%, respectively. This is more than the value permissible for transesterification reaction. Leung et al. (2010) recommended carrying out an acid catalysed esterification reaction to reduce the acid number of the vegetable oil. The acid catalysed esterification reaction was carried based on the optimum conditions published in Halder et al., (2015) work. The acid number was reduced from 2.54% to 1.42%. Since free fatty acid content was now below 2.5%, it was then transesterified with methanol in the presence of a base catalyst.

5.2 The transesterification of castor oil

The transesterification of the castor oil using methanol achieved a castor oil methyl ester (COME) yield of 83%. The COME produced was then prepared for the transesterification with TMP to produce TMP based esters.

5.3 The optimisation of the castor oil methyl ester transesterification reaction conditions

The castor oil TMP triesters yield optimisation has been described in paragraph 4.3. The results of the optimisation have been displayed in Table 5-1 below. The highest actual yield obtained was 72%. The reaction temperature, catalyst loading, reaction time and Molar ratio COME: TMP were at 140°C, 0.5 %wt,4 hours and 4:1, respectively. The lowest yield of 50% was obtained at a temperature of 80°C, 1 %wt. catalyst loading, 4 hours reaction time and 4:1 Molar ratio COME: TMP. From these results, it is eminent that the temperature greatly impacts the reaction. It appears that the increase in temperature increases the yield of castor oil TMP triesters.

In order to find the best model to fit the experimental data, a regression was performed on Minitab software. Different models were accessed on their suitability to represent the data. The accessed models included Linear, linear+square, Linear+interaction and quadratic regression models. The coefficient of determination (R^2) was used to determine if the model fits the experimental data. The higher the coefficient of determination (R^2), the more adequate the model is. The quadratic model was found to have the highest R^2 value of 0.9206. The R^2 value of 0.9325 means that the independent variable could best describe 92% of the yield response variation. The model could not describe only 8% of the variation. Therefore, the quadratic model was selected as the best model to predict the behaviour of the experimental data.

Table 5-1 The measured and predicted castor oil based TMP triesters yield at different experimental conditions

Run order	Temperature (°C)	Catalyst(%wt.)	Time(h)	Molar ratio COME:TMP	Actual Yield (%)	Predicted yield (%)
1	140	0,8	4	3	69,2	70,36
2	110	0,8	4	4	67,4	64,96
3	110	0,8	5	3	67,3	60,97
4	80	0,8	5	4	47,2	49,32
5	110	0,5	4	5	69,12	67,01
6	140	1	4	4	67,17	64,38
7	110	0,5	3	4	67,13	67,72
8	110	1	4	3	52	57,10
9	110	1	3	4	53	53,95
10	110	0,8	4	4	62	64,96
11	80	1	4	4	47	43,14
12	110	0,8	5	5	65,48	64,92
13	80	0,8	3	4	50	50,24
14	140	0,8	5	4	69,36	71,04
15	80	0,8	4	3	47	48,61
16	140	0,8	4	5	72	72,70
17	80	0,8	4	5	50	51,16
18	110	0,5	5	4	57	58,21
19	110	0,8	3	5	62,16	64,25
20	110	1	4	5	57,2	55,93
21	110	0,8	3	3	67	63,32
22	110	1	5	4	57	58,88
23	110	0,5	4	3	57	59,14
24	80	0,5	4	4	50,46	49,19
25	140	0,8	3	4	72	71,81
26	110	0,8	4	4	65,47	64,96
27	140	0,5	4	4	72	71,44

$$Yield = -61{,}2 + 1{,}246\,A + 95{,}9\,B - 8{,}4\,C + 11{,}6\,D - 0{,}00389\,A*A - 84{,}6\,B*B - 0{,}85\,C*C - 0{,}74\,D*D - 0{,}034\,A*B + 0{,}0013\,A*C - 0{,}0017\,A*D + 14{,}44\,B*C - 9{,}05\,B*D + 0{,}75\,C*D$$

A→Reaction temperature (°C)

B→ Catalyst loading

C→Reaction time

D→COME: TMP

According to Kamairudin et al. (2021), the positive sign represents an antagonistic effect while the negative showed a synergistic effect.

The variation analysis (ANOVA) was performed on the developed model to further determine its suitability to represent the yield of the TMP triesters. The results are shown in Table 5-2

Table 5-2 Analysis of variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	1787,56	127,683	9,94	0,000
Linear	4	113,58	28,395	2,21	0,129
A	1	67,92	67,923	5,29	0,040
B	1	31,21	31,215	2,43	0,145
C	1	3,19	3,194	0,25	0,627
D	1	6,14	6,142	0,48	0,502
Square	4	174,00	43,501	3,39	0,045
A*A	1	65,47	65,473	5,10	0,043
B*B	1	134,87	134,866	10,50	0,007
C*C	1	3,84	3,842	0,30	0,594
D*D	1	2,96	2,960	0,23	0,640
2-Way Interaction	6	77,09	12,848	1,00	0,468
A*B	1	0,26	0,264	0,02	0,888
A*C	1	0,01	0,006	0,00	0,983
A*D	1	0,01	0,010	0,00	0,978

B*C	1	53,53	53,525	4,17	0,064
B*D	1	21,00	21,001	1,63	0,225
C*D	1	2,28	2,280	0,18	0,681
Error	12	154,16	12,847		
Lack-of-Fit	10	139,19	13,919	1,86	0,400
Pure Error	2	14,98	7,488		
Total	26	1941,73			

According to Martín et al. (2020) a p-value, less than 0.05 indicate statistical significance; therefore, the developed model is statistically significant. As shown from Table 5-2, the developed model had a value of less than 0.05. This implies that the developed model is suitable for determining the relationship between the significant and response variable(yield). The lack of fit was determined to be insignificant as the p-value was greater than 0.05. The insignificant lack of fit implies that the quadratic model can represent the entire experimental data since there is no evidence that the model cannot fit the data. The large F-value for the lack of fit can be attributed to the experimental noise (Azman, et al., 2020).

In addition, the significance of the independent variables was also determined based on the p-value and the F-value. A small P-value and a large F value imply that the variable is significant. As a result, it can broadly impact the response variable when varied (Roselan, et al., 2020). From Table 4-5, B(catalyst loading), C (reaction time), D (COME: TMP) molar ratio, D^2 and C^2 are insignificant since the p-value is far greater than 0.05. Whereas A (reaction temperature), A^2, B^2 D (COME: TMP molar ratio) and B^2 are significant. The developed model showed slight significance for two-way interactions between (B)catalyst loading and (C)reaction time variables, implying that there might be a slight mutual interaction between the two variables. The insignificant terms were not eliminated as they only reduced the R^2 slightly.

The developed quadratic model was then used to determine the optimum conditions for the transesterification reaction. The results for the optimum conditions have been displayed in Table 5-3

Table 5-3 The optimum condition castor oil methyl ester transesterification reaction

Reaction temperature (°C)	Reaction time (h)	Catalyst loading (wt%)	Molar ratio COME: TMP	Predicted Yield	Actual yield
140	3	0.52	5	77.75	76.20

The predicted and actual yields were determined to be 77.75 and 76.20%, respectively. The error was calculated to be 2.03%. This proves that the developed correlation accurately predicts the yield with minimal error(<5%).

5.4 Characterization of the castor oil based TMP esters biolubricant

The GCMS method used to analyse the castor oil-based biolubricants was the same as the WCO characterisation method in paragraph 4.4. The method is explained in detail in the results and discussion section for WCO above (see paragraph 4.4). Figure 5-1 contains the chromatographs for the castor oil methyl esters (COME) and Castor oil based TMP esters produced through Method A. The Castor oil methyl esters were produced from the transesterification reaction between methanol and esterified castor oil. The number of picks produced from this reaction is much less than the waste cooking oil picks shown in Figure 4-2. This can be attributed to the few fatty acids found in the castor oil.

The main constituent of COME is the saturate content; Hexadecanoic acid methyl ester (2.15%), Methyl stearate (2.57%) and unsaturated content; 9,12-Octadecadienoic acid (Z, Z)-methyl ester (7.68%), 9-Octadecenoic acid methyl ester, (E)- (6.65%), 9-Octadecenoic acid, 12-hydroxy-methyl ester, (Z)- (78.63%). In summary, COME consists of 35 and 65% of saturated and unsaturated content, respectively. According to Heikal et al. (2017), a high amount of unsaturated content contributes to poor oxidative-thermal stability in biolubricants.

Figure 5-1 (b) shows the chromatogram of castor oil TMP based esters. The product picks are represented by peak 10 to peak 15. These peaks represent the triesters ,diesters and monoester that were produced during the transesterification reaction. Peak 2 to 8 shows the unreacted methyl ester that is in the product. The large presence of unreacted methyl esters in the product can be attributed to the excess molar ratio of COME to TMP that was added. Sripada et al. (2013) obtained similar results when studying the production of biolubricants from the canola diesel and methyl oleate. Before the product was characterised further for the physicochemical properties, it was subjected to the rotary evaporator to remove light components. The large presence of unreacted methyl esters in the product can be attributed to the excess molar ratio of COME to TMP that was added.

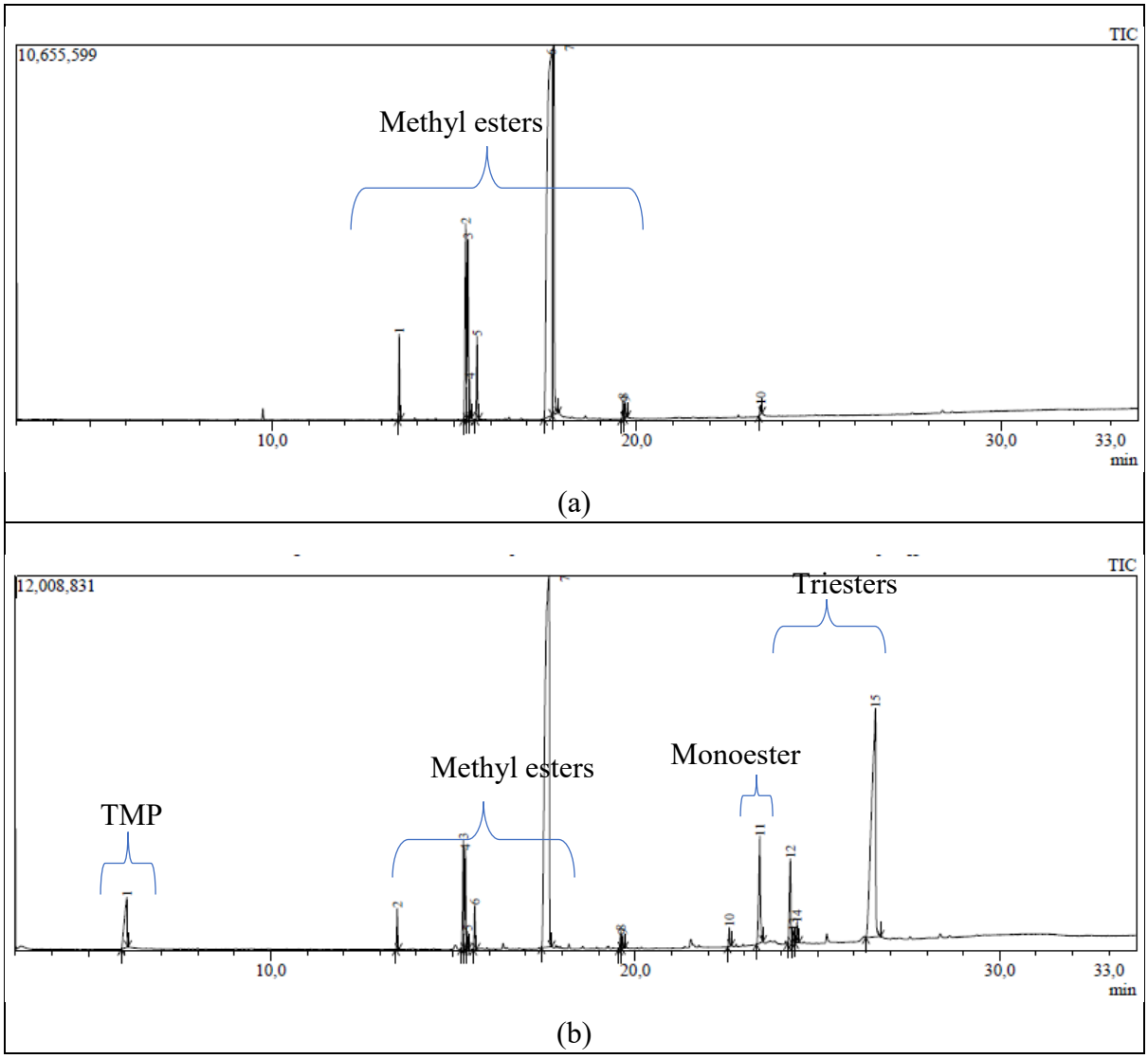


Figure 5-1 (a) Castor oil methyl ester and (b) Castor oil-based TMP ester Chromatograph produced through Method A

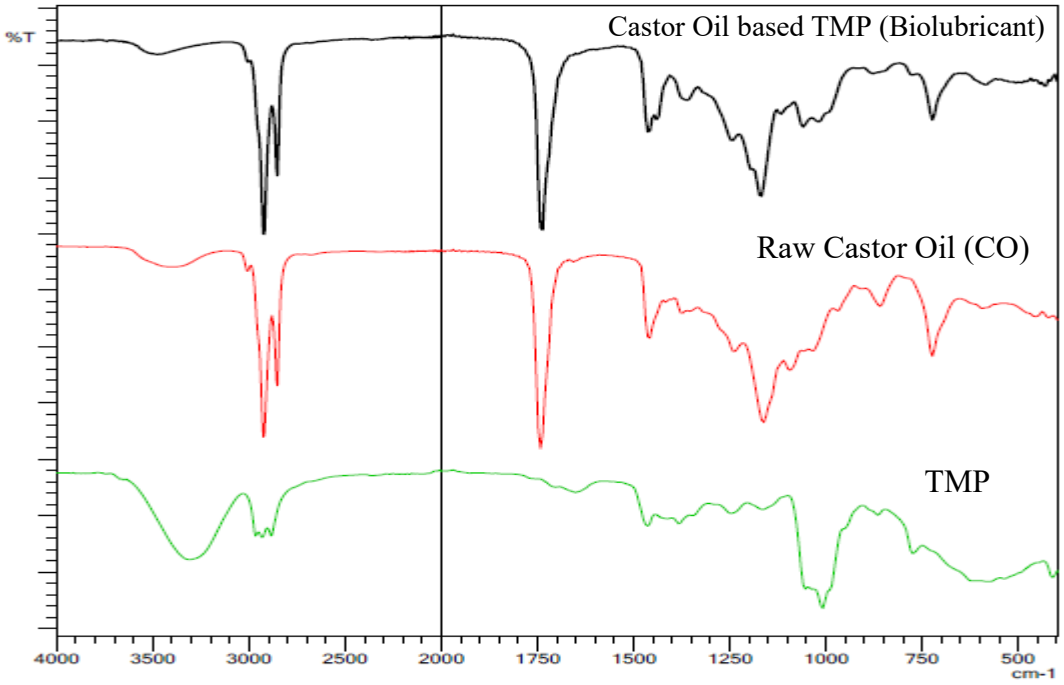


Figure 5-2 The FTIR spectra of Castor oil, Castor oil-based TMP esters and TMP

The product's characterisation was also carried out using a QATR™-S single-reflection ATR accessory with a diamond Crystal for Fourier transform infrared (FTIR) analysis. The analysis was done to identify the functional groups present within the product. The FTIR spectrum for the TMP based Castor oil is displayed together with the raw castor oil and TMP in Figure 5-3. The peaks identified in the passage below refer to the peaks appearing on the biolubricant's spectrum unless stated otherwise. The picks at 1170 cm^{-1} and 1740 cm^{-1} denote the presence of C-O stretch and C=O stretch vibration, respectively. This confirms the presence of an ester functional group in the biolubricant. A shallow pick is observed at 1460 cm^{1}, indicating the presence of the alkane functional group. The peaks at 2930 and 2860 cm^{-1} indicate the presence of C-H and CH2 stretching vibrations in the carboxylic acid. The appearance of the peak at 3400 cm^{-1} indicated the presence of water and phenols in the biolubricant. The TMP spectrum has a characteristic peak at 3307 cm^{1}, indicating the presence of hydroxide group (OH) in the compound. Based on the comparison between the three spectra in Figure 5-2, the OH peak disappears in the biolubricant spectrum. This implies that the transesterification of the Castor oil methyl ester was close to completion. The OH peak could be from some of the TMP that did not take part in the reaction.

5.5 The epoxidation of castor oil

The epoxide oxirane content for the epoxidized castor oil was calculated to be 5.36%, translating to 84% conversion. American Oil Chemists' Society (AOCS) Cd 9-57 method was used to determine the oxirane ring content. Malankara et al. (2012) reported an oxirane content of 5.6% for the epoxidized canola oil.

5.6 Optimisation of the epoxidized castor oil ring-opening reaction conditions

The optimisation of epoxidized castor oil was carried out as explained in paragraph 4.6. The same parameters analysed were also optimised except that the 2-hexyl decanol: eCO molar ratio was used instead of WCO. The results of the actual hydroxyl value obtained at different experimental conditions have been summarised in Table 5-4. Each of the experiments was run twice to increase reproducibility.

The Minitab software was used to regress the experimental data to obtain the model that will best describe the results. The hydroxyl value was selected as the response variable while the reaction temperature, reaction time, catalyst loading and 2-hexyl decanol to eCO ratio were set at the independent variable. Linear, linear+square, Linear+interaction and quadratic regression models were accessed for the regression of the experimental data. The coefficient of determination (R^2) for Linear, Linear+square, Linear+interaction and quadratic regression models was determined to be 0.8404, 0.9048, 0.8577, 0.9247, respectively. Among the four regression models examined for the experimental data, the quadratic model had the highest R^2 value. The R^2 value of 0.9247 means that the independent variable could best describe 92% of the hydroxyl value (HV) response variation. The model could not describe only 8% of the variation. Therefore, the quadratic model was selected as the best model to predict the behaviour of the experimental data.

Table 5-4 The conditions of the experiments with the measured and predicted ring-opened epoxidized castor oil hydroxyl value

Run Order	Temperature (°C)	Catalyst loading (%wt)	Time (h)	Molar ratio 2-hexyldecanol: eCO	Actual Hydroxyl value	Predicted Hydroxyl value
1	120	11,5	1,25	5,5	190,1	191,64
2	100	3	1,25	5,5	194,2	190,62
3	120	11,5	1,25	5,5	193	191,64
4	120	20	1,25	10	180,12	187,50
5	140	20	1,25	5,5	215,14	216,20
6	120	11,5	0,5	10	180,33	180,75
7	120	3	1,25	10	175,15	179,75
8	140	11,5	2	5,5	215	217,62
9	140	11,5	1,25	10	200,18	197,74
10	120	3	1,25	1	220,29	213,90
11	100	20	0,5	5,5	198	194,90
12	120	3	2	5,5	200	201,76
13	120	20	2	5,5	211,35	208,31
14	140	3	1,25	5,5	205	205,58
15	100	11,5	1,25	1	206	209,19
16	120	11,5	2	10	199	193,03
17	100	11,5	2	5,5	189,16	195,95
18	120	11,5	2	1	220,15	217,99
19	120	20	1,25	1	220,4	216,79
20	120	20	0,5	5,5	200,25	201,56
21	120	3	0,5	5,5	194,46	197,48
22	140	11,5	1,25	1	220,25	224,99
23	120	11,5	0,5	1	215	219,23
24	100	11,5	0,5	5,5	191,14	191,83
25	140	11,5	0,5	5,5	217,26	210,69
26	100	11,5	1,25	10	177	173,01
27	120	11,5	1,25	5,5	193,38	191,64

$$Y(Hydroxyl\ value) = 427.3 - 3{,}17\,A - 2{,}95\,B - 39{,}8\,C - 10{,}45\,D + 0{,}01373\,A * A + 0{,}0501\,B * B + 12{,}32\,C * C + 0{,}206\,D * D + 0{,}0153\,A * B + 0{,}051\,A * C + 0{,}0250\,A * D + 0{,}075\,B * C + 0{,}0327\,B * D + 1{,}037\,C * D$$

A→Reaction temperature (°C)

Reaction time (hr)

C→Catalyst loading

D→2-hexyl decanol to eCO

According to Kamairudin et al. (2021), the positive sign represents an antagonistic effect while the negative showed a synergistic effect.

An analysis of the variance (ANOVA) for the selected model was carried out to determine the model's fitness further. The primary function of the ANOVA analysis is to check the significance of the quadratic model. The ANOVA results have been displayed in Table 5-5 below.

Table 5-5 Analysis of the variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	4785,78	341,841	10,43	0,000
Linear	4	321,91	80,477	2,46	0,102
A	1	143,98	143,978	4,39	0,058
B	1	54,65	54,652	1,67	0,221
C	1	77,92	77,922	2,38	0,149
D	1	191,62	191,621	5,85	0,032
Square	4	345,20	86,300	2,63	0,087
A*A	1	161,63	161,634	4,93	0,046
B*B	1	74,40	74,396	2,27	0,158
C*C	1	255,65	255,655	7,80	0,016
D*D	1	90,36	90,358	2,76	0,123
2-Way Interaction	6	101,08	16,846	0,51	0,787
A*B	1	24,38	24,384	0,74	0,405
A*C	1	2,16	2,164	0,07	0,802
A*D	1	19,94	19,936	0,61	0,450
B*C	1	1,66	1,657	0,05	0,826
B*D	1	5,90	5,905	0,18	0,679
C*D	1	45,70	45,698	1,39	0,260
Error	12	393,20	32,766		
Lack-of-Fit	10	386,76	38,676	12,02	0,079
Pure Error	2	6,44	3,219		
Total	26	5178,97			

As can see in Table 5-5, the p-value of the developed model was determined to be extremely small (P<00000.1). According to Martín et al. (2020) a P-value, less than 0.05 indicate

statistical significance; therefore, the developed model is statistically significant. This implies that the developed model is suitable for determining the relationship between the significant and response variables. The lack of fit was determined to be insignificance (F-value =12.02), implying that the quadratic model can represent the entire experimental data. The large F-value for the lack of fit can be attributed to the experimental noise (Azman, et al., 2020).

The significance of the independent variables was also determined based on the P-value and the F-value. A small P-value and a large F value imply that the variable is significant. As a result, it can broadly impact the response variable when varied (Roselan, et al., 2020). From Table 5-5, B and C are insignificant since the p-value is far greater than 0.05. Whereas C (catalyst loading), A^2, C^2 are significant, and A (Temperature) is slightly significant. The developed model did not show any significance for any of the two-way interaction's variables, implying no interaction between any of the variables. Although these insignificance terms contribute to the error, they were not eliminated for this study. As they only reduce the R^2 slightly.

The developed quadratic model was then used to determine the optimum conditions for the epoxide ring-opening reaction. The results for the optimum conditions have been displayed in Table 5-6

Table 5-6 The optimum condition for the castor oil epoxide ring-opening

Reaction temperature (°C)	Reaction time (h)	Catalyst loading (wt%)	Molar ratio 2-hexyldecanol: eCO	Predicted Hydroxyl value (Mg KOH/g)	Experimental Hydroxyl value (Mg KOH/g)
140	20	2	1	239,952	236.4

The experimental hydroxyl value was 236.4 mg KOH/g, while the predicted was 239.95(mg KOH/g). This yielded an error of 1.10%. This proves that the developed correlation accurately predicts the actual hydroxyl value.

5.7 The Ring-opened epoxidized castor product confirmation

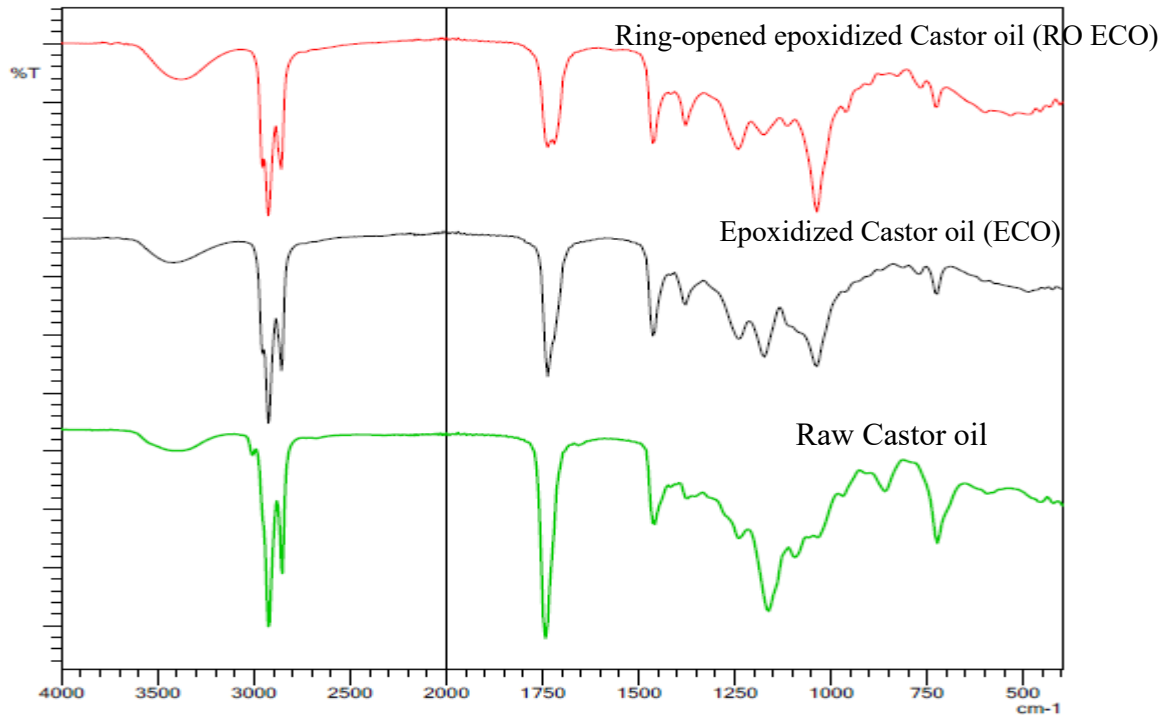


Figure 5-3 The FTIR spectra of raw castor oil (CO), epoxidized castor oil (ECO) and Ring opened castor oil (RO-CO)

Figure 5-3 shows the FTIR spectra of raw castor oil, epoxidized castor oil, and the ring-opened product. One of the most important signals that distinguish it from other vegetable oils is the broad peak at 3406 cm-1 that corresponds to the ricinoleic fatty acids hydroxyl group (O-H). The castor oil has a characteristic peak appearing at a wavenumber of 3009 cm ^{1}. The peak at 3009 cm^{-1} indicates the presence of C-H stretching from the C=C-H. However, the peak disappears once the epoxidation reaction is complete. This implies that the raw castor oil's alkene (-C=C-) bonds have completely reacted during the reaction. A new peak is observed at 810 cm^{-1} for the epoxidized castor oil, denoting the presence of the epoxy-functional group. The peak at 3400 cm^{-1} for the ring-opened is more pronounced compared to the other sample's spectrum. This can be attributed to the extent of O-H bond stretching present in the ring-opened epoxidized castor oil. The presence of the hydroxyl O-H group in the ring-opened product further confirms the opening of the oxirane ring from the epoxidized product.

5.8 Physicochemical properties

5.8.1 Acid number

The method described in paragraph 4.8.1 was applied for the total acid number analysis of the raw castor oil and castor oil-based biolubricants.

Table 5-7 shows the results obtained for the acid number for the castor oil biolubricant and raw oil. In addition to the biolubricants quality, an acid number can also be used to determine the oil's free fatty acid (FFA) content. According to Leung et al. (2010), % FFA must be less than 2.5% for the oil to undergo transesterification. According to the results shown in Table 5-7, the raw castor oil FFA content was calculated to be less than 2.5%. The percentage FFA content was reduced through acid esterification.

The RO-eCO had the highest acid number of 24.43 $mgKOH/g$ compared to the raw WCO and WCO-TMP. The high acid number can be attributed to the use of acid catalysts during epoxidation reaction. However, the acid number is still within the acceptable range of 0.20 to 50.00 mg KOH g-1 for engine oil, as stated by Danjuma and Dandago (2009) and Muhktar et al. (2014).

Table 5-7 The Total acid number measurement for the Castor Oil biolubricants

Sample	Test1 ($mgKOH/g$)	Test 2 ($mgKOH/g$)	Test 3 ($mgKOH/g$)	Average
Raw Castor Oil (WCO)	5.41	5.46	4.41	5.09
Esterified Castor oil	1.90	3.28	3.37	2.85
Castor Oil TMP esters (WCO-TMP)	1.44	2.24	3.97	2.55
Ring Opened epoxidized Castor Oil (RO-eWCO)	22.87	22.99	27.42	24.43

5.8.2 Density

The procedure and apparatus used for density analysis are described in paragraph 4.8.2. Figure 5-4 shows the density of castor oil biolubricants at different temperatures. The density of RO-eCO biolubricant was determined to be the highest compared to the other biolubricants. The

high density of the RO-eCO could be due to the extended chain length during the oxirane ring-opening reaction. Rios et al.(2020) also reported an increase in the castor oil's density after the ring-opening reaction. Various standards require the density of lubricant to be specified at 15°C. The density at 15°C of the raw CO, CO-TMP and RO-eCO was then determined to be 955, 948 and 967 kg/m^3, respectively.

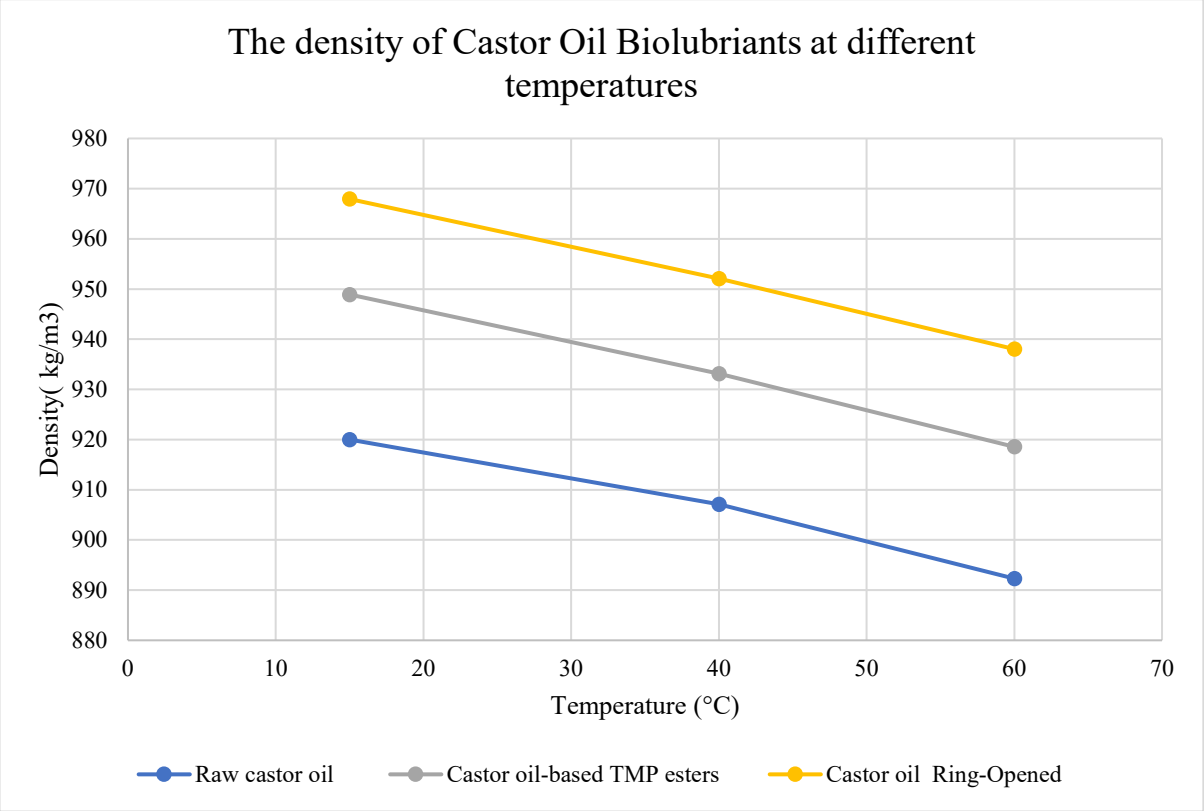


Figure 5-4 The density of Castor Oil based biolubricants at different temperatures

In an effort to improve the lubricity of the biolubricants nanoparticles were added to the synthesised biolubricants. The addition of nanoparticles on the base oil had increased the density of the nano-biolubricant. However, the trend of density with respect to temperature remains unchanged. The density decreases as the temperature increases. The effect of both SiO_2 and CuO nanoparticles were the same irrespective of the biolubricant.

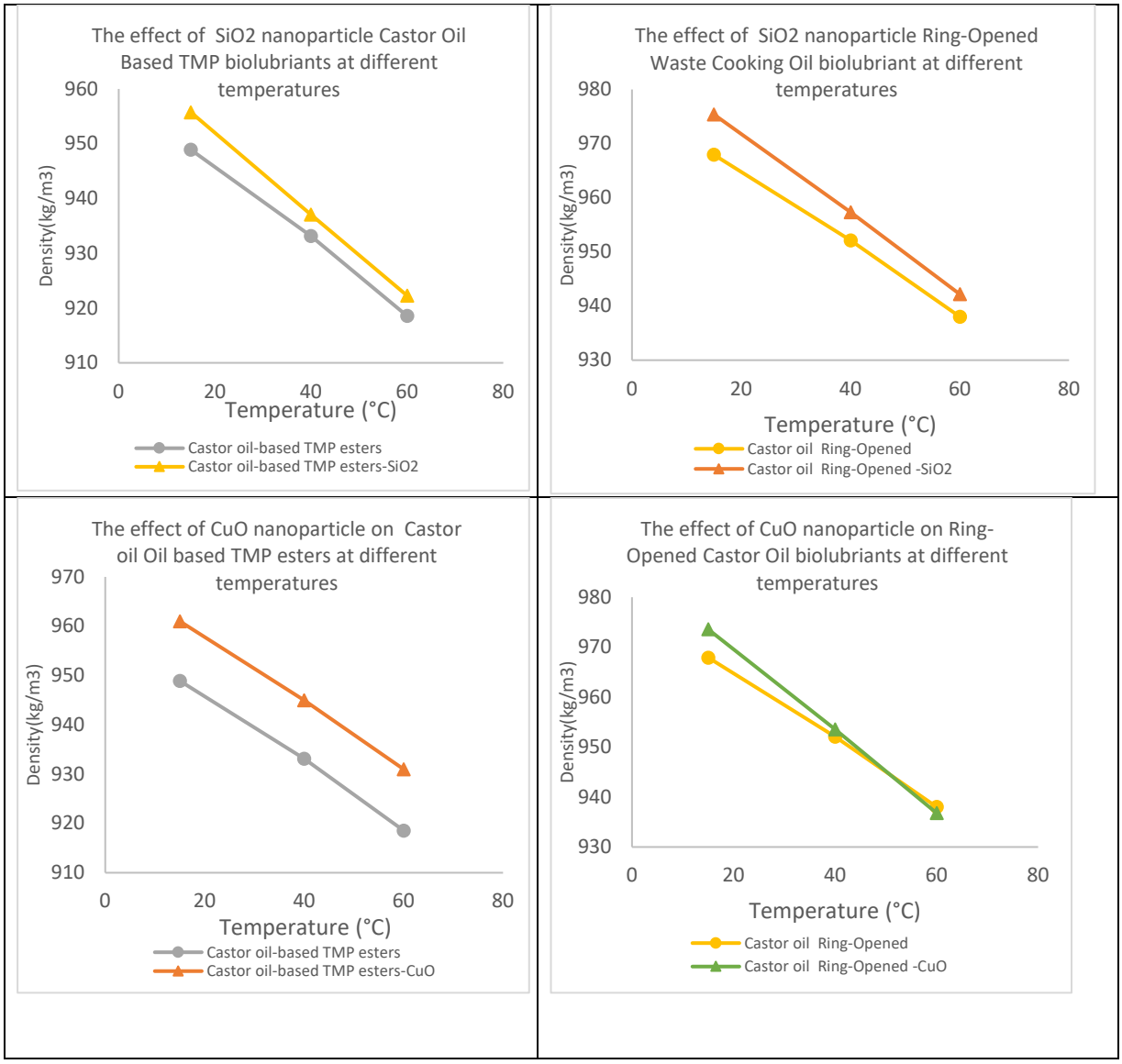
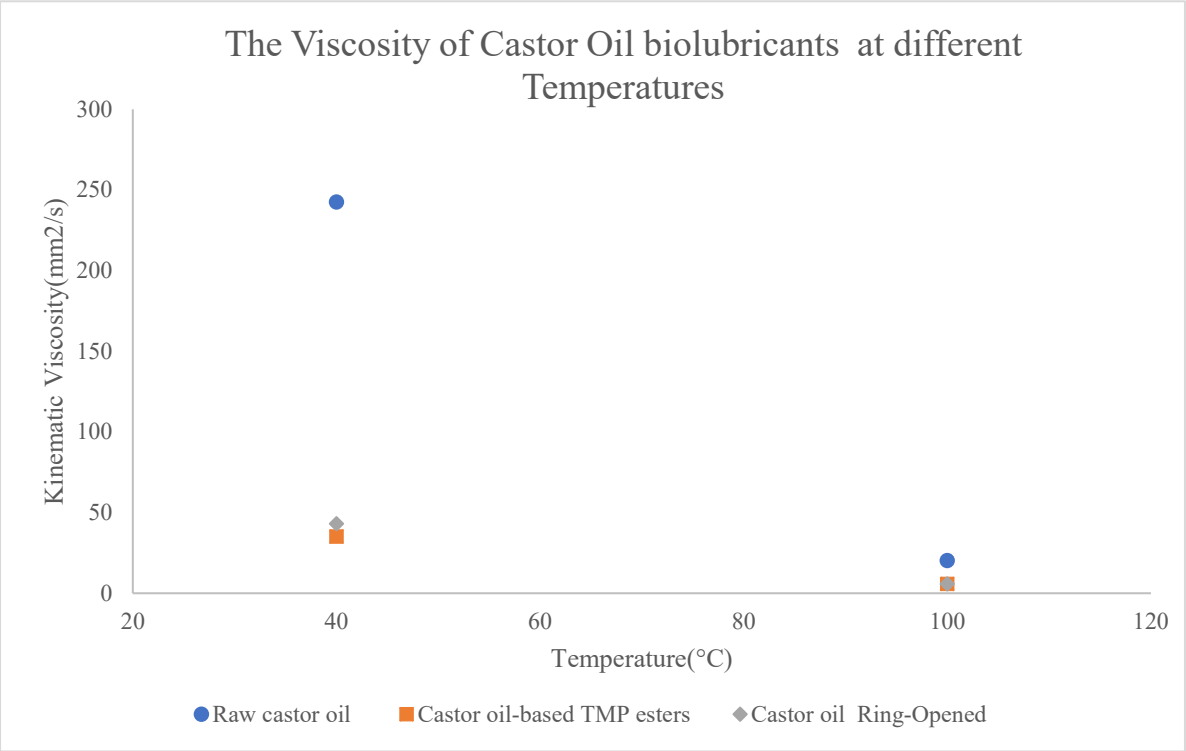


Figure 5-5 The effect of nanoparticles on the castor oil-based biolubricants

5.8.3 Viscosity and viscosity index

The procedure and apparatus described in paragraph 4.8.3 were used to determine the kinematic viscosity of castor oil-based biolubricant. The raw castor oil kinematic viscosity was determined to be used as a reference. The kinematic viscosity was determined to be 223 and 21 mm^2/s at 40 and 100°C, respectively. In earlier work, the kinematic viscosity of 226.6 and 19.72 mm^2/s at 40 and 100°C were determined for castor oil (Salih, et al., 2011). Similar results were also reported by Yunus et al. (2004). The viscosity index was calculated to be 67. The low viscosity index is due to the significant change in the oil's kinematic viscosity when the temperature is varied. Castor oil generally has a very high kinematic viscosity compared to most vegetables but an extremely low viscosity index (Gokdogan, et al., 2015) .



The kinematic viscosity of the castor oil-based TMP esters was determined to be 35 and 5.7 mm^2/s at 40 and 100°C, respectively. Other researchers have reported the value of 45.3 and 9.31 mm^2/s at 40 and 100°C (Musa, et al., 2015). Similarly, the values of 20.94 and 4.5 mm^2/s were reported by Silva et al. (2013). The difference between the values could be attributed to the different fatty acids present in the raw castor oil and process conditions. Based on Automotive Lubricant Viscosity Grades: Engine Oils – SAE J 300, Dec. 1999, the castor oil-based TMP biolubricant conforms to the SAE 20 viscosity grade. The viscosity index of CO-TMP was determined to be 101.05. Based on the engine oil specifications reported by Inkerd et al.(2015), the CO-TMP biolubricant viscosity index is within the engine oil standard (VI>90).

Numerous studies have shown that epoxidized vegetable oils often have poor low-temperature properties; hence, it is necessary to carry out further processes to improve the lubricity of the biolubricant (McNutt & He, 2016; Syahir, et al., 2017). Although the epoxidized product is not required as the final product in the current study, the viscosity was measured to determine the effect of the oxirane ring-opening reaction. The kinematic viscosity of the epoxidized CO biolubricant was determined to be 230 and 25mm^2/s at 40 and 100°C, respectively. There was

a slight increase in the kinematic viscosity from the raw CO. This can be attributed to the decrease in the degree of unsaturation(C=C) as the raw castor oil goes through the epoxidation reaction. Similar results were reported by Somidi et al. (2014).

The kinematic viscosity of the ring-opened epoxidized castor oil (RO-eCO) biolubricant was determined to be 55.00 and 7.86 mm^2/s at 40 and 100°C, respectively. Due to the ring-opening reaction, the kinematic viscosity has decreased from the epoxy castor oil. These results agree with the observation made by Madankar et al.(2013) on the ring-opened epoxidized canola oil biolubricant. Particularly the results obtained for the epoxidized canola oil that was ring-opened with 2-ethylhexanol. According to the Automotive Lubricant Viscosity Grades: Engine Oils – SAE J 300, Dec. 1999, the RO-eCO biolubricant conforms to the SAE 20 viscosity grade. The viscosity index was calculated to be 101.05.

1.1.1.3 The effects of nanoparticle additives on kinematic viscosity of the castor oil-based biolubricants

The silicon dioxide and copper oxide nanoparticles were added to the castor oil-based lubricants. The same procedure performed for the biolubricant without the additives was followed. Figure 5-6 below shows the effect of the nanoparticle on the kinematic viscosity of the synthesised biolubricants. Based on Figure 5-6, the kinematic viscosity increases as the nanoparticles are added. However, the SiO_2 nanoparticles are observed to have superior effect on the base biolubricant compared to CuO. For instance, the change in kinematic viscosity was calculated to be between 3 to 10% for CuO and 11 to 16% for SiO_2. Similar results were observed by Cortes and Ortega (2019) after adding the nanoparticles into the sunflower oil flower oil.

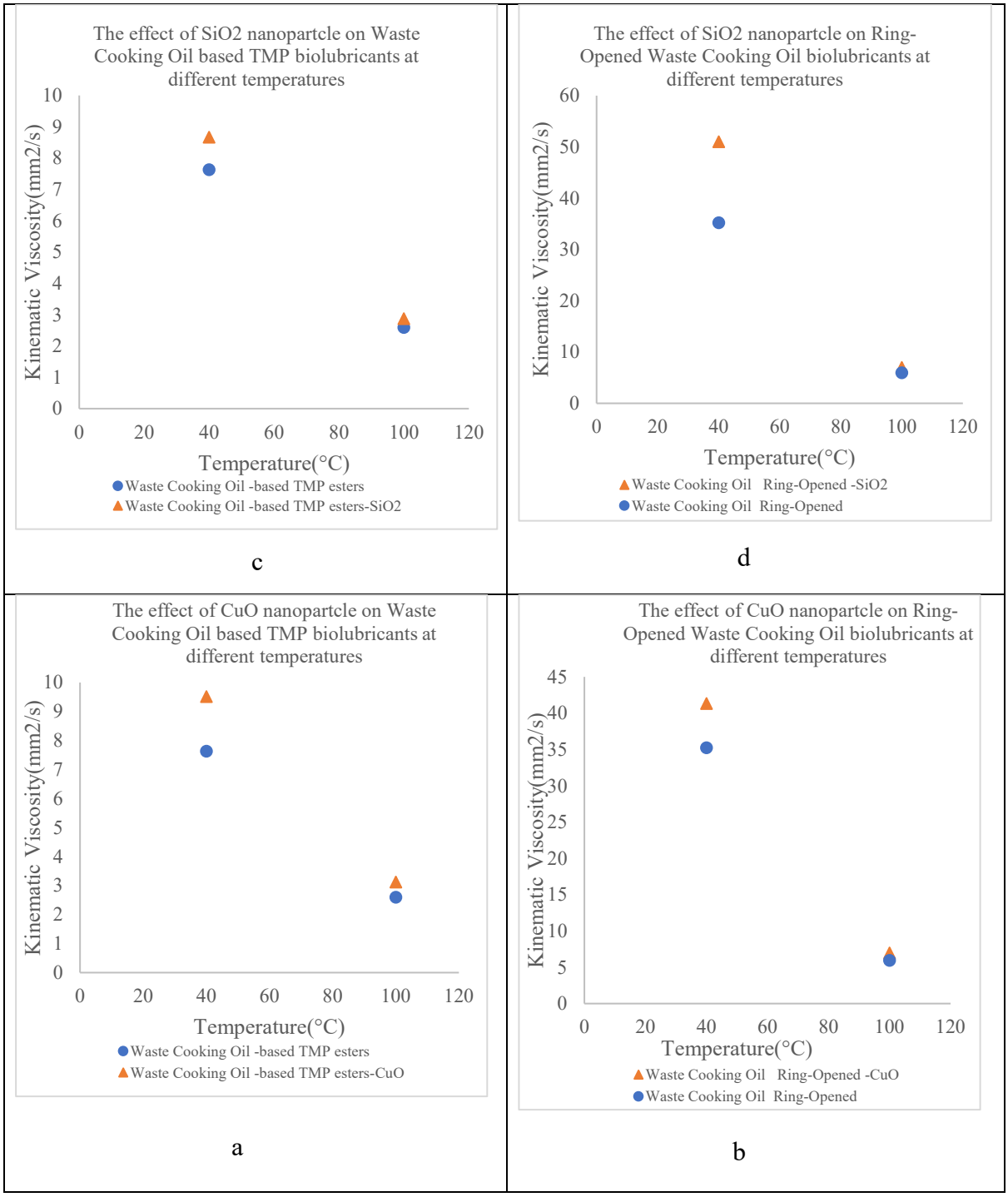


Figure 5-6 The effect of silicon dioxide and copper oxide nanoparticles on the castor oil produced biolubricants

5.8.4 The pour point and cloud point

Pour point is one of the crucial low-temperature properties of biolubricant. This property is used to tell if the oil will flow in between the two sliding metals at low temperatures. In regions where the temperature becomes very low, it is required that the lubricant has the lowest possible pour point. Low pour points are required to ensure that the engine is well lubricated during cold conditions. According to the literature, the pour point depends on the structure and the viscosity (Menkiti, et al., 2017).

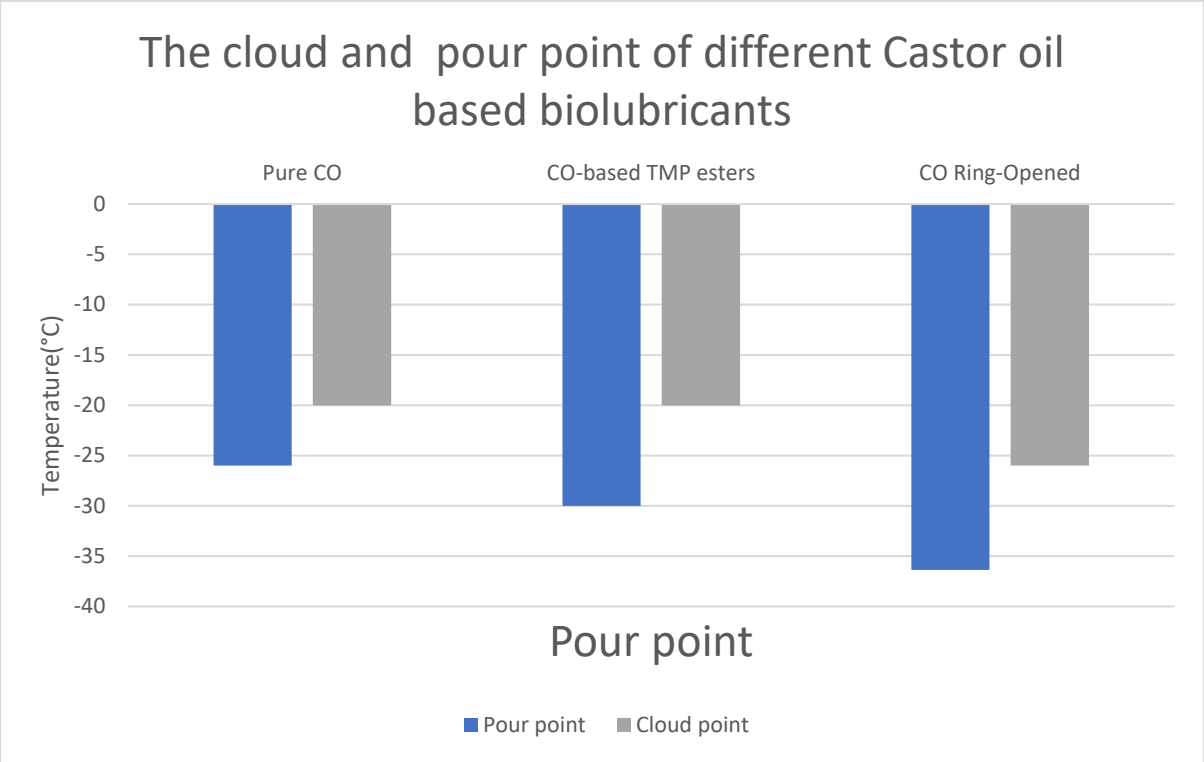


Figure 5-7 The cloud and pour point of castor oil-based biolubricants

The determination of the pour point was done in accordance with ASTM -97. Figure 5-7 presents the pour point temperature of the raw Castor Oil (raw CO), Castor Oil-based TMP esters (CO-TMP) and Ring-Opened epoxidized Castor Oil (RO-eCO). The pour point of the raw CO was determined to be -26°C. Previous researchers have reported the value of -27°C for the raw castor oil pour point (Salih, et al., 2011; Syahir, et al., 2017).

The pour point of castor oil methyl ester before it was reacted with TMP was determined. The COME's pour point was determined to help understand the effect of transesterification reaction with TMP. The pour point 5°C was measured for the COME. After the reaction was complete, the CO-TMP biolubricant was measured. The CO-TMP biolubricant had the recorded pour

point temperature of -30°C, indicating an improvement after the transesterification of the COME. According to Arbain and Salimon (2009), the pour point can be improved due to the higher degree of branching esters. The low pour point for castor oil biolubricant can be attributed to the higher degree of saturation(C=C) present in the castor oil biolubricant. According to the GCMS analysis performed earlier, the castor oil methyl ester contained over 60% of the unsaturated content.

The cloud and pour points of RO-eCO were determined to be -30°C and -36°C, respectively. The decrease in the pour point from -26°C of the raw castor oil could be due to the increase in the chain length of the ring-opened product. According to Madanhire and Mbohwa (2016), molecular crystalization is inhibited by the presence of a large branching point which creates a steric barrier around the individual molecule. As a result, the cloud and pour point decreases due to the presence of a large branching point. The low pour point of the RO-eCO follows the same trend observed by Madanhire and Mbohwa (2016) for the ring-opened epoxidized canola oil. Similar results were reported by Riosa et al. (2020) for the chemical modification of castor oil fatty acids.

1.1.1.4 The effects of nanoparticle additives on cloud and pour point of the castor oil-based biolubricants

The silicon dioxide and copper oxide nanoparticles were added to the castor oil-based lubricants (base oil). A 1wt% fraction of the additive was added to the based oil. There was no effect on both the cloud and pour point of the biolubricant observed.

Chapter 6 -Tribological study

One critical part of the lubricant is to understand the tribological performance. The tribological study focuses on the friction and wear of interacting surfaces. When a lubricant is applied, it forms a layer between two interacting surfaces. As a result, less heat is generated, and wear is reduced. Tribometers such as four-ball tribometer and ring on disc tribometers are often used to conduct the tribological performance. However, this equipment is expensive and not readily available. Previously researchers have studied the relationship between different physicochemical properties and tribological parameters (Thapliyal & Thakre, 2017; Abdo, 2008; Trzos, et al., 2013). Various mathematical and statistical strategies have been used to establish empirical relationships between physicochemical parameters. In this context, different vegetable oils in literature were studied and a correlation between the tribological parameters and physicochemical properties was established.

Table 6-1 The physicochemical and tribological properties of the biolubricants oil

Biolubricant /Vegetable oil	Density (15°C) g/cm^3	Viscosity(mm^2/s) @40°C	Coefficient of friction	Reference
TMP Palm oil	0.8549	101.86	0.68	(Yunus, et al., 2013)
Palm Olein	0.8975	38.08	0.105	(Bahari, 2017)
Soybean Oil	0.9075	30.72	0.112	(Bahari, 2017)
TMP ester added with nanoparticle	0.8553	108.75	0.8553	(Yunus, et al., 2013)
OL	0.8549	101.86	0.069	(Zulkifli, et al., 2013)
TMP1	0.8553	108.75	0.065	(Zulkifli, et al., 2013)
TMP3	0.8558	107.21	0.05	(Zulkifli, et al., 2013)
TMP5	0.8562	101.42	0.055	(Zulkifli, et al., 2013)
TMP7	0.8568	102.15	0.054	(Zulkifli, et al., 2013)
TMP10	0,8583	97,637	0,065	(Zulkifli, et al., 2013)

The causal correlations between the coefficient of friction (COF) and physicochemical characteristic features were estimated using regression analysis. The linear regression technique is used to determine a causal relationship between a dependent variable and two or more independent variables. The parameters of interest in the study included the dependent variable viz. COF and independent variables kinematic viscosity at 40°C and density at 15°C. The variables for the selected biolubricants obtained from different literature sources are displayed in Table 6-1.

The data in Table 6-1 was regressed using a single order multiple regression. Subsequently, the regression statistics were established. The correlation coefficient(R^2) and standard error(E) were determined to be 0.8711 and 0.0087282, respectively. These results indicate a strong relationship between the variables. The predicted R^2 was calculated to be 0.9615. This value implies that the model can predict the COF with 78.53% accuracy. Additionally, the Analysis of variance (ANOVA) was done to determine how much variability is in the regression model. The ANOVA table with the relevant parameters has been displayed in Table 6-2 below.

Table 6-2 Analysis of variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	2	0,005665	0,002833	37,18	0,000
Density	1	0,000047	0,000047	0,62	0,448
Kinematic Viscosity	1	0,000206	0,000206	2,70	0,128
Error	11	0,000838	0,000076		
Lack-of-Fit	6	0,000833	0,000139	134,33	0,000
Pure Error	5	0,000005	0,000001		
Total	13	0,006503			

The p-value and the F-value of the regression model were determined to be 0.048 and 215, respectively. According to Martín et al.(2020) P-value, less than 0.05 indicate statistical significance; therefore, the regression model is statistically significant. Density has a P-Value of 0.448, which is greater than the P-value determined for the viscosity. A P-value greater than 0.1 indicates that the variable is statistically insignificant (Zhang & Zheng, 2009) . Additionally, viscosity is considered less insignificant than the density since the P-value of the viscosity is closer to 0.05 compared to density. This implies that the density does not greatly affect the COF compared to viscosity. Table 6-3 contains the coded coefficients for analysing variability. Coefficients represent the magnitude and direction of the relationship between

variables and response variables in the model. All coefficients are in coded units to minimize multicollinearity between variables. While the other variables are held constant, the coefficient for a variable shows the change in the mean response associated with an increase of one coded unit in that variable. The coefficient sign indicates the direction of the relationship between the dependent and independent variables.

Table 6-3 Coded coefficients table for Analyse Variability

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0,881	0,961	0,92	0,379	
Density	-0,82	1,04	-0,79	0,448	99,36
Kinematic viscosity	-0,001166	0,000709	-1,64	0,128	99,36

The coefficient of intercepts and independent variables are then determined, as shown in Table 6-3. The regressed linear equation is written as follows:

$$COF = 0.881 - 0.82 * \rho_{15°C} + 0{,}001166 * \nu_{40°C} \ldots. \ (6-1)$$

$$\nu_{40°C} = Kinematic\ viscosty\ at\ 40°C\ in \frac{mm\text{^}2}{s}$$

$$\rho_{15°C} = Density\ at\ 15°C\ in \frac{g}{cm^3}$$

The model was validated using further experimental data available in the literature (Kiu, et al., 2017). The model was found to be reasonably accurate, within an error of less than 10%.

6.1 Estimation of the Waste Cooking Oil biolubricants coefficient of friction

The regressed equation 6-1 above was used to estimate the coefficient of friction for the produced waste cooking oil biolubricants. A decrease in the coefficient of friction implies that the biolubricant is efficient in reducing friction and subsequently saves energy and ensure a long life for the engine. The results for the estimated COF have been shown in Table 6-4. The RO-eWCO had the lowest COF compared to the other biolubricants.

Table 6-4 The estimated Coefficient of friction for Waste Cooking Oil biolubricants

	WCO	WCO-TMP	RO-eWCO
Density ($\frac{g}{cm^{-1}}$)	0,923	0,884	0,955
Kinematic viscosity ($\frac{mm^2}{s}$)	43,59	7,63	35,23
Coefficient of friction	0,073	0,147	0,057

6.1.1 The effect of nanoparticles on the estimated Coefficient of friction for waste cooking oil biolubricants

The results shown in Table 6-5 illustrate nanoparticles' effect in WCO-TMP and RO-eWCO. The RO-eWCO had, on average, the lowest COF compared to WCO-TMP. The addition of 1wt% of SiO_2 and CuO decreased the COF of WCO-TMP. The most significant decrease in the COF of the WCO-TMP biolubricant was recorded for the WCO-TMP biolubricant with CuO. However, the CuO had a different effect on the RO-eWCO's COF, where an increase of 52% was observed. Trajano and Moura (2014) observed similar results when studying the effect of CuO on epoxidised sunflower oil. Chiñas-Castillo and Spikes (2000) also warned about the detrimental effect of nanoparticles on the biolubricants. The SiO_2 still maintained the same effect it had on the WCO-TMP. The COF decreased by 38%, from 0.057 to 0.035. Based on the results presented in Table 6-5, it is evident that the addition of nanoparticles has a significant effect on the friction reduction of lubricants. In addition, the SiO_2 nanoparticles are better than the CuO.

Table 6-5 The estimated coefficient of friction for waste cooking oil biolubricants with nanoparticles

	WCO-TMP			RO-eWCO		
	Pure	SiO_2	CuO	Pure	SiO_2	CuO
Density ($\frac{g}{cm^{-1}}$)	0.898	0.911	0.964	0.955	0.959	0.91
Kinematic viscosity ($\frac{mm^2}{s}$)	7.63	10.63	9.52	35.23	51.01	41.34
Coefficient of friction	0.147	0.122	0.079	0.057	0.035	0.087

6.2 Estimation of the Castor oil biolubricants coefficient of friction

Similarly to the waste cooking oil biolubricant, the regressed equation was used to estimate the coefficient of friction for the castor oil biolubricant. The results have been displayed in Table 6-6. It is clear from the results that the chemical modification methods applied to the raw castor oil had reduced COF. A reduced COF means less friction and subsequently, less wear occurs. As a result, the energy used by the engine is reduced. The RO-eCO had the lowest COF of 0.024 compared to the CO-TMP.

Table 6-6 The estimated Coefficient of friction for castor oil biolubricants

	CO	CO-TMP	RO-eCO
Density	0.955	0.948	0.967
Kinematic viscosity	223	35.09	55
Coefficient of friction	0.162	0.063	0.024

6.2.1 The effect of nanoparticles on the estimated Coefficient of friction for castor biolubricants

The regressed equation for COF was also applied to determine the effect of nanoparticles on the coefficient of friction for castor oil biolubricants. Table 6-7 shows the effect of adding wt% of SiO_2 and CuO nanoparticles on the coefficient of friction for the produced castor oil biolubricants. According to the results shown in Table 6-7, the addition of SiO_2 and CuO decreased the COF for the biolubricant. The addition of SiO_2 into CO-TMP and RO-eCO biolubricant decreased COF by 17% and 58%, respectively. On the other hand, CuO nanoparticle added into the CO-TMP and RO-eCO biolubricant decreased COF by 23% and 37%, respectively. Based on these results, it can be concluded that the addition of 1wt% nanoparticles improves the tribology of the biolubricants.

Table 6-7 The estimated Coefficient of friction for castor oil biolubricants with nanoparticles

	CO-TMP			RO-eCO		
	Pure	SiO_2	CuO	Pure	SiO_2	CuO
Density ($\frac{g}{cm^{-1}}$)	0.948	0.955	0.961	0.967	0.975	0.973
Kinematic viscosity ($\frac{mm^2}{s}$)	35.09	39.48	38.62	55.00	61.199	58.5
Coefficient of friction	0.063	0.052	0.048	0.024	0.010	0.015

Chapter 7 Conclusions

The production of environmentally friendly biolubricants through chemical modification methods, viz. two-step base-catalysed transesterification method, epoxy ring-opening of the epoxidized vegetable oil and addition of nanoparticles, was achieved. The synthesised biolubricants were subjected to various characterizations methods to investigate their suitability for engine application. Therefore, based on the investigations made, the following broad conclusions are made:

- A yield of 70% was achieved for the production of waste cooking oil methyl ester (WCOME) through the abased catalysed transesterification method.
- The optimisation to produce waste cooking oil TMP triesters was achieved using a four-factor Box-Behnken design of experiment in Minitab
- The optimised conditions to produce waste cooking oil TMP triesters were obtained at the temperature of 140°C, catalyst loading of 0.5wt%, the reaction time 3 hours of and WCOME to TMP ratio of 4.55:1 molar ratio
- The epoxidation of the WCO achieved an oxirane content of 5.2%
- The optimised conditions for the production of ring-opened epoxidized waste cooking oil using 2-hexyldecanol were obtained at the temperature of 120°C, catalyst loading of 1.06wt%, the reaction time 20 hours of and 2-hexyldecanol to eWCO molar ratio of 1:1
- The WCO based TMP esters and ring-opened were successfully confirmed through a GCMS and FITR analysis.
- The total acid number of the WCO based TMP esters and RO-eWCO were determined to be 0.88 and 14.26 mg KOH/g respectively. They were all within the acceptable range of the engine biolubricants.
- The density of Ring-opened eWCO was higher than WCO based TMP esters biolubricant
- The nanoparticles increased the density of the WCO based biolubricants
- WCO-TMP biolubricant had the lowest kinematic viscosity compared to the rest of WCO-TMP biolubricant. As a result, it could not be used as an engine lubricant
- RO-eWCO conforms to SAE20 engine oil requirements
- RO-eWCO had the lowest pour point and met the requirements for engine oil application. While did not meet the maximum required Pour point of -5°C
- The thermal stability of the RO-eWCO increased from 339 to 360°C while TMP

- The castor oil was first subjected to acid esterification to reduce the free fatty acid from 2.59 to 1.42% FFA
- A yield of 83% was achieved for the production of castor methyl ester (COME) through the base catalysed transesterification method.
- The optimisation for the production of CO TMP triesters was achieved using a four-factor Box-Behnken design of the experiment in Minitab
- The optimised conditions to produce castor oil TMP triesters were obtained at the temperature of 140°C, catalyst loading of 0.52wt%, the reaction time 3 hours of and COME to TMP ratio of 5:1 molar ratio
- The epoxidation of the CO achieved an oxirane content of being 5.36%
- The optimised conditions for the production of ring-opened epoxidized castor oil using 2-hexyldecanol were obtained at the temperature of 140°C, catalyst loading of 2wt%, the reaction time of 20 hours and 2-hexyl decanol to eCO molar ratio of 1:1
- The CO based TMP esters and RO-eCO were successfully confirmed through a GC-MS and FITR analysis.
- The total acid number of the CO based TMP esters and RO-eCO were determined to be 2.55 and 24.43 mg KOH/g respectively. They were all within the acceptable range of the engine biolubricants.
- The density of Ring-opened eCO was higher than CO-based TMP esters biolubricant
- The nanoparticles increased the density of the CO-based biolubricants
- CO-TMP biolubricant had the lowest kinematic viscosity compared to CO-TMP based biolubricant. As a result, it could not be used as an engine lubricant
- RO-eCO and CO-TMP biolubricants conform to SAE20 engine oil requirements
- RO-eCO had the lowest pour point and met the requirements for engine oil application.
- The COF correlation was developed to estimate the coefficient of friction for the produced biolubricant.
- It was found that the nanoparticles increased both the density and viscosity of the biolubricant. As a result, the COF was also affected.

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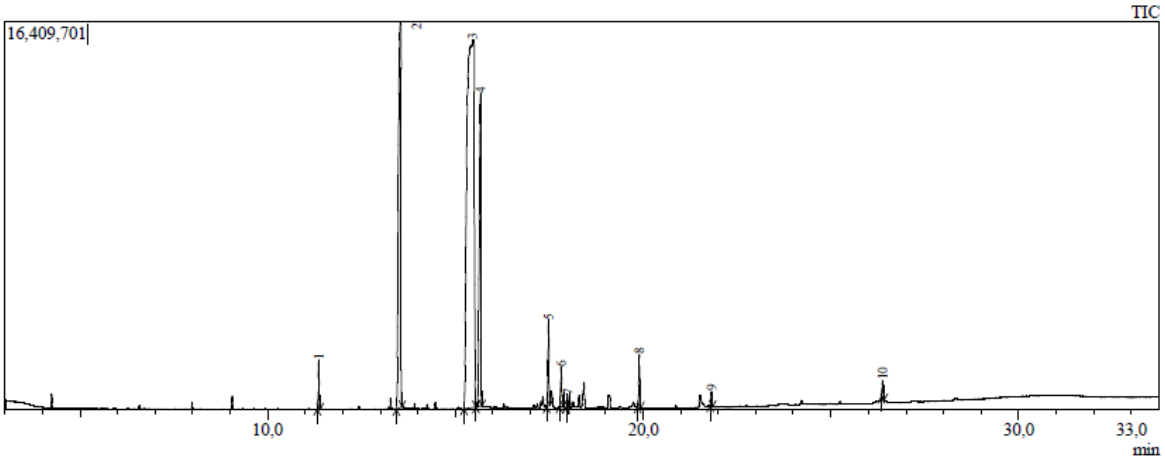
Appendix A -Sample calculations

Molar mass of WCOME



Peak NO.	Name	Composition	Molar mass	
1	Methyl tetradecanoate	0.0086	245	2.10
2	Hexadecanoic acid. methyl ester	0.2278	270	61.50
3	9-Octadecenoic acid, methyl ester, (E)-	0.5992	294	176.16
4	Methyl stearate	0.1096	298	32.66
5	9-Octadecenoic acid, 12-hydroxy-, methyl ester, (Z)-	0.0207	312	6.45
6	Eicosanoic acid, methyl ester	0,0114	374	4.26
7	4S,8aR,9R,12S,12aR)-9,12-Dihydroxy-4-methyldodecahydro-2H-benz	0.0029	256	0.74
8	Methyl 20-methyl-heneicosanoate	0.0115	354	4.07
9	Tetracosanoic acid, methyl ester	0.0031	384	1.19
10	1-Glyceryl ricinoleate	0.0053	298	1.57
				290,74

Malar mass of WCOME

$$Avg\ MM_{Biodiesel} = \sum_i Average\ composition_i \times MM_i = 290.74 \frac{g}{mol}$$

50 g of WCOME Added

$$m_{WCOME} = 50\ g$$

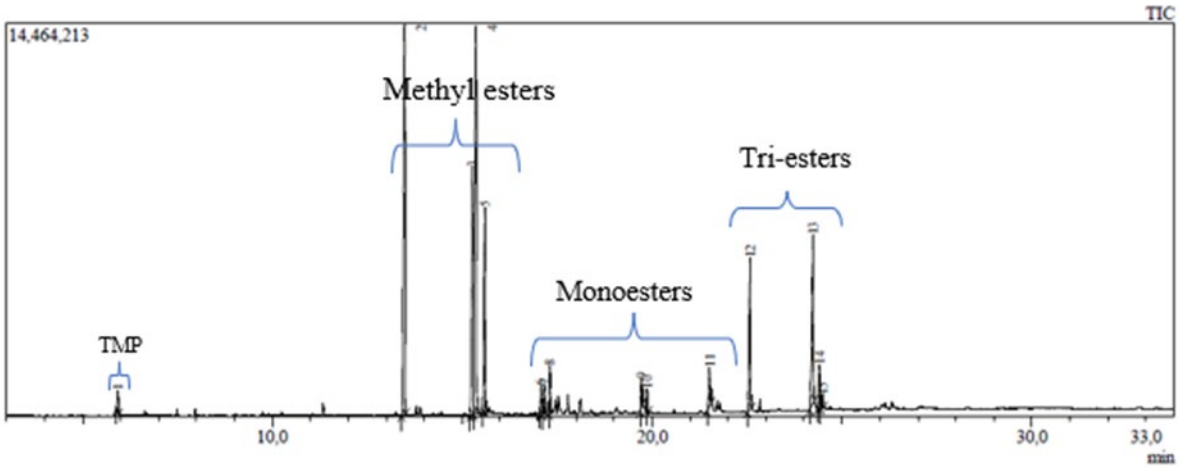
$$n_{WCOME} = \frac{50}{290} = 0.1724\ moles$$

For WCOME: TMP of 3:1

$$TMP\ moles\ required = 0.1724 * \frac{1}{3} = 0.05747\ mooles$$

$$TMP\ mass\ required = n * MM_{2-hexyldecanol} = 0.05747 * 242.44 = 13.93g$$

Yield calculations



$$\%\ TMP\ Coversion = \frac{initial\ mass\ of\ TMP - final\ mass\ of\ TMP}{Inital\ mass\ of\ TMP} \ldots (3-2)$$

The reaction mixture at the end of reaction =60 g

$$\%\ TMP\ Coversion = \frac{initial\ mass\ of\ TMP - final\ mass\ of\ TMP}{Inital\ mass\ of\ TMP}$$

$$= \frac{13.93 - 0.0071 * 60}{13.93} = 96.7$$

Composition of the product

Monoesters=0.035

Diesters=0

Triesters=0.178

Mass of each product

Monoesters=0.035*60=2.1g

Diesters=0

Triesters=0.178*60=10.68g

$$product\ selectivity = \frac{mass\ of\ the\ desired\ product}{mass\ of\ all\ the\ products\ produced} = \frac{10.68}{10.68 + 2.1} = 0.8356$$

$$\%\ yield = \frac{0.8356\ \times\ 96.7}{100} = 80.8\ \%$$

The oxirane oxygen content calculations

$$The\ oxirane\ oxygen\ content(Epoxide\ value) = \frac{1.60 * N * Volume\ of\ Hbr}{mass\ of\ a\ sample\ (g)} \ldots . (3-5)$$

$$The\ oxirane\ oxygen\ content(Epoxide\ value) = \frac{1.60 * 0.5 * 5.2}{3} = 5.2\%$$

$$Relative\ conversion\ to\ oxirane\ = \frac{experinmental\ oxirane\ oxygen\ content}{Theoretical\ oxirane\ content}$$

$$= \frac{5.2}{6.4} * 100 = 81.25\%$$

Hydroxyl value calculations

$$HV\left(\frac{mgKOH}{g}\right) = \frac{[(blank\ volume(ml) - sample\ volume(ml)\ ]) * Normality * 56.1}{sample\ mass(g)} + acid\ number$$

$$HV\left(\frac{mgKOH}{g}\right) = \frac{[(10 - 4.3\ ]) * 0.5 * 56.1}{1} + 14.26 = 174.45\ mgKOH/g$$

Viscosity index calculations

Waste cooking oil viscosity index

Kinematic viscosity at 40°C= 43.59 mm2/s
Kinematic viscosity at 100°C= 9.53 mm2/s

Using TABLE 1 of Designation: D2270 – 10.

L = 135.3
H = 76.91

U=43.59 mm2/s

Since U < H = , the equation below was used

$$VI = \frac{[(antiLogN) - 1]}{0.00715} + 100$$

$$N = \frac{\log H - logU}{logY}$$

$$Y^N = \frac{H}{U}$$

Using the values obtained above

$$N = \frac{\log H - logU}{logY} = 0.2518$$

$$VI = \frac{[(antiLogN) - 1]}{0.00715} + 100 = 209.90$$