



A critical review on vegetable oil-based bio-lubricants: preparation, characterization, and challenges

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Abstract

Lubrication is a procedure that involves the use of a chemical called lubricant to reduce wear on surfaces that are in relative motion with each other. It aids in the transmission of pressure created between opposing surfaces. Lubricants serve as anti-friction agents. They allow for flat-level operations by retaining superior machine functionality and reducing the likelihood of recurring breakdowns. In today's world, the price of crude oil is rising in tandem with the depletion of reservoirs (oil). As a result, protecting a pollution-free environment is a major responsibility. The focus of current research is on creating and using an ecologically friendly lubricant made from renewable resources. This paper discusses the preparation, characteristics, characterization advantages, and uses of vegetable oil-based non-edible lubricants. Chemical changes are required since vegetable oil-based lubricants have lower thermal and oxidative stability. The article explores the required chemical modification approaches for improving the properties of bio-lubricants. The characterization of bio-lubricants has been elaborately discussed, highlighting the major pros and cons. The drawbacks and also future scope of the bio-lubricants have been highlighted.

Keywords Lubricants · Vegetable oil · Transesterification · Epoxidation · Characterization · Nanoparticle's additives

Abbreviations

VI	Viscosity Index
IMR	Infant mortality rate
IC	Internal Combustion
UBHC	Unburnt hydrocarbons
TMP	Trimethylol propane
NaHCO ₃	Sodium methoxide
C ₂ H ₆ CaO ₂	Calcium methoxide
PP	Pour point
ME	Methyl esters
WCO	Waste cooking oil

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Ti	Titanium
SiO ₂	Silicon dioxide
H ₂ SO ₄	Sulphuric acid
H ₂ O ₂	Hydrogen peroxide
cSt	Centistokes
cP	Centipoise
GA	Guizotia abyssinica
TiO ₂	Titanium dioxide
TGA	Thermogravimetric analyser
KOPTE	Karanja polyol tryster
ECO	Epoxidized canola oil
BCO	N-butanol
ACO	Amyl alcohol
EHCO	2-Ethyl hexanol
HRC	Hardness Rockwell C
WVO	Waste vegetable oil
SAE	Society of automotive engineers
Fe	Iron
Cu	Copper
Co	Cobalt
BN	Boron nitride
Cu	Copper
CuO	Cupric oxide
AW	Anti-wear
PAO	Polyalphaolefin
EP	Extreme pressure
MoS ₂	Molybdenum disulphide
Al ₂ O ₃	Aluminium oxide
Fe ₂ O ₃	Ferric oxide
ZrO ₂	Zirconium dioxide
HFRR	High-frequency reciprocating rig
COF	Coefficient of friction
CeO ₂	Cerium dioxide
NO	Nitric oxide
NO _x	Oxides of nitrogen
CO	Carbon monoxide
CO ₂	Carbon dioxide
THC	Total hydrocarbon
HC	Hydrocarbon
O ₂	Oxygen
C ₁₈ H ₃₄ O ₂	Oleic acid
CH ₂ O ₂	Formic acid
CH ₃ COOH	Acetic acid
C ₁₉ H ₃₆ O ₂	Methyl oleate
C ₁₉ H ₃₄ O ₂	Methyl linoleate
hBN	Hexagonal boron nitride
C ₃₂ H ₆₄ O ₄ Sn	Dibutyltin dilaurate
KOH	Potassium hydroxide
Zr (SO ₄) ₂	Sulphated zirconia

1 Introduction

Lubricants are the substances used to reduce the friction between surfaces in contact, and as a result, it reduces the amount of heat generated by these surfaces. It could also transmit forces, move foreign particles, and heat or cool surfaces. Reduced friction is the characteristic of lubricity (Trotsek, 2017). For friction and wear to be reduced, lubrication is necessary. Usually, it is caused by numerous types of sliding, moving, and rotating components (Tung & McMillan, 2004). It can also lower the temperature in the metal-to-metal proximity area. One of the main causes of energy loss is friction. Friction between sliding and moving parts wastes one-third of the world's total energy. Lubricating oil's quality and its kind are essential factors in minimizing the friction. Friction reduction requires a substantial amount of energy in the industries that provide power, industry, and transportation. Additionally, the replacement of mechanical parts, transmission systems, and their processes results in large economic losses (Holmberg & Erdemir, 2007).

Lubricants are commonly utilized in industries, machinery, and engine oil applications (Ahmed et al., 2016). A lubricant aids in the reduction of wear and the avoidance of heat loss from moving contact surfaces. It serves as an insulator in transformer applications. It acts as a medium to defend two mating surfaces from getting corroded and lessen oxidation. It also acts as a sealing agent against smut, dusty powder, water, and dirt. Lubricant acts as an agent to reduce the temperature at the contact zones of metals. High boiling point and low freezing point (to stay liquid over a wide temperature range), high viscosity index (VI), strong thermal stability, hydraulic stability, corrosion prevention, and high resistance to oxidation are all properties of an excellent lubricant (Singh et al., 2017).

1.1 Types of conventional lubricants

1.1.1 Mineral oil

Conventional lubricants are classified into 2 types: mineral oil based and synthetic. Mineral oils are made from highly refined, purified, and processed petroleum. Refining hydrocarbons produce them in crude oil by distillation process. They act as carriers of additives for boundary or solid-film lubrication and are applied as hydrodynamic lubricants (Singh et al., 2017). Mineral oil is one of the petroleum products used as a lubricant for various applications from the past several years and an ingredient for cosmetic and personal care items. Due to its favourable properties as a lubricant for different applications, its consumption is enormous. Crude mineral oil is extensively used in the automotive, railroad, and aviation industries as a lubricant (Sadriwala et al., 2020). Mineral oil is commonly disposed away in the environment during oil changes, resulting in pollution and having an impact on global eco-systems. Mineral oil is a complex mixture of substances with unknown biological activity that causes mutation and carcinogenesis. When it comes to public concern in many developing countries, little attention is paid to managing or reducing health risks caused by mineral oil disposal. It can sometimes contribute to child malnutrition and an increase in infant death rates (IMR) (Salimon et al., 2010). In case its usage in internal combustion (IC) engines is not completely miscible with the basic fuels such as diesel, due to their leakage into the combustion chamber will partially burn to lead to the pollutant formation. Hence, use of mineral oils will increase unburnt hydrocarbons (UBHC), and smoke emissions from the engines. Therefore, mineral oils are amended from being used,

because of severe environmental pollution due to the contamination of combustion products and also damaging the cylinder surface due to the increased rubbing action of metallic additives added to the lubricant (Syahrullail et al., 2013).

1.1.2 Synthetic oil

Synthetic oil is a lubricant composed of chemical compounds that have been artificially synthesized. Chemically modified petroleum components can be made into synthetic lubricants instead of crude oil. The most common starting material is crude oil, which is distilled and then physically and chemically transformed. Compared to traditional mineral-based oils, synthetic lubricants can provide exceptional performance (Afifah et al., 2019). Owing to their low volatility and increased thermal stability, they have a longer service life, promoting environmental sustainability. Synthetic lubricating oil has numerous advantages over mineral lubricating oils, including better low-temperature fluidity, oxidation stability, and thermal stability. It is used as a substitute for petroleum-refined oils when operating in extreme temperature conditions. When opposed to traditional petroleum and animal-fat based lubricants, synthetic oils are utilized in metal stamping to provide environmental and other benefits. (Adhvaryu et al., 2005). In addition to the above advantages, even several shortcomings have limited their use as lubricant. Probably, the most glaring downside of synthetic oil is the higher cost. Synthetic oil costs two to four times as much as conventional oil. Cold storage may increase the risk of additive precipitation for synthetic oils (do Valle et al. 2018; Cavalcanti et al., 2018).

2 Bio-lubricants

On the other hand, vegetable oils can become the substitute for mineral oil-based for various applications including lubrication. Vegetable oils are obtained from plants and plant seeds. They consist of mainly triacylglycerols (91–96%), polar lipids (phospholipids and galactolipids), monoacylglycerols, diacylglycerols, and minor amounts of free fatty acids and polyisoprenoids. Various vegetable oils and their applications are shown in Table 1.

One of the potential and future application of the vegetable-based oils is lubrication. A comparison between mineral oils and vegetable oils, in general, is given in Table 2. When compared to mineral oil, bio-lubricants made from vegetable oil show higher levels of lubricity, flash point, volatility, and viscosity index. For instance, the viscosity index of most mineral oil's ranges from 90 to 100, while that of non-edible vegetable oil is around 220. Vegetable oil-based lubricants with a high viscosity index work well to keep the lubricating coating intact at high temperatures. Flash and fire points determine the volatility and fire-resistance qualities of lubricants (Alves et al., 2013). Additionally, it reduces operating temperature and yields energy savings of at least 16 per cent. Because they include a lot of polyunsaturated fatty acids, bio-based lubricants have good heat stability and low pour and cloud points. They have higher heat content and minimum sulphur content and are biodegradable. Vegetable oil-based bio-lubricants can replace mineral oils as gear box oil, hydraulic oils, engine oils, lubricants for two-stroke engine, tractor, insulating oils, aviation oil, grease, metal grinding oils or multi-purpose oils (Singh et al., 2015).

Of the various advantages of vegetable oils, biodegradability is the most important property for it to be used as an alternative to conventional lubricants (Erhan & Asadauskas, 2000a, 2000b a, b) (Kumar et al. 2011). A lubricant is deemed biodegradable if it can be

Table 1 Various vegetable oils and their applications (Shashidhara & Jayaram, 2010), Liew Yun Hsien, W. (2015) and Panchal et al. (2017)

Sl. No	Vegetable oil	Major applications
1	Canola oil	Hydraulic oils, tractor transmission fluids, metal working fluids
2	Coconut oil	Gas engine oils
3	Palm oil	Grease, rolling lubricant
4	Rapeseed oil	Air compressor-farm equipment, chain saw bar lubricant
5	Safflower oil	Enamels, light-coloured paints, diesel fuel, resins
6	Linseed oil	Stains, varnishes, lacquers
7	Soybean oil	Plasticizers, hydraulic oil, printing inks, pesticides, disinfectants
8	Castor oil	Gear lubricants, greases
9	Jobba oil	Cosmetic industry, lubricant applications
10	Crambe oil	Intermediate chemicals, surfactants
11	Sunflower oil	Grease, diesel fuel substitutes
12	Cuphea oil	Motor oil, cosmetics
13	Tallow oil	Lubricants, plastics
14	Olive oil	Automotive lubricants

Table 2 Oil comparison between vegetable and mineral oils.

Mobarak et al. (2014), Singh et al., (2015) and (Singh et al., 2017)

Characteristics	Vegetable oils	Mineral oils
Density@20 °C(kg/m ³)	940	880
Viscosity index	100–200	100
Oxidation stability	Neutral	Satisfactory
Pour point °C	–20–+10	–15
Solubility in water	Insoluble	Insoluble
Hydrolytic stability	Not satisfactory	Satisfactory
Cold flow behaviour	Not satisfactory	Satisfactory
Sludge forming tendency	Not satisfactory	Satisfactory
Seal swelling tendency	Slender	Slender
Shear stability	Satisfactory	Satisfactory
Miscibility with mineral oils	Satisfactory	–

digested by organisms or their enzymes in renewable raw materials produced through aerobic or anaerobic processes (Haase et al., 1989). A lubricant is considered to be degradable when it is biodegraded at least 80% within 28 days or at least 60% after 28 days (Reeves et al., 2017). Several processes contribute to a lubricant's biodegradability. The initial process involves the disappearance of the original bio-lubricant and the formation of a new compound, which may or may not be fully biodegradable. By using infrared spectroscopy to analyse the C–H bond, this main breakdown is quantified (Perin et al., 2008). The second stage is when the organic chemical calculates how quickly it will biodegrade into CO₂ and water (within 28 days) (Battersby & Morgan, 1997).

Since some components of lubricant formulations are ecologically toxic and can have a permanent negative impact on the environment or living beings, ecotoxicity is a crucial characteristic that must be regulated. Dumping the waste mineral oil-based lubricants causes long term pollution of the environment and also the ecosystem. The

contaminants from these oils will harm the plant and animal life. Aquatic ecosystems are more vulnerable to severe harm. As a result, it's important to determine how toxicant water will be to aquatic life, including bacteria, algae, small fish, and laboratory rats. As the vegetable-based oil is 100% biodegradable, it is free from all the above-mentioned ill effects and can protect the environment and existing ecosystems for future generations. A renewable and biodegradable fuel, biodiesel can be produced using fresh or leftover oilseed plants, vegetable oils, and animal fats as the raw material. Biodiesel can be used in its pure form or combined with petroleum diesel, and burning it produces significantly fewer emissions than burning fossil fuels (Vignesh & Barik, 2019). The highest risk factor that affects the environment through acid rain, human diseases, etc. is the high NO_x emission caused by the use of mineral oil-based lubricants. Furthermore, the production of atmospheric ozone, a significant greenhouse gas, is mostly influenced by CO and NO pollution. Therefore, methyl esters of vegetable oil in diesel engines suggest a reduction of undesirable exhaust emissions such as CO and smoke by 14% and 12%, respectively, by chemical modification (Aalam & Saravanan, 2017). Rapeseed methyl ester decreased the CO, CO₂ and smoke opacity of exhaust gas emissions by 10% 12% and 8%, respectively, while NO_x emissions increased significantly (Yukseket al., 2009). A comparative study was done in four stroke engine oil by usage of engine oil, coconut oil and palm oil as lubricants. The emissions such as HC (ppm), CO (%), CO₂ (%), O₂ (%) and NO (ppm) were calculated. For engine oil, the emission values were 104, 0.92, 4.5, 14.02, and 12, respectively, whereas for of coconut oil as lubricant, the reduction in emission values were 99, 0.67, 2.9, 15.82, and 11, respectively. Similarly, for palm oil, the emissions values were found to be 102, 0.73, 3.4, 15.66, and 14, respectively (Mannekote & Kailas, 2011).

The two categories of vegetable oil include edible and non-edible oils. The physiochemical properties of edible oils and non-edible oils are shown in Table 3 and Table 4. Even though edible oils are good candidates for bio-lubricants, they are extensively used in cooking especially in developing countries. On the other hand, non-edible oils are presently used in chemical industries in manufacturing of soaps, detergents, and cosmetics, etc.; current utilization is very low. This indicates there is large potential of non-vegetable oils that could be used for lubrication. Hence, they could be good candidates for future lubricants.

Table 3 Physical and chemical characteristics of edible oils (Mobarak et al., 2014), (Azam et al., 2005) and (Gui et al., 2008)

Various edible oils	Density (Kg/m ³)	Kinematic viscosity at 40 °C (mm ² /s)	Oxidation stability 110 °C, h	Cloud point °C	Flash point
Palm	875	5.72	4.0	13.0	165
Sunflower	878	4.45	0.9	3.42	185
Coconut	805	2.75	35.4	0	112
Soyabean	885	4.05	2.1	1.0	176
Linseed	890	3.74	0.2	-3.8	178
Olive	892	4.52	3.4	-	179
Peanut	882	4.92	2.1	5.0	177
Rape seed	880	4.45	7.5	-3.3	62
Rice bran	886	4.95	0.5	0.3	-

Table 4 Physio-chemical properties of non-edible oils (Singh et al., 2017), (Mobarak et al., 2014) and (Karmakar et al., 2010)

Non-edible oils	Cloud point °C	Density (kg/m ³)	Oxidation stability 110 °C, h	Kinematic viscosity at 40 °C (mm ² /s)	Density (kg/m ³)
Karanja	9.0	918	6.0	4.80	918
Castor	-13.5	898	1.2	15.25	898
Tobacco	-	887	0.8	4.25	887
Mahua	-	850	-	3.40	850
Jatropha	2.75	878	2.3	4.82	878
Neem	14.5	885	7.2	5.20	885
Camellia Japonica and Vernicia Fordii	11.7	882.6	-	3.7	882.6
Guizotia Absyssinica	1.4	-	-	4.1	-
Sapium sebiferum	-	877	-	19.4	877
Ricinus Communis	-13.1	907	0.31	15.4	907

3 Need of chemical modifications of vegetable oil

Vegetable oils have a huge potential as bio-lubricants, but they are not generally commercialized due to their high heterogeneity and other undesirable physical characteristics, such as poor oxidation stability and low temperature properties. The natural oils are composed of fatty acids that are derived from triacyl-glyceride molecules, which contain glycerol. The presence of glycerol in the natural oils gives rise to a tertiary β -hydrogen (secondary hydrogen) attached to the β -carbon (secondary carbon) of the functional hydroxyl group. The unsaturated fatty acids which consist of β -hydrogen, which is known to have oxidative instability, are what causes the rapid oxidation of natural oils, commonly known as autoxidation. Hence, there is a need to alter the physico-chemical qualities of vegetable oils via different chemical pathways to improve critical properties such as oxidative stability, biodegradability, thereby retaining and even enhancing certain properties to suit various uses. The most common ways for altering vegetable oils are transesterification/esterification processes, epoxidation, hydrogenation, and estolide synthesis. (Salih et al., 2012). A transesterification reaction occurs when an ester's organic group reacts with its alcohol's organic group. An acid or base catalyst is often added to catalyze the reaction. During epoxidation, the carbon-carbon double bond is converted into oxiranes (epoxides) by hydrogen peroxide, organic peroxides, etc.

Hydrogenation is chemical process applied to reduce or saturated organic compounds, usually through a catalyst such as palladium, nickel, or platinum. Hydrogenated vegetable oil is processed to improve the product's taste, texture, and shelf life. In case of estolide formation, as fatty acids are unsaturated, they form a carbocation that may undergo nucleophilic addition by a second fat, either with or without the carbocation migrating along the chain, to form ester bonds. However, the initial estolide synthesis step frequently necessitates the use of pricey capping fatty acids (Cecilia et al., 2020).

4 Transesterification of vegetable oils

Oil transesterification involves the conversion of triglycerides from oils to usable oils which are less viscous than their neat forms. The transesterification stage involves a vegetable oil basically triglyceride reacting with alcohol and producing methyl ester (ME) and glycerol in the presence of a catalyst (Hsien, 2015) as shown in Fig. 1. A triglyceride contains three hydrocarbon chains, namely R1, R2 and R3 that represent its hydrocarbon chain of fatty acid. In recent years, many studies have concluded that transesterification of vegetable oils can enhance their properties (Salih et al., 2012).

Sulaiman et al. (2007) studied palm oil derivative wherein trimethylolpropane (TMP) is produced under vacuum in a transesterification reactor. Result showed that the conversion rate was 61% at a temperature of 110 °C for two hours. Koh et al. (2014) evaluated the studies on bio-lubricant production using a sodium methoxide catalyst (NaOCH₃), palm methyl ester and TMP. Transesterification reaction was performed at 110 °C to 150 °C. Their results showed that 140 °C is the most suited reaction temperature for a 25-min reaction. Aziz et al. (2014) used palm oil methyl ester as the raw material and sodium methoxide catalyst for his research. The optimal reaction conditions were found to be 158 °C, catalyst concentration of 1.56%, molar ratio of 4:1, and reaction time of 55 min. The yield of 37.56% was obtained from these optimal conditions. McNutt (2016) performed transesterification studies and his experimental studies showed a reduction in pour point and rise in thermo-oxidative stability of esters as compared to the neat oil.

Methyl esters obtained from the primary reactions are further transesterified or converted into, triesters in subsequent stages. Heikal et al. (2017) used palm oil and Jatropha oil, for a two-stage transesterification process to produce a bio-lubricant. Methanol was used in conjunction with potassium hydroxide and sodium methoxide as the catalyst. Results showed TMP esters extracted from palm oil gave a yield of 97.8% after a 4-h reaction at 130 °C. Similarly, TMP esters were obtained from Jatropha oil based on similar reaction conditions gave a yield of 98.2%. TMP esters derived from Jatropha oil showed a high viscosity index (138), minimal pour point temperatures (−3 °C), and moderate thermal stability, which met industrial oil requirements. Uosukainen et al. (1998) evaluated the transesterification of rapeseed oil fatty acids and candida rugosa lipase as a catalyst. At 42 °C, 5.2 kPa, and 12% added water, bio-catalysts achieved up to 98% conversion of TMP esters. They observed a slightly higher temperature of 47 °C; the maximum conversion rate of the triester was about 70%. Their results also showed an increase in triester yield when the temperature was initially held between 80 and 115 °C for 2 h and then further increased to 110 °C for 8 h. Ghazi et al. (2009) evaluated the studies on TMP triesters and have

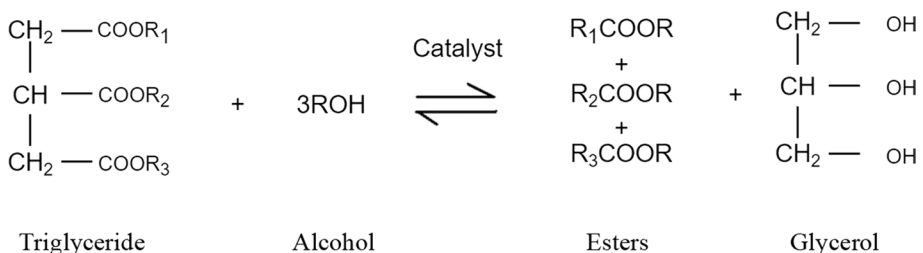


Fig. 1 Schematic representation of transesterification

shown significant oxidative stability with sodium methoxide, with degradation temperatures surpassing 325 °C. Yunus et al. (2005) conducted experiments on the palm oil derived triesters synthesized at a temperature range of 125–150 °C with sodium methoxide as the catalyst. Results have shown pour point reaching as low as –37 °C. The palm TMP triesters were also synthesized using calcium methoxide (C₂H₆CaO₂) heterogeneous catalyst, but it ended up showing a longer reaction time of 8 h than using a homogeneous catalyst, which took less time. Abd Hamid et al. (2012) performed the experiments employing a combination of palm methyl ester and TMP to form palm bio-lubricant using an oscillatory flow reactor. They noticed an improvement in the final product's thermal and oxidative stability. Studies conducted by Sripada et al. (2013) showed that TMP-based triesters can be synthesized by mixing methyl/ethyl esters with fatty acids in addition to biodiesel. Similar works were conducted by Chowdhury et al. (2013) using waste cooking oil (WCO) methyl esters to produce TMP triesters. Encinar et al. (2020) performed experimental work on rapeseed and castor oil methyl esters, which were further transesterified using several alcohols with titanium isopropoxide as a catalyst. Reaction parameters such as temperature, molar ratio of alcohol to methyl ester, and catalyst concentration were varied. Results revealed about 93% yield for rape seed and castor oils in a time period of 2 h. The optimal temperature and catalyst concentration for bio-lubricant generation were found to be at temperature 165 °C and for catalyst 2%. Table 5 shows the detailed transesterification reaction conditions, catalysts, and different bio-lubricants properties achieved after the process.

4.1 Summary

The literature review on transesterification can be summarized as bio-lubricant can be realized using several methods, but transesterification from vegetable oils is the most popular because of its renewability and sustainability. In transesterification, molar ratio of glyceride to alcohol, catalyst type, and feedstock fatty acid content will influence the conversion. The most common catalysts used in transesterification studies are hydroxides, alkoxides, and carbonates, which usually yield greater than 80%. In general, biodiesel plants use methanol since it is economic and short-chain branching (to avoid steric hindrance effects). Most researchers recommend a 6:1 molar ratio for methanol, while for ethanol, they recommend a 9:1 molar ratio. The proportion of fatty acids plays a vital role in bio-lubricant properties. As a result, the structure of these fatty acids, particularly their unsaturation, chain length, and hydroxyl group, influences numerous characteristics of the final bio-lubricant. Important qualities of bio-lubricants such as viscosity and pour point appeared to be affected by the type of alcohol employed during transesterification process. Proper alcohol selection could improve the performance of the bio-lubricant, particularly in terms of tribological characteristics.

5 Epoxidation of vegetable oils

An epoxide functional group, a 3-atom ring with two carbon atoms and one oxygen atom, is created when two carbon atoms undergo epoxidation, which is the elimination of double bonds between them with the assistance of an oxygen atom. Most plant oils have a low friction coefficient and make good boundary bio-lubricant. Many researchers argue that the wear rate is significant despite the low coefficient of friction (COF) of plant oils as boundary bio-lubricants (Bowden & Tabor, 2001). To circumvent these

Table 5 Transesterification details of bio-lubricants (McNutt, 2016) (da Silva et al., 2015a, 2015b) and (Encinar et al., 2020)

Reactants	Product	Catalyst	Reaction conditions	Oxidative/thermal stability	Pour point (°C)	Viscosity index (cSt)	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	Yield (%)
Palm methyl ester and trimethylolpropane	Trimethylolpropane triesters	NaHCO ₃	140 °C, 25 mbar, 25 min	355 °C Degradation temperature	-2	176	9.0	47.1	94.6
Canola biodiesel ester and trimethylolpropane	Trimethylolpropane triester	NaHCO ₃	110 °C, 1 mbar, 5 h	Induction duration: 0.74 h	-66	204	40.5	7.8	90.9
Rubber methyl ester and trimethylolpropane	Trimethylolpropane triesters	p-Toluenesulphonic acid	135–140 °C, until theoretical reaction complete	12–18 min (Rotary bomb oxidation test) Flash point: 272–308 °C	(-15)–(-3)	206–222	23.1–62.6	5.9–12.6	94.5–96.5
Thumba methyl ester, xylene and trimethylolpropane	Trimethylolpropane triesters	p-Toluenesulphonic acid	135–140 °C, until complete	12–18 min (Rotary bomb oxidation test) flash point: 270–318 °C	(-12)–(-3)	209–220	20.65–60.26	5.45–11.89	89–95
Soybean oil and various alcohols	n-alcohol-esters	Zr (SO ₄) ₂	140 °C, 4 h	-	-	45–195	10.3–432.7	3.0–34.4	> 80
Pentaerythritol and oleic acid	Pentaerythritol tetraoleate ester	Ion exchange resin, Indion-130	110 °C, 7 h toluene solvent	-	-24	190	63.08	12.00	-
Sunflower oil and octanol	fatty acid-n-octyl esters	Iron-Zinc double-metal cyanide (DMC) complexes	170 °C, 8 h	23 min (Rotary bomb oxidation test)	-3	226	7.93	2.74	96

Table 5 (continued)

Reactants	Product	Catalyst	Reaction conditions	Oxidative/thermal stability	Pour point (°C)	Viscosity index (cSt)	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	Yield (%)
Valeric trimethylolpropane acid	Valeric acid Trimethylolpropane ester	Silica-sulphuric acid	70 °C molar ratio of 3:1, toluene	–	–75	82	9.5	2.5	–
Castor biodiesel and trimethylolpropane	Trimethylolpropane triester	$C_{32}H_{64}O_4Sn$	170 °C, 0.01 bar	Rotating pressure vessel oxidation test: 43 min (Addition of butylated hydroxytoluene)	–27	119	287.2	26.13	89.7
Castor biodiesel and trimethylolpropane	Trimethylolpropane triester	Amberlyst 15 ionic exchange resin	120 °C, 0.01 bar	–	–	127	20.94	4.467	–
Castor biodiesel and trimethylolpropane	Trimethylolpropane triester	$NaHCO_3$	120 °C, 0.01 bar	Rotating pressure vessel oxidation test: 150 min (Addition of Butylated hydroxytoluene)	–	141	11.28	3.100	–
Palm methyl ester and trimethylolpropane	Trimethylolpropane triesters	$C_2H_6CaO_2$	180 °C, 50 mbar, 8 h	–	–	–	–	–	92.38

Table 5 (continued)

Reactants	Product	Catalyst	Reaction conditions	Oxidative/thermal stability	Pour point (°C)	Viscosity index	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	Yield (%)
High oleic palm methyl ester and trimethylolpropane	Trimethylolpropane triesters	NaHCO ₃	120–155 °C, 0.3 mbar, 30 min	–	(–37)–(–9)	183–200	45.5–50.7	9.2–10	–
Waste cooking oil methyl ester and trimethylolpropane	Trimethylolpropane triester	KOH	128 °C, 180 Pa, 1.5 h	Flash point: 240 °C	–8	204	38.60	8.44	85.7
Jatropha methyl ester and trimethylolpropane	Trimethylolpropane triesters	NaHCO ₃	150 °C, 55 min	325 °C Degradation temperature	–6	183	42.57	9.37	–
Jatropha and trimethylolpropane	Trimethylolpropane triesters	NaHCO ₃	150 °C, 10 mbar, 3 h	–	–6	180	43.90	8.71	>80

issues, chemical changes such as epoxidation and transesterification of plant oils with polyols have been utilized (Salimon et al., 2010). Chemical intermediates such as lubricants, plasticizers, and non-isocyanate polyurethanes are formed when unsaturated vegetable oils undergo epoxidation. (Tan & Chow, 2010).

Epoxidized vegetable oils present an opportunity to create a more sustainable and eco-friendly economy. The epoxidation process is often accelerated through heterogeneous and homogeneous catalysts, such as sulphuric acid and ion exchange resin, to obtain higher yields in fewer hours (Aguilera et al., 2019). Amorphous titanium (Ti) or silicon dioxide (SiO₂), rhenium, and tungsten-based catalysts have also produced high yields (Goud et al., 2007). Mineral acids such as sulphuric acid, acidic cation exchange resins such as sulphonated polystyrene-type Amberlite, tungsten-based catalysts, Ti (IV)-grafted silica catalysts, and methyl-tri-n-octylammonium diperoxotungsto phosphate are the most frequent catalysts used in epoxidation reactions (Chakrapani & Crivello, 1998). Usually, heterogeneous catalysts are utilized as alternatives to mineral acids in epoxidation (Yadav & Borkar, 2006).

Goud et al. (2006) evaluated the studies on the epoxidation of Mahua oil employing mineral acids as catalysts, hydrogen peroxide as an oxygen donor, and acetic acid as an active oxygen carrier. At the end of the experiments, higher yield in lower time period was obtained. Studies performed by Doll et al. (2017) revealed that the carbonated and epoxidized estolides were created by ring-opening them with carbon dioxide using tetrabutylammonium bromide as a catalyst after epoxidizing them with hydrogen peroxide and formic acid. Their findings said that epoxidized estolides had substantially higher viscosities than the initial estolides. Experimental study conducted by Sharma et al. (2007) showed that the pour points of each of estolides increased by 4–16 °C after epoxidation. Sharma and Dalai (2013) conducted studies using 0.5:1 acid-to-ethylenic unsaturation molar ratio along with an Amberlite IR-120 catalyst (20% of oil). The outcome of the studies revealed that in comparison with other commercial catalysts, novel sulphated Ti-SBA-15(10) was shown to be the most active and highly selective one. Dinda et al. (2008) conducted a kinetic study on epoxidation of cotton oil using peroxyacetic acid generated in situ by reacting hydrogen peroxide and glacial acetic acid with mineral acid, which helped to obtain higher yields. Meshram et al. (2011) conducted a study on epoxidation with hydrogen peroxide and acetic acid utilizing acidic cation exchange resin Amberlite IR-122 catalyst for wild safflower oil and achieved better yields. Mungroo et al. (2008) evaluated the studies on epoxidation of canola oil with hydrogen peroxide and acetic acid/formic acid utilizing Amberlite IR-120H resin. They found that acetic acid is superior oxygen transporter than formic acid. Unsaturated fatty acid-rich soybean (Adhvaryu & Erhan, 2002) and rape seed oils (Wu et al., 2000), exhibited improved oxidation stability and friction-reducing abilities when epoxidized as compared to their original forms. Kulkarni et al. (2013) evaluated the studies on epoxidized mustard oil by using H₂SO₄ catalyst. They concluded that after epoxidation, oil fulfilled low-temperature flow properties (PP = 28 to 35 °C), high-temperature lubrication characteristics (VI = 150–177) and oxidative stability requirements of the commercial lubricant market. As a result, H₂SO₄ was chosen as the most effective ring-opening catalyst. According to McNutt (2016), epoxidation of vegetable oil leads to decrease in viscosity index and a raise in pour point. As observed, this modification was often advantageous due to the low reaction temperature, although the product's pour points are not suitable for utilization purposes. The details of epoxidized vegetable oil with the type of catalysts used, reaction conditions, and their physical characteristics are shown in Table 6.

Table 6 Epoxidized vegetable oil with their physical characteristics (McNutt, 2016) (Salih et al., 2012) and (Silva et al., 2015a, 2015b)

Reactants	Products	Catalyst	Reaction conditions	Oxidative/thermal stability	Pour point (°C)	Viscosity index	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	Yield (%)
Jatropha oil, CH ₂ O ₂ , and H ₂ O ₂	Epoxidized Jat-ropha oil	H ₂ SO ₄	10 °C, 2 h while H ₂ O ₂ added, then 60 °C	Rotary bomb oxidation test: 20min/Flash point: 288 °C	0	139	146.5	18.2	96
C ₁₉ H ₃₄ O ₂ , CH ₂ O ₂ and H ₂ O ₂	Epoxidized C ₁₉ H ₃₄ O ₂	–	–	Oxidation onset temperature: 180.3 °C	–1.5	132	14.3	3.5	95
Canola oil, CH ₃ COOH and H ₂ O ₂	Epoxidized canola oil	Amberlite IR-120H	65 °C, 8 h	Thermal Stability: 319 °C	9	–	–	–	–
Canola oil, CH ₃ COOH and H ₂ O ₂	Epoxidized canola oil	Amberlite IR-120H	65 °C, 8 h	Thermal Stability: 320 °C	10	151	–	–	–
C ₁₈ H ₃₄ O ₂ , CH ₂ O ₂ and H ₂ O ₂	Epoxidized oleic acid	–	4 °C, 2 h	Flash point: 113.11 °C	0	45.44	–	–	–
Passion fruit oil, CH ₂ O ₂ , and H ₂ O ₂	Epoxidized passion fruit oil	–	30 °C, 3 h	Rapid small scale oxidation test: 16.89 min	–	185.65	–	–	–
C ₁₉ H ₃₄ O ₂ , CH ₂ O ₂ and H ₂ O ₂	Epoxidized C ₁₉ H ₃₄ O ₂	–	–	Oxidation onset temperature: 131.2 °C	–7.5	308	19.3	63	85
Canola biodiesel, CH ₃ COOH and H ₂ O ₂	Epoxidized bio-diesel	Amberlite IR-120H	65 °C, 8 h	Thermal Stability: 160 °C	0	–	–	–	–
Thumba oil, CH ₂ O ₂ and H ₂ O ₂	Epoxidized Thumba oil	–	5–10 °C, Before adding H ₂ O ₂ and heating to 60 °C for 7 h	Rotary bomb oxidation test: 20 min	–3	128	216.9	22.7	–

Table 6 (continued)

Reactants	Products	Catalyst	Reaction conditions	Oxidative/thermal stability	Pour point (°C)	Viscosity index	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	Yield (%)
$C_{19}H_{36}O_2$, CH_2O_2 and H_2O_2	Epoxidized $C_{19}H_{36}O_2$	–	–	Oxidation onset temp: 187.75 °C	0	151	8.0	2.5	97
Moringa oil, CH_2O_2 , and H_2O_2	Epoxidized moringa oil	–	30 °C, 3 h	Rapid small scale oxidation test: 24.57 min	–	–	–	–	–
Canola oil, CH_3COOH and H_2O_2	Epoxidized canola oil	Sulphated-stannic oxide catalyst	70 °C, 6.5 h	Oxidation induction duration: 60 h	9	141	114	19	–

5.1 Summary

The derivatives of epoxy oil provide a number of benefits, including improved low temperature characteristics, viscosity, thermal stability, and lubricity as the product's branching rises. Low pour point value, enhanced lubricity, and excellent heat stability are all features of the ring-opening product. Moreover, the epoxidized oil showed an improvement in additive solubilization, increasing the fluid performance. Based on the extensive study on epoxidation, it can be concluded that the vegetable oils' lubricity and stability are improved at low temperatures. Simultaneously, there will be a significant rise in the pour point value and an increase in the viscosity index. Epoxy oils have a higher heat stability than triglycerides.

On the other hand, epoxy oils rapidly oxidize when exposed to higher temperatures over an extended period of time. According to the research review, increasing the temperature, increases the conversion of epoxidized vegetable oil, and adjusting the molar ratio affects the yield of the epoxidized oil. To improve the quality and quantity of the epoxy bio-lubricant, the temperature, catalyst, and molar ratios of alcohol are to be maintained at optimum levels. Reduction in friction effects is also governed by the nature of chemical structure and type of oil used. Hence, further studies on various edible and non-edible oils are necessary to claim for the most suitable oil that shows comprehensive improvement in properties compared to either synthetic or mineral oil. In general, it is observed that researchers have used chemical modification technique such as esterification and epoxidation reactions to alter the bio-lubricant properties and make them as suitable candidates for lubrication purposes, but further research is necessary to optimize the catalyst selections and operating conditions for a particular type bio-lubricant especially derived from non-edible oils.

6 Characterization of bio-lubricants

After chemical modification, proper characterization is essential to assess the bio-efficiency of the lubricants for diverse applications. In this regard, various tests have been conducted on bio-lubricants to analyse their efficacy related to viscosity/viscosity index, thermal stability, oxidative stability, friction and wear, etc. The principle, method followed, and the various findings of bio lubricant characterization are discussed below.

6.1 Viscosity/viscosity index

A lubricant's viscosity or viscosity index plays a vital role in minimizing collisions and rubbings among mechanical components in action and improving the effectiveness of the mechanical device. Therefore, increasing the temperature of lubricant causes its molecular potential energy to increase and intermolecular forces to decrease those results in decreased viscosity (Ting & Chen, 2011). It is considered highly advantageous and outstanding if viscosity index exceeds 200. The viscosity of a lubricant will rise when there is a double bond, but will decline when there are two or more double bonds (Rodrigues et al., 2006). To minimize friction variations caused by temperature fluctuations, fluids are often rated based on their viscosity index. If viscosity index is high, lesser will be the viscosity affected by the temperature (Shahabuddin et al., 2013). Viscometers and rheometers are used for measuring the viscosities of the bio-lubricants

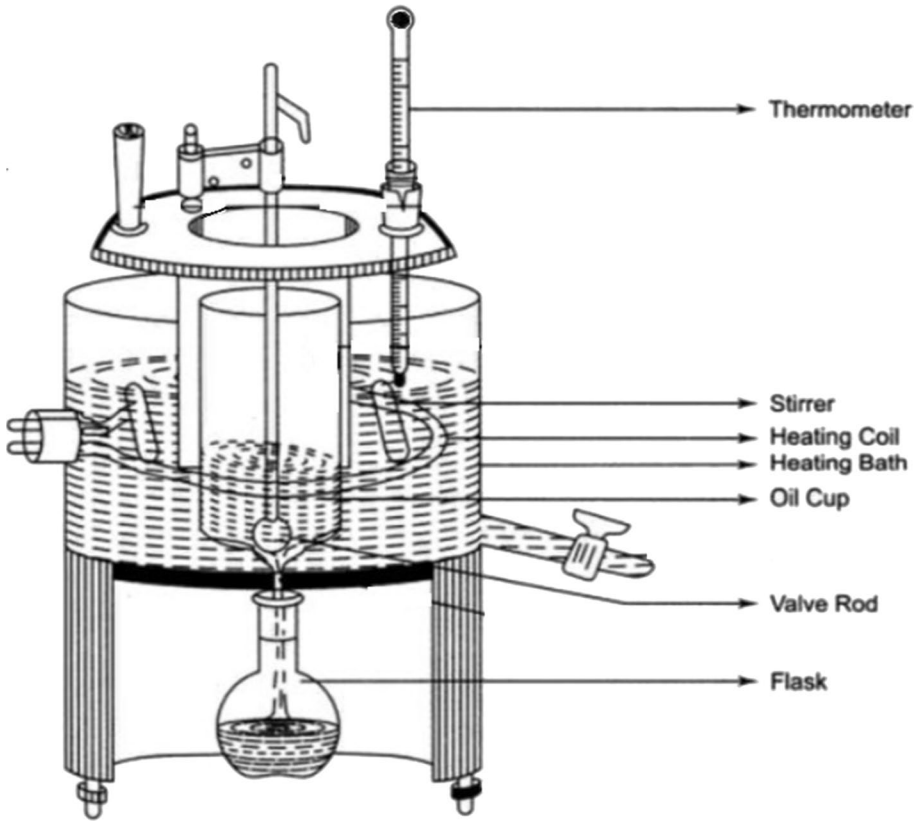
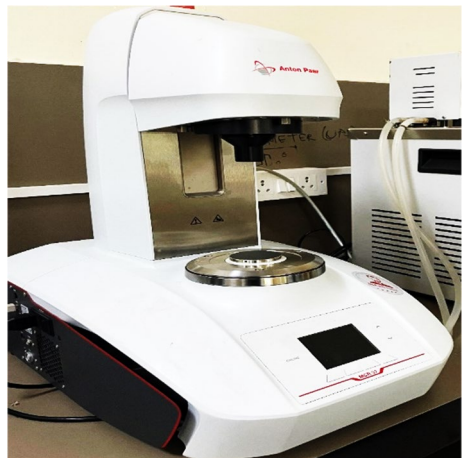


Fig. 2 Viscometer

Fig. 3 Rheometer



as shown in Figs. 2 and 3, respectively. A viscometer is a simple device used for measuring only the viscosity, whereas a rheometer is more flexible and has a much wider dynamic range of control, characterization and measurement of fluid parameters.

It was demonstrated that the canola biodiesel-based lubricant had a viscosity index of 204, which was attributed to the polyunsaturated fatty acids found in it (Sripada et al., 2013). Vegetable oils contain triglycerides, which maintain intermolecular connections as temperature rises, hence the palm oil-based lubricant has a viscosity index higher than mineral oils (Masjuki et al., 1999). Heikal et al. (2017) evaluated kinematic viscosity of palm TMP. It exhibited a high viscosity index (140), and a low pour point temperature ($-3\text{ }^{\circ}\text{C}$) as compared to mineral oil. Shahabuddin et al. (2012) studied a novel ecologically acceptable lubricant formulation with enhanced viscosities, using ethylene–vinyl acetate and styrene–butadiene–styrene copolymers to extend the viscosity range of high-oleic sunflower oil. At $40\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$, the highest kinematic viscosities were roughly between 140 and 240 cSt and 25–35 cSt, respectively. Asadauskas et al. (1997) tested a biodegradable bio-lubricant and found that vegetable oils had a superior viscosity index than mineral oils, according to their experimental results. Bekal and Bhat (2012) conducted an experimental study on an IC engine using a bio-lubricant (Pongamia oil) and concluded that for lower viscosity, Pongamia oil lubricant ensured highest brake thermal efficiency. Ting and Chen (2011) developed engine bio-lubricant and studied the viscosity and efficacy of soybean oil-based bio-lubricant. Their study concluded that epoxidized soybean oil had a higher viscosity. Azad (2017) investigated on an oil-rich mandarin seed and evaluated them as a potential, substitute, and second-generation transportation fuel. An ARES rheometer was used to measure the kinematic viscosity at $40\text{ }^{\circ}\text{C}$. In addition, the study found that at low temperatures, oil had a higher viscosity and at high temperatures it had a lower viscosity than diesel. Reeves et al. (2015) studied the properties of bio-lubricants from non-edible oil and edible oils and further they were examined for friction and wear qualities. Viscosity and temperature analysis was done to discover correlations between them and the effect of the differing composition of fatty acids within the natural selection of oils. At room temperature ($21\text{ }^{\circ}\text{C}$), the viscosity of natural oils ranged from 54cP for Corn oil to 71cP for Peanut oil. Rani et al. (2015) evaluated viscosity of rice bran oil with a redwood viscometer as per ASTM D2270. Vegetable oil exhibited a very low range of viscosity in comparison with SAE20W40.

Zaid et al. (2021) conducted the experiments with raw Jojoba oil and measured viscosity using the redwood viscometer as per ASTM D445-06. When the raw Jojoba oil was blended with nanoparticles, the viscosity was increased. Sarin et al. (2009) investigated the physico-chemical properties of *Guizotia abyssinica* (GA) oil and compared it with *Jatropha* and *Pongamia* oils. Density of oils were 912 kg/m^3 , 910 kg/m^3 , and 930 kg/m^3 for GA, *Jatropha* and *Pongamia* oils, respectively. As compared to *Jatropha* ($36.0\text{ mm}^2/\text{s}$) and *Pongamia* ($37.5\text{ mm}^2/\text{s}$) oils, GA oil ($27.4\text{ mm}^2/\text{s}$) exhibited a lower kinematic viscosity. Abramovic and Kloufutar (1998) and Fasina et al. (2006) revealed that the viscosities of vegetable oil increased when monounsaturated fatty acids increased but decreased when polyunsaturated fatty acids increased. Kumar et al. (2017) investigated the physico-chemical and tribological properties of a titanium dioxide (TiO_2)-doped nano-lubricant using a redwood viscometer. At room temperature, the viscosity for nano-lubricants with 0.8% TiO_2 (100.61 cSt) was highest due to the high concentration of nanoparticles. Thottackad et al. (2012) evaluated nano-lubricant viscosities for coconut oil at various temperatures and with varying nanoparticle concentrations of cupric oxide (CuO). It was observed from the experiments that the kinematic and dynamic viscosities were increased marginally

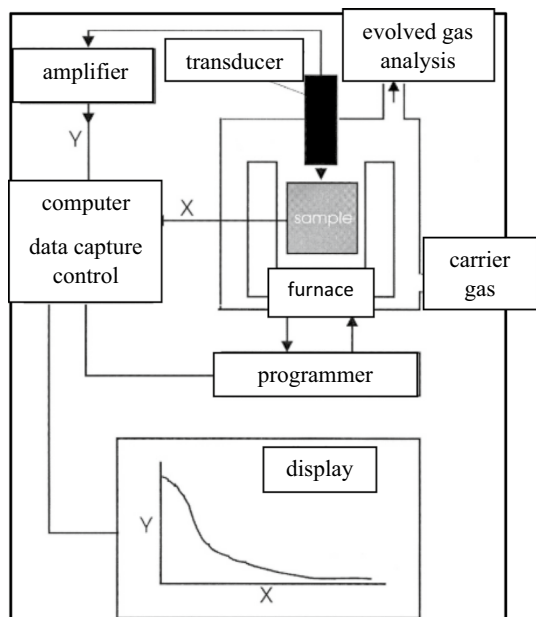
when nanoparticles were added. The reduction in density had resulted in larger kinematic viscosity variations at higher temperatures than dynamic viscosity.

It can be summarized that viscosity is the most essential feature of oil since it affects tribological behaviour. Coefficient of friction will be lowered, if viscosity is high and parallelly it also results in working temperature of the lubricant. Viscosity variations also depend on the type of the oil and its composition. Vegetable oil bio-lubricants' fatty acid composition will influence the oil's viscosity at room temperature. Strong lubricity qualities will be observed for the oils with the viscosity index greater than 100 which allows it to be used in a wide temperature range while maintaining its original physico-chemical features.

6.2 Thermogravimetric analysis

The most crucial oil characteristic, particularly when using vegetable oil as a lubricant in high-temperature conditions, is thermal stability. A thermal analysis technique is one in which a sample is heated under controlled conditions to measure changes in chemical or physical properties. Using thermal gravimetric analysis, the thermal stability of base oils and derivatives could be determined. Figure 4 shows the general set up of thermogravimetric analyser used for measuring the material's thermal stability and also composition. Sharma and Sachan (2017) assessed thermal stability of synthesized Karanja polyol tryster (KOPTE), obtained from base lubricant Karanja oil, under nitrogen atmosphere using the Mettler Toledo thermogravimetric analyser. An inert nitrogen atmosphere of 40 ml/min was used to conduct a thermal analysis at a heating rate of 12 °C/min from 30 to 800 °C. The thermogravimetric analyser (TGA) profiles showed that weight losses of 1%, 50% and 90% occurred at 180.36 °C, 312 °C and 451.11 °C,

Fig. 4 A generalized thermal analysis instrument and resulting thermal analysis curve



respectively. TGA data of KOPTE synthesized at elevated temperatures showed good thermal stability, which can be further enhanced further by combining with certain additives.

Madankar et al. (2013) evaluated the thermal behaviour of the hydroxy esters under a flow of argon, at the rate of 40 ml/min, by PerkinElmer's thermogravimetric differential thermal analyser for epoxidized canola oil, heating at a constant rate of 10°C/min. From the results, the thermal stability of epoxidized canola oil (ECO) was found to be below a temperature of 320 °C. Within the temperature range of 320 °C to 445 °C, ECO suffered a 95% weight loss. The ring-opening products of ECO mixed with n-butanol (BCO), amyl alcohol (ACO), and 2-ethyl hexanol (EHCO) were thermally stable below 355 °C, 361 °C, and 405 °C, respectively. Further, a 94% weight loss of BCO, ACO, and EHCO were observed within the temperature ranges of 355–475 °C, 361–510 °C, and 405–516 °C, respectively. Reeves et al. (2015) evaluated thermogravimetric analysis to determine the lubricants' thermal sensitivity in a high-temperature environment. Isothermal decomposition tests were performed in which the samples were subjected to heating at a rate of 20 °C /min till 50 °C and 100 °C below the onset of decomposition temperature of 378 °C. In order to exhibit thermal mass loss in a constant heat setting, the samples were maintained at about 327 °C temperature and 277 °C for 480 min. For peanut oil, 91% of the oil has decomposed at a temperature of 327 °C, while 18% of the oil has decomposed at a temperature of 277 °C within 480 min. Kalam et al. (2017) evaluated the thermogravimetric analysis for olive oil and SAE15W40. The decomposition temperature of olive oil and SAE15W40 are 395.15 °C and 249.20 °C. As a result, as compared to lubricating oil, olive oil demonstrated greater temperature stability. The increased thermal stability of the biodegradable oil is primarily due to the high amount of unsaturated fatty acids present. Borugadda and Goud (2016) evaluated the studies using waste cooking oil methyl esters (WCOME) and its epoxide in inert atmosphere (N₂) to determine the onset temperature. They observed that WCOME, and its epoxide were stable up to temperatures of 175 °C and 187 °C (on-set temperatures) relatively in an inert atmosphere. Similarly, maximum decomposition temperature corresponding to maximum weight loss was examined. The values were 224.5 °C and 245.5 °C for WCOME and its epoxide, respectively. The lack of un-saturation percentage of epoxide is responsible for its higher heat stability. Since all the double bonds were converted into oxirane rings during epoxidation, it was predicted that epoxide would have greater thermal stability than WCOME that had not undergone modification. Sharma et al. (2015) evaluated the thermal stability of canola oil and epoxidized canola oil using thermogravimetric differential thermal analyser (TG/DTA). They observed that canola oil and epoxidized canola oil were thermally stable below 305 °C. Maximum weight loss (90–95% wt) was observed in two samples at the temperatures 460 and 461 °C, respectively. Hence, it was concluded that epoxidized canola oil was thermally more stable and hence can be used for high temperature applications as compared to canola oil which has poor thermos-oxidative stability.

According to the literature, when using vegetable oil as a lubricant at high temperatures, its thermal stability is the most significant feature to consider. Thermal stability primarily depends on the chemical structure and fatty acid composition of the oil. Due to the presence of oleic acid and incorporation of some additives, it is seen that the thermal stability of biodegradable oil can be improved. Unsaturated vegetable oils are susceptible to chemical changes that alter the physico-chemical properties of the bio-lubricant, which limits the lubricant's ability to be employed at high temperatures. Generally, the transesterification and epoxidation of methyl esters leads to increase in thermo-oxidative stability, while maintaining lubricity characteristics of the base oils.

6.3 Friction and wear

Friction is the force that occurs between two contact surfaces in relative motion, whereas wear is the phenomenon of mechanical and/or chemical damage that affects the quality of the materials in contact with each other. A lubricant act as a layer between the contacting surfaces and protects it from wear. Friction and wear also depend on the type and composition of the oil used as a lubricant. The efficacy of lubricants is also measured by its capacity to minimize friction, wear and also the generation of heat. Several techniques and equipment have been used for determining friction and wear, of which four-ball tribo-tester and pin-on-disc tribometer are quite important amongst them. A four-ball tribo-tester determines bio-lubricant's anti-wear and extreme pressure characteristics. For testing, ASTM D 4172 and D 2783 methods are followed. The four-ball tribo-tester representation is shown in Fig. 5. It consists of three stationary balls put in a cup beneath a fourth ball connected to a spinning shaft through a chuck. It can measure the frictional torque exerted on the three lower balls by a calibrated arm attached to a friction recording device's spring. The revolving of three balls against the higher ball under pressure, created friction and wear. Between the thrust bearing and the cup, mounting discs were put. The loads that would be tested will be put on the load lever.

Figure 6 represents the pin-on-disc tribometer, where in friction and wear tests are conducted according to ASTM standards D4172. The pin and disc of the machine are made of Al-7% Si alloy and EN31 steel with a hardness of 60 HRC. The linear wear loss could be continuously measured during each test using a high-precision ball screw actuator with an encoder.

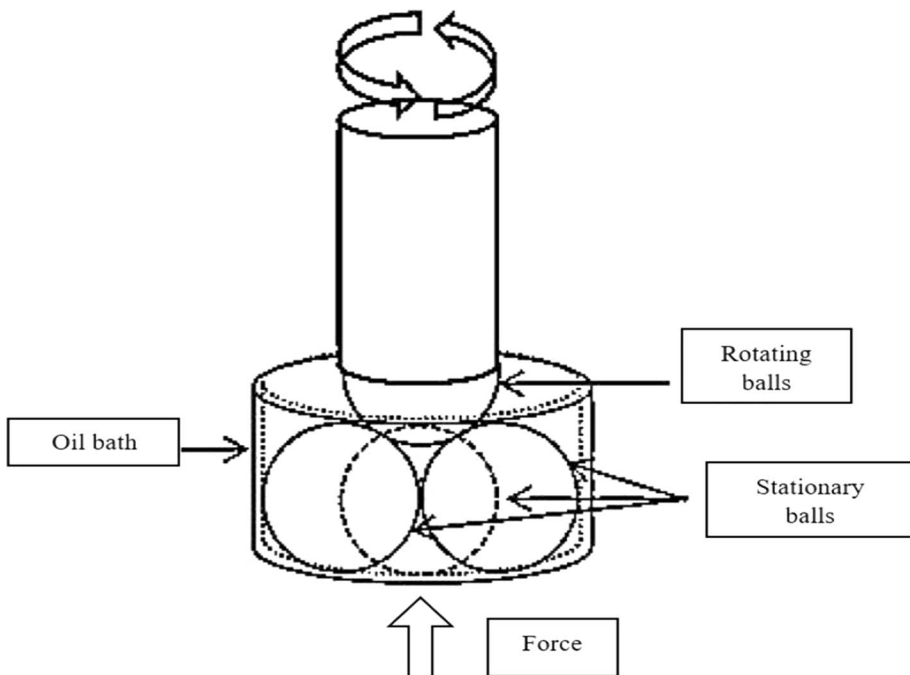


Fig. 5 Layout of four ball tribotester

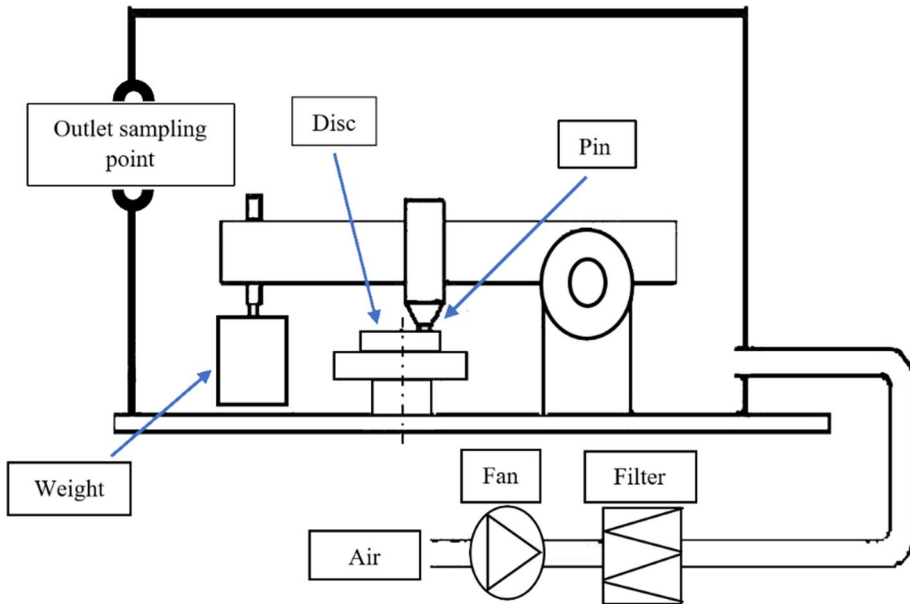


Fig. 6 Layout of pin-on-disc

Several researchers have performed tribological testing of the wear and frictional effects using different types of mineral oils, bio-lubricants with and without additives. Sulek et al. (2010) evaluated the studies on methyl esters of fatty acids derived from rape-seed oil with additives. Using high-frequency reciprocating rig-ball-on-flat apparatus. It was found that with 5% of the additive, the COF decreased by nearly 20% while wear rate decreased gradually. Mannekote and Kailas (2011) evaluated the studies on coconut oil, palm oil and mineral oil as a lubricant in a four-stroke engine oil using four-ball tests. They observed that the palm and coconut oil have better anti-friction properties compared to the engine oil. The findings of their experiments also showed that the palm oil-based lubricating oil performed better in terms of wear than the mineral oil-based lubricating. Arumugam and Sriram (2012) investigated the effect of bio-lubricants on the tribological behaviour of a cylinder liner piston ring combination by using a pin-on-disc tribometer. The bio-lubricant reduced the COF including frictional force and wear. Furthermore, under comparable working conditions, the bio-lubricants demonstrated greater lubricity than the other test samples. The wear resistance of bio-lubricants was increased by the long-chain fatty acids in them because they created a hydrocarbon layer that shielded surfaces from abrasion. They concluded from the aforementioned studies that engine lubricants made from vegetable oils are renewable, environmentally friendly, biodegradable, and have minimal volatility. Investigation carried out by Kalam et al. (2011) tested the friction and wear properties of a conventional lubricant, lubricants with additives, and lubricants polluted with waste vegetable oil (WVO). The results showed that there was a reduction in wear as well as friction coefficient when lubricants polluted with WVO. The amine phosphate in the lubricant with WVO is responsible for the anti-wear property. Jayadas et al. (2007) evaluated the studies on coconut oil bio-lubricant and tested the anti-wear characteristics by a four-ball tester and obtained higher anti-wear properties and less frictional co-efficient for the coconut oil-based lubricant.

Zulkifli et al. (2013a, 2013b) investigated the studies on palm oil-based TMP ester under fluid film lubrication using high-frequency reciprocating rig (HFRR) to evaluate the wear test. Several blends of palm oil-based TMP ester including 1%, 3%, 5%, 7%, and 10% were tested and analysed. It was found that 3% addition of palm oil-based TMP ester in OL (ordinary lubricant) decreased coefficient of friction up to 30%. For hydrodynamic lubrication, addition of 7% of TMP reduced the friction up to 50% and thus it is responsible for increasing the mechanical efficiency of the components. Bhale et al. (2008) evaluated the test samples from pin-on-disc with lube oil contaminated with methyl ester derived from *Jatropha* oil and diesel fuel. Oxygenated components mixed with the double bond in the *Jatropha* oil resulted in higher lubricity, leading to the lowest wear and friction coefficient. Awang et al. (2019) evaluated the studies using piston-skirt liner tribometer by mixing CNC nanoparticles (various concentrations) in engine oil. They observed significantly reduction in the friction and wear rate and hence improving the lubricating properties of engine oil. Base oil containing 0.1% CNC demonstrated excellent tribological properties including the lowest COF and the strongest wear resistance under all lubrication conditions. The CNC nano-lubricant chemically reacts with surfaces to form a tribo-boundary film that deposits above the frictional surfaces and hence can reduce the friction coefficient. Sadriwala et al. (2020) analysed the research on jojoba oil and its combinations with mineral oil to determine whether it was practical for tribological purposes. A blend of 10% jojoba oil made a substantial contribution to the study by offering the lowest COF and wear. In comparison with the other mixes, 10 per cent blends maintained a better fluid layer throughout the process. The least COF and wear were around 0.037 and 0.32, respectively. Singh (2015) evaluated the studies on tribological behaviour as lubricant additive and physiochemical characterization of *Jatropha* oil blends. SAE-40 was used as conventional lubricant. According to the experimental findings, the wear scar diameter increased as lubricating oil load increased and decreased with the addition of *Jatropha* oil. They also observed that the addition of 15% *Jatropha* oil with base lubricant produced better performance and anti-wear characteristics. Arumugam and Sriram (2013) evaluated the tribological effects of chemically modified bio-lubricants and commercial synthetic lubricants on cylinder liners and piston rings of a diesel engine with a high-frequency reciprocating tribometer. Compared to synthetic lubricants, bio-lubricants with chemical changes had greater oxidative stability, enhanced cold flow, and superior frictional forces and friction coefficients. During boundary lubrication, the chemically modified bio-lubricant had a coefficient of friction 23% lower than commercial synthetic lubricants. Similar studies have been conducted by Bekal and Bhat (2012) on *Jatropha* oil as a bio-lubricant with pin-on-disc machine and found a reduction in wear and engine emission. Shahabuddin et al. (2013) evaluated *Jatropha* oil by blending it in different proportions with mineral oil and tested for friction and wear properties. When *Jatropha* oil was blended with the reference oil, the coefficient of friction and wear reduced by 10%. The overall research conducted by using vegetable oil-based bio-lubricants and their influence on wear and friction is shown in Table 7.

6.4 Nanoparticles additives

Nanoparticles of different origins were added with bio-lubricants to improve the tribological performance such as friction and wear. Nanoparticles were added as additives to the mineral oil, synthetic oil as well as to the vegetable oil bio-lubricants. Several studies were conducted using nanoparticle additives to mineral oil-based lubricants to analyse the

Table 7 Overview of the research conducted using vegetable oil-based bio-lubricants and their influence on wear and friction (Mobarak et al., 2014)

Researchers	Test method and condition	Bio-lubricants	Reference lubricant	Result
Bhale et al. (2008)	Pin-on-disc machine	Jatropha methyl ester	Lube oil	Due to the presence of oxygenated moieties in jatropha oil methyl ester, which together with double bonds improved overall lubricity further, the lube oil contaminated with jatropha oil showed lower wear; cumulative weight loss, and friction coefficient than the lube oil contaminated with diesel under similar operating conditions
Arumugam and Sriram, (2013)	High-frequency reciprocating tribometer test rig	Chemically modified rapeseed oil bio-lubricant	SAE20W40	Rapeseed oil underwent chemical modification via the epoxidation, hydroxylation, and esterification processes. The bio-lubricant made from chemically modified rapeseed oil performs better in terms of frictional force and coefficient of friction as well as good oxidative stability and improved cold flow properties
Bekal and Bhat, (2012)	Pin-on-disc machine	Pongamia oil	SAE 20W40	The use of pongamia oil as a lubricant can improve efficiency and totally stop the emission of metal residues, in contrast to the use of mineral oil

Table 7 (continued)

Researchers	Test method and condition	Bio-lubricants	Reference lubricant	Result
Asadauskas et al. (1997), Adh-varyu et al. (2005)	Four-ball tribo-tester	Soybean oil	Petroleum-based mineral oils	The FA chain can exhibit excellent low-temperature flow and stability with an ideal chain length of six carbons connected to the unsaturated carbon. Thermal and oxidative stability of the chemically modified oils were the best as compared to raw soybean oil
Chauthan and Chhibber, (2013)	Different tribo-tester with high flash point standard test method	Vegetable oils (Jatropha, Neem, Karanja, Soybean, Palm, Coconut, Castor, Olive, Mahua, Sunflower, etc.)	Petroleum based mineral oils	Since they can be made readily from stable vegetable oils and their ester, it is recommended that the majority of mineral oil-based greases be replaced with quickly biodegradable greases
Ting and Chen, (2011)	High-frequency reciprocating tribometer test rig	Soybean oil	Commercial synthetic lubricant	The results showed that the viscosity of the epoxidized soybean oil is significantly greater than that of the engine lubricants and the original soybean oil. By combining the three soybean oils as base oils, viscosity analysis delivers effective forms to fit the viscosity of engine lubricants
Jayadas et al. (2007)	Four-ball tester	Coconut oil	SAE 20W50	Wear with coconut oil has been significantly reduced by the inclusion of the anti-wear/extreme pressure ingredient as 2-T oil

Table 7 (continued)

Researchers	Test method and condition	Bio-lubricants	Reference lubricant	Result
Lebedevas et al. (2013) Fazal et al. (2012) Maleque et al. (2000)	High-frequency reciprocating rig (ball-on-flat). steel-steel pair contacts	Palm oil	SAE20W50	Results showed that at lower loads (up to 500 N) and temperatures (up to 100 °C), the wear rates under 5% Palm oil methyl ester lubricant are lower, whereas at higher loads and temperatures, the wear rates are higher
Arumugam and Sriram, (2012) Zulkifli et al., (2013a, 2013b)	Pin-on-disc tribo wear tribometer	Castor oil and palm oil	SAE 20W40	
The biodegradable palm oil used to make the TMP ester has excellent lubricity characteristics, including a higher flashpoint temperature and VI				
Kalam et al. (2011)	Four-ball tribo-tester, with standard test method Ip-239	Waste palm oil	SAE 40	Waste palm oil with a normal lubricant and an amine phosphate additive might be used as a lubricant substitute (maximum 4%) since amine phosphate's anti-wear properties lowered wear and friction coefficient and enhanced viscosity

Table 7 (continued)

Researchers	Test method and condition	Bio-lubricants	Reference lubricant	Result
Erhan et al. (2000b)	High-frequency reciprocating machine	Palm oil-based TMP ester	SAE 40	Vegetable oil-based lubricants with a combination of chemical additives, diluent (polyalphaolefin), and high-oleic vegetable oils show superior oxidative stability and improved low temperature properties like pour points in comparison with commercially available industrial oils like bio-based hydraulic fluids

influence on friction and wear, COF and other tribological properties. Sulgani and Karimipour (2019) investigated the effect of a hybrid nano-powder of aluminium oxide (Al_2O_3) and iron (III) oxide (Fe_2O_3) on the thermal characteristics of 10w40 engine oil. Influence of nanoparticle concentration at varied mass fractions (0, 0.25, 0.5, 1, 2, and 4) was investigated. The KD2-Pro thermal analyser was used to evaluate the thermal conductivity of the hybrid nano-fluid. The result showed that even the smallest mass concentration improved the thermal characteristics of the nano-lubricant. For friction testing, CuO was added to API-SF oil (engine oil SAE 30) and base oil. This resulted in friction coefficients that were 18.4% and 5.8% lower than those of the oils without nanoparticles. The application of Fe, Cu, and Co nanoparticles dramatically reduced the friction coefficient and wear of friction pairs (up to 1.5 times), according to a tribological study of mineral oils with nano-additives. Tribological tests revealed that using combinations of nanoparticles was superior to using them alone. Celik et al. (2013) reviewed the research on engine oil that had nano-hBN added, which altered the coefficients of friction. Direct contact was avoided because to the presence of enough nano-hBN additions in the oil, which also reduced wear and friction. Jatti and Kumar (2015) conducted research on the tribological behaviour of titanium oxide nanoparticles added to multi-grade engine oil based on minerals. Tests were conducted with loads of 40, 60, and 90 N, sliding speeds of 0.5 m/s, 1.0 m/s, and 1.5 m/s, and nanoparticle concentrations of 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt%. They noticed that, when compared to base oil, all nano-lubricants tested showed decreased friction and wear. The deposition of soft TiO_2 nanoparticles on the worn surface was thought to be the cause of the anti-friction and anti-wear behaviour because they reduced shearing resistance and so improved tribological qualities. Studies conducted by Singh et al., (2020a, 2020b) showed that the addition of nanoparticles to mineral oil significantly improved lubricant properties like load carrying capacity, coefficient of friction (COF), wear scar diameter (WSD). 0.01% vol fraction of titanium dioxide (TiO_2) increased the load carrying capacity of journal bearing by 40%.

Some researchers have also worked on addition of nanoparticles to synthetic oil, to improve the lubricating properties. Padgurskas et al. (2013) evaluated tribological properties of lubricant additives of Co, Cu, and Fe nanoparticles in SAE 10 oil. Oil friction coefficients and wear were lowered by the inclusion of nanoparticles by up to 1.5 times when compared to oil without such additives. Tribological tests revealed that using copper nanoparticles alone or in conjunction with other nanoparticles was the most effective way to reduce wear and friction. They came to the conclusion that combinations of nanoparticles were more efficient than pure nanoparticles. Wan et al. (2015) evaluated the tribological behaviour of lubricative oil (SAE 15 W-40), containing nanoparticles of boron nitride (BN). They measured the rheological behaviour of the lubricant oil with a rheometer, while they tested the anti-wear and anti-friction properties of the nano-lubricant using a tribometer. The nano-BN oils significantly improved the base oil's anti-friction and anti-wear (AW) properties, with lower nanoparticle concentration exhibited better tribological performance. Asnida et al. (2018) improved the durability of piston-liner contact, by employing copper oxide nanoparticles as an additive in engine oil. To minimize wear and friction on the piston skirt, copper oxide nanoparticles were distributed in SAE10W-30. CuO nanoparticles, added to syntium oil as an additive, effectively reduced friction and wear in the lubricating oil. Raina and Anand (2018) investigated the impact of diamond nanoparticle concentration on the friction and wear properties of polyalphaolefin (PAO) oil. The near spherical shape of nanoparticles reduced sliding contact between interacting surfaces and smoothed acute asperities, decreased both co-efficient of friction and wear loss. For a 0.2 wt% concentration, the minimal wear loss is obtained.

Addition of nanoparticles to the vegetable oil bio-lubricant has been studied by few researchers; Zulkifli et al., (2013a, 2013b), using a four-ball machine tribo-tester, assessed the tribological properties of two lubricating oils, paraffin oil and palm oil bio-lubricant containing TiO_2 nanoparticles as additives. As TiO_2 nanoparticles were added to the TMP ester, the friction coefficient was lowered by 14% and 10% reduction in wear scar diameter compared to the TMP ester without TiO_2 nanoparticles. Gulzar et al. (2015) evaluated molybdenum disulphide (MoS_2) nanoparticles on modified Palm oil and they claimed that for a 1 wt% concentration of the nanoparticles, the extreme pressure (EP) properties were increased by 1.5 times. Shafi and Charoo et al. (2020) studied rheological behaviour of Hazelnut oil blended with different concentrations of zirconium dioxide (ZrO_2) nano-additives. The viscosity of the mixture was found to be highest (5.8%) when 1.5% ZrO_2 by weight was added to Hazelnut oil. Singh et al., (2020a, 2020b) evaluated the tribological properties of modified juliflora oil with the addition of TiO_2 nanoparticles. After chemical modification of juliflora oil, the iodine value of the oil decreased, and adding nanoparticles helped to increase oil's kinematic viscosity. With a nanoparticle addition of 1.2%, the maximum increase was observed. Adding nanoparticles increased the flash point, and the maximum reached at a concentration of 0.6%. Tribological tests showed that 0.6% of TiO_2 nanoparticles significantly decreased the COF and pin wear.

Hence, it can be summarized as, adding nanoparticles to a base synthetic oil increases anti-friction qualities while reducing wear. Comprehensive studies have been undertaken by adding nano-additives to the mineral or synthetic oil. The studies related to the addition of nanoparticles to vegetable oil-based bio-lubricants are scanty or limited. Formerly conducted studies have revealed that dispersion and anti-wear property of epoxidized oil improved with the addition of nanoparticles at the optimum concentration. Results also depend on the type of oil, nanoparticle type, its concentration, and size. Hence, comprehensive studies are required to claim the advantage of using nanoparticles as additive to bio-lubricants in terms of physiochemical and rheological properties, agglomeration of nanoparticles, concentration of nanoparticles, volume and size variation, etc. It was observed that as the nanoparticle concentration increased, the flash point of epoxidized oil increased; however, there was a reduction in pour point which may be a factor of concern for lubricant to be used at low temperatures.

7 Conclusions

In the present paper, applicability of vegetable oils as bio-lubricants has been comprehensively discussed with focusing on the chemical modifications required, tribological characteristics and additives added to the bio lubricant. The conclusions drawn from the current study can be summarized as.

1. The major challenge with the utilization of vegetable oils is their thermo-oxidative instability. These vegetable oils can be transesterified and epoxidized to address this issue.
2. Improved lubricity, oxidative stability, and low temperature qualities are provided via estolide production, which often calls for lower reaction temperatures. A wide range of lubricants with radically diverse properties can be created using a variety of fatty acids, and the resulting estolides can be esterified to further enhance their low-temperature capabilities and stability. However, the process becomes expensive.

3. Due to the exothermic nature of the reaction, epoxidation has relatively modest reaction temperatures, but it dramatically raises the pour point and lowers the viscosity index. It also improves the lubricity properties and stability of the vegetable oil.
4. Catalyst, molar ratio and the reaction temperature are the most influencing parameters for epoxidation. However, optimization of these parameters is required for a better yield which also depend on the type of the vegetable oil.
5. Compared to synthetic and mineral lubricants, bio-lubricants with chemical changes had greater oxidative stability, enhanced cold flow, and superior frictional forces and friction coefficients.
6. The nanoparticles were effective additives for bio-lubricants, as they reduce wear and friction co-efficient significantly and enhanced thermal stability compared with oil without additives.
7. Despite the fact that the use of bio-lubricants is currently extremely low, the trend is expanding and is dependent on spending money on research and development (R&D). Although bio-lubricants are more environmentally friendly than minerals and have better quality and longer lifespans, their expensive price in relation to minerals prohibits their development from being expedited further. The technology needed to produce renewable lubricants at competitive prices and in the scale required to make a bigger impact on the market is currently lacking. An expansion in scale, which is directly dependent on the supply security of vegetable oils as the primary raw material, could result in more affordable costs.
8. Cost-effectiveness of production techniques of the vegetable oil based lubricants should be continuously improved. The study of bio-lubricants will require the creation of less expensive feedstocks, more effective catalysts, and improved reaction methods.
9. Additional research will also be required to demonstrate the benefits of using vegetable oils in place of mineral oils and persuade producers and operators of these benefits. These initiatives will undoubtedly result in the widespread use of bio-lubricants in the future, providing significant advantages such as great biodegradability, decreased dependency on petroleum, less detrimental effects on human health, and minimal environmental harm.
10. The creation of diverse biodegradable industrial lubricants, however, has the potential to bring about a significant shift in the global lubricant sector. The laws governing disposal and environmental standards are becoming tougher, which may push consumers to switch to using biodegradable items. The market share of environmentally friendly lubricants is expected to increase to 15% within the next 15–20 years, and up to 30% in some areas. Within the next 10 to 15 years, the world's lubricant market will witness a significant replacement of the current products, and it will undoubtedly continue to be an exciting area of development for lubricant makers.
11. Plant oils may be chemically altered to improve properties including vulnerability to hydrolysis and oxidative attacks, poor low temperature behaviour, and low viscosity index coefficients. Finding a balance between the commercial potential of bio-lubricants and their ecological constraints will grow more challenging. If a product poses a serious risk to human health, it must be removed from further use in lubricants because of toxicological and ecological concerns. In conclusion, plant bio-based oils are a crucial component of new strategies, laws, and subsidies that help to lessen reliance on fossil fuels like mineral oil.

8 Challenges and future perspective of bio lubricants

When it comes to the pour point, most vegetable oils freeze at roughly $-11\text{ }^{\circ}\text{C}$, preventing them from being used. Unsaturated vegetable oils possess low thermo-oxidative stability, making them vulnerable to chemical attack, which changes their bio-physico-chemical characteristics. The fundamental problem stems from the feedstock's great variability and seasonality, which means that varied chemical compositions of the initial vegetable oil are possible, creating ambiguity with their use. Another problem is deciding which non-edible oil to use. Because their use could lead to price speculation and societal disruption, most previous research could disrupt the food chain. As a result, non-edible oils like have become increasingly popular as a sustainable alternative in recent years.

In comparison with standard mineral oils, bio-lubricants future prospects should focus on improved lubricating qualities and non-toxicity. Chemical alterations of the initial vegetable oils are also crucial for improving the final formulation of bio-lubricants. In recent years, enzyme methods have proven to be viable options for obtaining precursors or bio-lubricants at low temperatures.

Nanoparticles have been proven to improve bio-lubricant by reducing asperity contact and wear. Despite the many benefits of using nanoparticles as oil additives that were examined and summarized in this research, there are some inherent restrictions on their use that need to be further researched in the future. Preparing and maintaining homogeneous mixes of nanostructure particles and oils is the first and perhaps most difficult issue. To create lubricants that are both physically and chemically stable, numerous nanoparticle stability modification strategies should be researched in all types of base oils. Another challenge with nanoparticle applications, they face high production costs because high-tech equipment must be used to create them. As a result, efforts should be focused on enhancing nanoparticle production techniques to make their uses more economically viable. The nanoparticle size and its concentration to be optimized for a basic type of vegetable oil bio-lubricant which shows the maximum performance. But despite all these, lubricants prepared from the vegetable oils have a great prospect in the future as they can overcome most of the shortcomings and challenges with conventional mineral or synthetic lubricants.

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Data availability The data that support the findings of this study are available on request from the corresponding author.

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