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Review

A Review on Bio-Lubricants as an Alternative Green Product: Tribological Performance, Mechanism, Challenges and Future Opportunities

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Abstract

Industries, especially those related to transportation, have relied extensively on petroleum products for lubrication, raising serious questions about the security of the world energy supply in the future. Observed that the end-products might be released back into the environment, posing major environmental risks. As a result, bio-based products have attracted increasing interest as prospective replacement to mineral-based type due to their important role in resolving the issues of pollution. With renewability and biodegradability as their greatest points, bio-based lubricants have been discovered to offer superior lubricating qualities to those of traditional mineral lubricants but currently have some undesirable qualities that need to be improved based on the literatures. Therefore, this research objective is to showcase the potential of bio-lubricants, both in terms of their environmental benefits and for technical applications, based on studies that have been published over the years. Review of the natural oil's molecular structures, physio-chemical characteristics, and lubricating ability is crucial for the creation and choice of lubricants. Owing to their accessibility in a wide range of characteristics, which are necessary for specific applications, bio-based lubricant is a possible replacement for a variety of applications, according to the primary findings. The results showed that sunflower oil improved in reducing friction and wear by 93.7% and 70.1%; and 77.7% and 74.1%, under TiO_2 and SiO_2 studied, against base lubricant values of 0.0511 and 11.2414 (mm^3), respectively. However, to get beyond some of the restrictions such as poor low temperature and oxidative stability, adequate chemical modification is necessary in solving agglomeration challenges.

Keywords

vegetable lubricant, bio-lubricant potentials, sustainability, tribological performance

1 Introduction

In industries (transportation and production) or any sliding operations, lubricants are used to reduce wear and friction on interacting surfaces [1]. Apart from minimizing wear and friction, lubricants also help prevent corrosion [2], distribute power, remove heat [3], and provide a liquid seal at moving contacts. From large gear like industrial metal-rolling mills to small equipment like computer hard drives, lubricants are employed in a variety of equipment to maintain dependable machine performance [4]. Although not all lubricants are liquids, that way 19th century's industrial growth generated a demand for liquid lubricants that quickly outpaced the supply of every other type, thus meeting the expectations [4, 5]. In solving the lubrication challenges, mineral oil, a raw material made possible using petroleum source, was also produced. However, since ordinary base lubricant cannot withstand the working conditions, enhancement through inclusion of sui additives were introduced. In this synergistic approach, while the additives offer extra features to the final product, base stocks contribute unique basic characteristics. As to foster development via industrialization, the demand for lubricants around the world has increased at a rate of 2% annually over the past ten years, and by 2017 recorded approximately 42.1

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million metric tons [4], mostly products of petroleum.

Additionally, it has been demonstrated that the combustion of mineral oils used as lubricants releases some amounts of heavy metals like calcium, magnesium, phosphorus, iron, zinc particulates [6, 7]. Again, Tung and McMillan [8] predicted gloomy future prospects after analyzing the current and potential uses of mineral oils as lubricants in automotive engines. According to sustainability development goal drive that defined sustainability, as the process of advanced modification in a balanced environment, whereby the exploitation of resources and technological development are compounded to improve immediate and future application to meet human requirements and objectives [9].

The automobile and equipment industries are particularly interested in enhancing long term sustainability, dependability, durability, and energy efficiency [10]. To lessen the environmental issues posed by automobiles and machinery, new technological solutions could be developed, such as the use of lightweight materials, low toxic lubricants/fuels and controlled exhaust pollution as well as fuel consumption [1]. For example, internal combustion (IC) engines produce high-pressure gases and high-temperature expansion as a result of combustion, which exert direct force on the parts of engine-like pistons and convert chemical energy into useful mechanical energy [2]. To achieve maximum output, effective lubrication of moving parts is necessary in order to operate reliably and safely under intended operating circumstances and for them to move smoothly past one another without seize. Since energy losses are mostly caused by wear and friction, especially in engines and drive trains, as explained thermodynamically. As a result, efforts are conducted to find suitable mineral oil substitutes for industrial applications. However, the environmental impact from the use of these petroleum derived products becomes worrisome due to emission of some poisonous, thus needed replacement that are eco-friendly. Singh [11], conducted experiment on Castor oil-based lubricant ability to minimize smoke emission during engine operation. The results showed that the reference oil had a smoke of 7.5 (%) on the chassis dynamometer at 40 km/h with wide open throttle, whereas the oil samples A, B, and C had smoke of 3, 2.5, and 2.8%, respectively. The best performed oil had an average smoke level of 2.77, which was less than half of the reference mineral oils. At 40 kmph, this indicated a significant decrease in smoke, thus found within JASO "FC" specification. Again, Reddy et al., [12], affirmed emission reduction with vegetable lubricant during investigation on usage of vegetable palm oil as a Lubricant to replace mineral counterpart in CI Engines. Comparing mineral oil to blends of mineral oil and palm oil evidently shows that mineral oil emits greater NOx emissions. However, lower NOx emissions were obtained with 25% palm oil blend than 50% palm oil blend. The study further revealed similar HC emissions when using 100% mineral oil and a 25% palm oil blend, but marginally decreased when using a 50% palm oil blend.

Bio-products, due to their natural technical characteristics and ability to break down through biodegradation [13], bio-oils are viewed as replacement to mineral oils. Vegetable oil-based bio-lubricants often display high flash point, high viscosity index (VI), high lubricity, and moderate evaporative losses in relative to mineral oils [14-16]. Owning to the length of bio-oil fatty acid chains together the polar groups in the structure of bio oils, the lubricants can be used for different lubrications regime [16, 17]. Seeds that contain oil are widely available and can be used to make vegetable oil. In categorizing bio-lubricants, both edible and inedible vegetable oils are considered vegetable lubricants. Lubricants like; Jatropha [18-20], karanja [21], neem [16], rapeseed [22, 23], castor [24], linseed [25], palm [12, 26], sunflower [27], coconut [28], soybean [29], olive [30], and canola [31] are a few examples.

Vegetable oil has been used as engine fuel by many studies [32, 33], but only a small number have mentioned employing vegetable oil-based lubricants for automotive applications [34]. Numerous research studies from the last few decades have covered the usage of bio lubricants as substitutes in lubrication applications. Only a small number of these investigations have examined and evaluated bio-lubricants thoroughly to understand their operational tendencies. Therefore, the primary goal of this study is to review bio-lubricant lubrications with presentation of their performances and mechanism of operation. Challenges and future expectations in bio lubricants for tribologist, policymakers, industrialists, and researchers were elucidated. This provides a thorough analysis of the possibilities for using bio lubricants as substitute lubricants for industrial applications, including information on the features of vegetable oils and their possibility to serve as lubricants. In this research, the most recent articles as well as several published reports in highly regarded journals in scientific indices are evaluated.

2 Lubricating oil sources and their nature

High molecular weight hydrocarbons that are building stocks for conventional lubricants are obtained from vacuum residue in the refinery. Unsaturated fatty acids are used as base stocks in bio-lubricants, which until now have been based on vegetable oil [32]. Due to their weak heat stability and poor oxidation stability from the presence of oxidizable functional groups brought on by an unsaturated bond, pure vegetable lubricants are found inappropriate for use in applications like lubricating fluids [35]. Vegetable oils can have their unsaturated fatty acid content decreased to make them appropriate for use in engines and make them equivalent to conventional lubricants via chemical modification methods like hydrogenation, transesterification and epoxidation [30, 36, 37]. The various base stocks applied to make lubricating oils are listed in Table 1 based on the literature reviewed. Depending on whether they are made of synthetic or mineral oil, the base oils are divided into five classes (I–V) by the American Petroleum Institute (API) [38, 39]. The categorization is also influenced by the oils' sulfur content and hydrocarbon composition, thus makes bio-lubricant promising in lubricant formulation [2, 40].

To enhance the final lubricant formulation's, physical, chemical and thermal qualities, as well as stability through additives, added new features to base stocks. Based on their function in lubrication systems, lubricant additives are divided into different categories: friction modifiers, anti-oxidation agents and anti-wear. Additionally, they are categorized according to their working environment and role, like tribo-improvers, rheo-improvers, and maintainers [39]. Lubricant tribological performance is improved by tribo-improvers; rheo-improvers are designed for base oil's fluidity, while maintainers prevent the lubricants and machine parts from degrading, as well as the breakdown of the substances involved in the lubrication system.

3 Why bio-based lubricants a greener product

In lubricant classifications, plants like coconut, palm, soybean, sunflower and rapeseed are used to produce bio-

Table 1 Categories and sources of various base stocks for formulation of lubricant oils

Base stocks oil	Biomass base oil stocks [4, 14]	Synthetic oil base stocks [39, 40]	Mineral base oil stocks [14, 37, 40]	Re-refined base oil stocks [14, 41]
Sources	Bio-oils, lipids, and oils produced from agro-residues and wastes through thermochemical and catalytic processing are among the plant- and animal-based oils.	Generated from petroleum crude oil using hydro-treating and hydro-processing after chemical modification. They mostly consist of oils based on poly-olefins, silicones, polyolesters. Most of them are API Group IV and V oils.	They are produced during the processing of crude oil, which includes solvent refinement and hydrocracking. They might have a naphthenic, aromatic, or paraffinic composition. The majority of these are oils from API Groups I, II, and III.	Obtained from refined petroleum products that have undergone acid/clay treatment to remove impurities and volatile and insoluble parts. API Group I, II, and III oils are primarily present.

lubricants [4, 41]. Petroleum oils and synthetic esters that meet recognized renewability and less toxic standards can also be used to make bio-lubricants. Generally, bio-lubricants are normally referred to as lubricants with high biodegradable tendency and eco-friendly. The need for lubricants made from plant-based materials is being prompted by increasing environmental concerns and the ensuing environmental restrictions. Since they are non-toxic, renewable and biodegradable, vegetable oils have emerged as the top option for substantial lubricant applications, including hydraulic oils and grease [4]. If a lubricant satisfies the requirements listed in Fig. 1, it is considered sustainable and ecologically friendly:

Vegetable oils have been used as lubricants for machinery for a long time. Due to the discovery of petroleum and the accessibility of cheaper oils, this notion was abandoned. However, there is a growing interest in using lubricants made from vegetable oils because of the negative effects that fossil fuels have on the environment. A variety of companies have created and sold bio-based lubricants [42]. As they maintain the technical requirements of traditional lubricants, bio-based lubricants offer a possible replacement for mineral oils. But there are a few drawbacks to using bio-based lubricants as well. For instance, the poor cold flow characteristics and oxidation stability of these lubricants will cause polymerization and deterioration [34]. This issue can be solved by chemically altering vegetable oils to remove the β-hydrogen atoms in glycerol [43, 44]. Vegetable oil tribological qualities are primarily influenced by the length of the carbon chain, the kind of fatty acids present, and the polarity [45]. A thorough understanding that focuses on their physicochemical qualities, techniques to improve their physicochemical properties, and the suitable additives as to increase lubrication is necessary. This is to ascertain the appropriate renewable feedstock for a given lubrication as well as the working conditions. As lubricant performs many functions as in Fig. 2, knowing the suitable lubricants is essential.

However, their significant limitation is a narrow ability to withstand thermo-oxidation and hydrolysis, which can be fixed by adding additives or chemically altering the oil through transesterification, epoxidation, estolide production, or hydrogenation [46-48]. The triglyceride of ricin-oleic acid makes up most of it as presented in Fig. 3. It has a higher additive solubility due to the existence of hydroxyl content in its building, which increases its polarity and gives it better qualities including improved lubricity, metal affinity, viscosity, and low-temperature performance. Such structures are preferred base oil for lubricant formulations because of these qualities. Among the many industries where such base lubricants normally used are lubricants, fuels, paints, coatings, polymer synthesis, chemicals, and medications.

One of the main barriers to industrial adoption of vegetable oil-based lubricants is low oxidation stability. The effectiveness of natural antioxidants such lignin and its derivatives in lubricants made from vegetable oils was assessed. The most

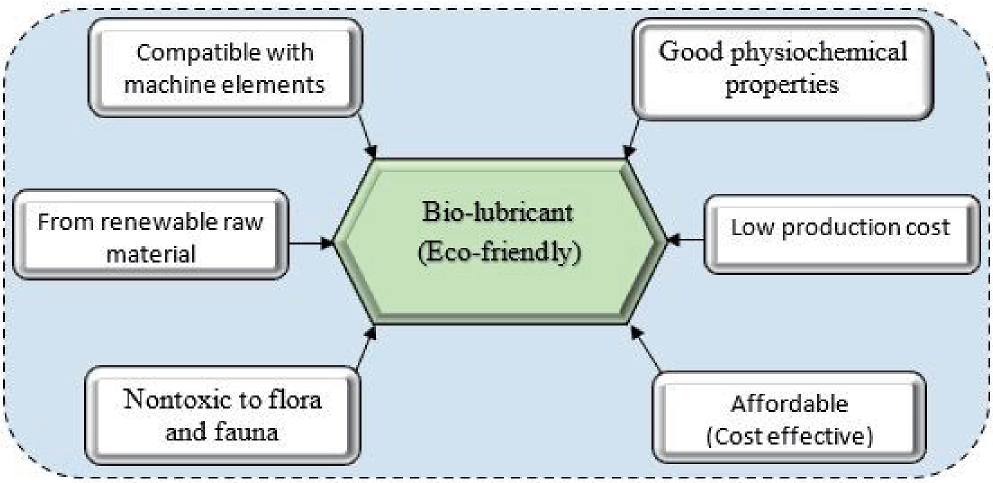

Fig. 1 Sustainability characteristics of bio-lubricant

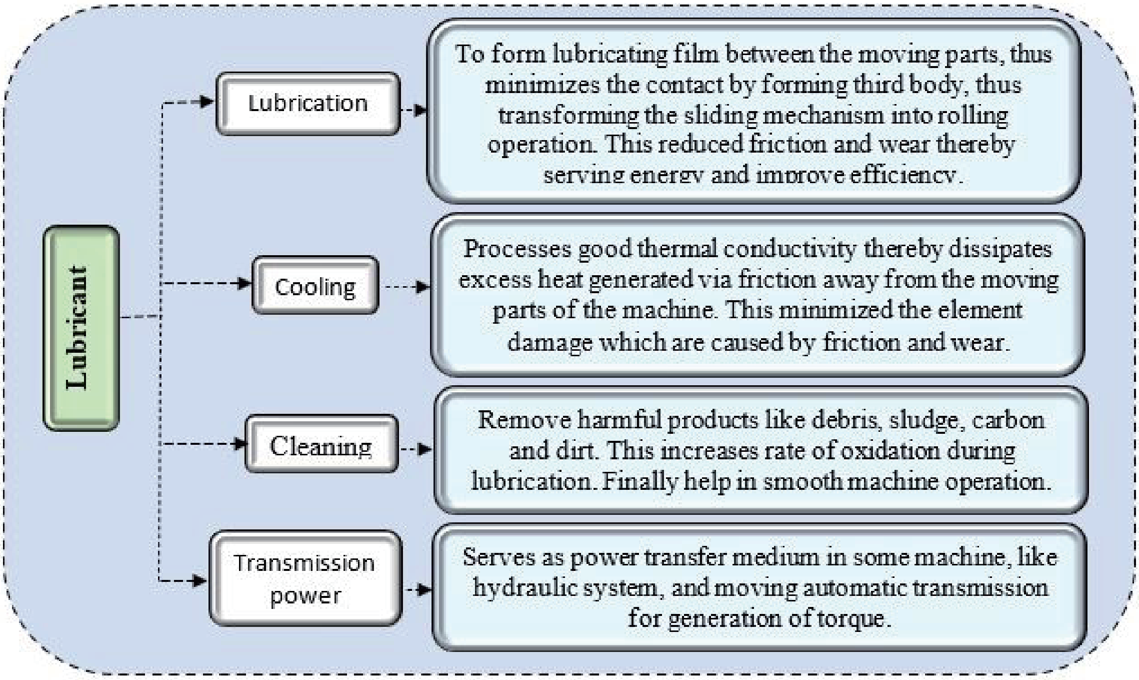

Fig. 2 Categorized functions of lubricants

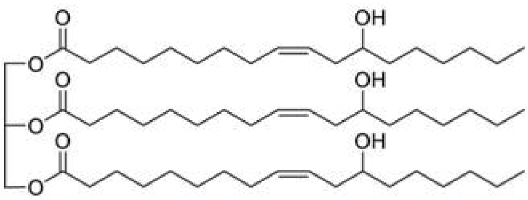

Fig. 3 Chemical structure of most base bio-lubricant showing triglyceride [49, 50]

prevalent polyphenolic substance in nature, lignin is found in biomass derived from land. Monolignols (syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units, as illustrated in Fig. 4, are cross-linked to create it. In addition to lignin's antioxidant characteristics, improved anti-oxidant activity against particular species has been suggested for lignin. Furthermore, under some conditions, lignin has already been shown to have low toxicity and to be compatible with other additives and varieties of lubricants. Different methods of separation, fractionation, and depolymerization can be used to create lignin fractions, as discussed by Wan et al., [51]. Products made from lignin have been highly valued as ingredients in a variety of materials, including polymeric polymers, fuels, adhesives, antioxidants, additives, coatings and platform chemicals [52-55]. The main fatty acids that make up the bio-lubricants made from vegetable oils are presented in Table 2.

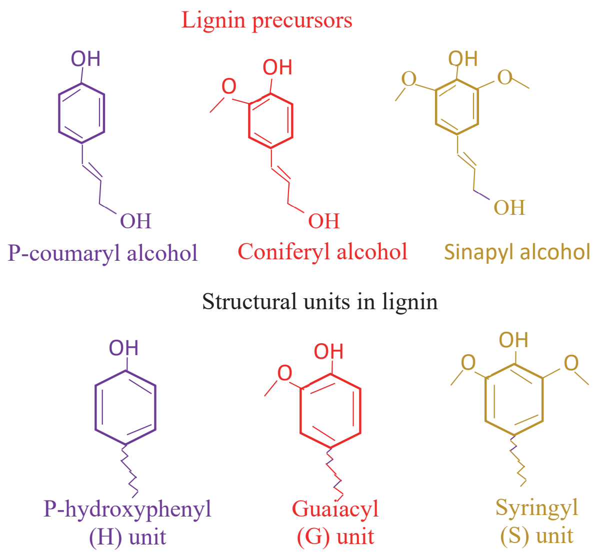

Fig. 4 The structural unit and building blocks of Lignin [56]

Table 2 Various fatty acids present in vegetable base oil for lubricant use

General name	Fatty acid type	Molecular formula	Ref.
Oleic acid	Monounsaturated	$H_{18}H_{34}O_2$	[58-60]
Linolenic acid	Tri unsaturated	$H_{18}H_{30}O_2$	[59, 60]
Palmitic acid	Saturated	$H_{16}H_{32}O_2$	[59, 60]
Ricinoleic acid	Unsaturated	$H_{18}H_{34}O_3$	[59, 60]
Stearic acid	Saturated	$H_{18}H_{36}O_2$	[58-60]
Linoleic acid	Diunsaturated	$H_{18}H_{32}O_2$	[59, 60]

4 Modification of base-bio lubricant

The objective of bio-lubricant research has been to comprehend the connection between chemical assembly and molecular structure and to address the shortcomings of both natural and manufactured lubricants. For instance, bio-lubricants made of branched fatty acids, like isostearic acid, display outstanding low-temperature performance, including a low pour point, low viscosity, good chemical stability, and flashpoint [7, 16]. Polyunsaturated C_{18} fatty acids are thermally isomerized and then hydrogenated to produce isostearic acid. Only the inside of the molecule has branching sites. Similar to that, 12-hydroxystearic acid, which is produced by hydrogenating ricin oleic acid, can also be employed. As was previously mentioned, the performance of the bio lubricant is improved by eliminating the double bonds and the glycerol molecules from the triacylglycerols. In the modifications, several approaches are used including; esterification/transesterification, hydrogenation [57], oligomerization/estoloides and epoxidation, but in course of this research, only transesterification synthesis of formulation of fatty acid methyl esters and ethylene glycol di-esters were considered.

4.1 Synthesis of fatty acid methyl esters (FAMEs)

As emphasised that fatty acid present in lubricant influences its physio-chemical properties, which in turn affect the tribological performance, thus need to modify. In enhancing the physio-chemical characteristics of pure bio-oil, fatty acids methyl esters (FAMEs) and glycerol were produced as by-products of the transesterification method, which altered the carboxylic groups in all oils using methanol and KOH as catalysts [58]. The transesterification reaction was conducted in line with the plan shown in Fig. 5. Triglycerides due transformed into diglycerides, which are then changed to monoglycerides [59] and glycerol in the third and final reversible process of transesterification. Oil, catalyst and the used alcohol are combined and agitated in a reaction vessel to initiate the transesterification reaction [36]. Optimal conditions for transesterification reactions lead to the production of FAMEs [58]. The ideal conditions for optimal transesterification conversion were through application of 20% methanol to oil (w/w), a molar ratio of 6:1, and a catalyst concentration of 1.0% of KOH to oil (w/w). After 60 minutes at 60°C reaction temperature, a maximum methyl ester yield of 98% was attained [60].

Under analysis conducted [58], on soybean, sunflower, Jatropha oils together waste cooking oil applying ethylene glycol as a di-alcohol. All of the generated FAMEs have high levels of linoleic acid (18:2), which correspond to the amounts of waste, sunflower, soybean, and Jatropha oils, respectively, at 68.55, 48.53, 33.51, and 31.82%. A small quantity of linolenic (18:3) is also present, which together with linoleic acid makes up the polyunsaturated fatty acids. Monounsaturated palmitic (16:1) and oleic acids are also present in significant levels in FAMEs (18:1). The fatty acid constituent of the oil will have an influence on the chemical/physical characteristics of the bio lubricants that are created. Low oxidative stability may be caused by the significant amount of unsaturated fatty acids present [58].

4.2 Bio lubricants synthesis from oil-derived FAMEs

A transesterification procedure was employed to create ethylene glycol di-esters (EGDEs) from each oil's generated FAMEs for the various used vegetable oils. In this reaction, as shown in Fig. 6 (a), CaO was utilised as a base-strength heterogeneous catalyst classified by Lewis natures [58]. CaO

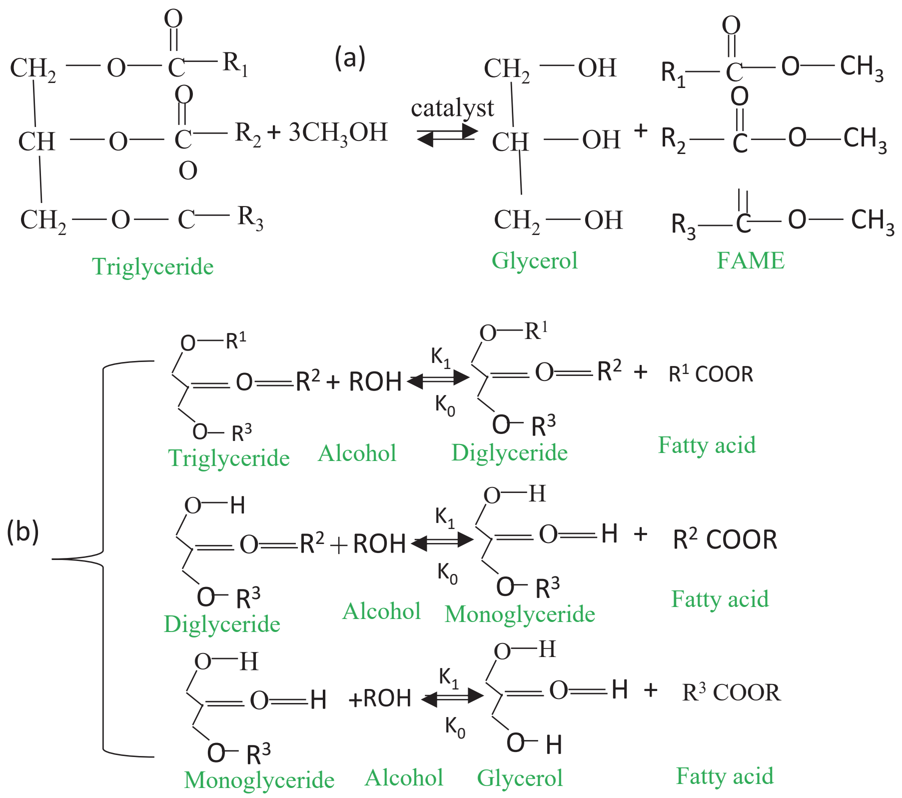

Fig. 5 Triglycerides reaction to produce FAMEs via Transesterification technique [58]

was used because it provides advantages for the environment, including being noncorrosive, recyclable, and having fewer disposal issues. It encourages simple recovery, reusability, and an economical green procedure. In the schematic transesterification reaction shown in Fig. 6, 500 g of each oil-derived FAME was introduced to the reactor setup [60], one at a time, and 53 g of ethylene glycol was added in the stoichiometric value. The end products were sent for assessment after being filtered to remove catalyst and contaminants. To determine the transesterification conversion, the reaction's released methanol was gathered and quantified. The ratio of the actual amount of produced methanol to the theoretically predicted amount was used to compute the transesterification conversion [58, 60].

As presented in Fig. 6 (b), the high selectivity of the corresponding esters produced by transesterification with other alcohols, particularly primary alcohols (2-ethyl-1-butanol, 1-hexanol, 3-buten-1-ol, and 10-undecen-1-ol), suggests the potential for using plant oils to effectively produce a variety of fine chemicals, including the monomer for the synthesis of polyesters [61]. By trans-esterifying aliphatic polyesters, poly (ethylene adipate) and poly (butylene adipate), with ethanol and cyclohexane methanol, and obtaining the corresponding adipates and only ethylene glycol or butylene glycol, efficient acid-, base-free depolymerization of these polyesters has been demonstrated [62]. It has also been shown that a CaO catalyst is efficient [60].

In order to outperform mineral oil lubricants, bio lubricants have been created from plain plant oils by chemically altering their properties [64]. Vegetable oils' physiochemical properties are improved by chemical modification of their fatty acids (Table 3), which also gives bio lubricants the ability to tolerate a variety of working conditions [34, 65]. Some of the essential characteristics features that require for good lubricants are;

i. **Viscosity:** This always refers to as key elements that affects how a bio lubricant is applied [66, 67]. While greater viscosity stocks are used in vehicle engine oil, low viscosity stocks can be used for car transmission oils. The ability of a company to effectively separate the workpiece from the tool (in order to control friction and wear) in a metal forming application is determined by the bio lubricant viscosity. At 40 and 100°C, bio-lubricants' kinematic viscosities are tested, and the results are compared to an observational standard range [17].

ii. **Fire point and flash point:** The minimum temperature at which an external source can ignite vaporised oil is known as a bio-lubricant's flash point (FP), while the temperature at which bio-lubricant combustion would continue for at least five minutes after the ignition source has been removed is known as a bio-lubricant's FP [68]. The volatility and fire resistance of a bio-lubricant are determined by its flash point and fire point, respectively. The flash point of a bio-lubricant determines its needs for storage and transportation. Normally, precautions are needed for safe handling of products with flash points lower than 38°C (100°F). Thus, the flash point and fire point [24, 67] of lubricating oils dictate their flammability risk. According to Owuna et al., [64], the triglycerides' quantity of carbon atoms determines a bio-lubricant's flash point.

iii. **Viscosity index:** Bio lubricant's viscosity index (VI) is a metric used to describe how viscosity changes as temperature changes [25]. A bio-lubricant's viscosity is inversely correlated with its temperature, so a machine that operates in a wide range of temperatures will need a lubricant with a greater viscosity index. The influence of temperature on a lubricant's viscosity is lessened [45] the greater the viscosity index.

iv. **Pour point:** The bio-lubricant will resist flow owing to its extremely high viscosity at low temperatures. The pour point of the lubricant is the minimum point at which a bio-lubricant sample can flow exclusively by gravity. Additionally, it is not the temperature at which solidification takes place, but rather the last temperature

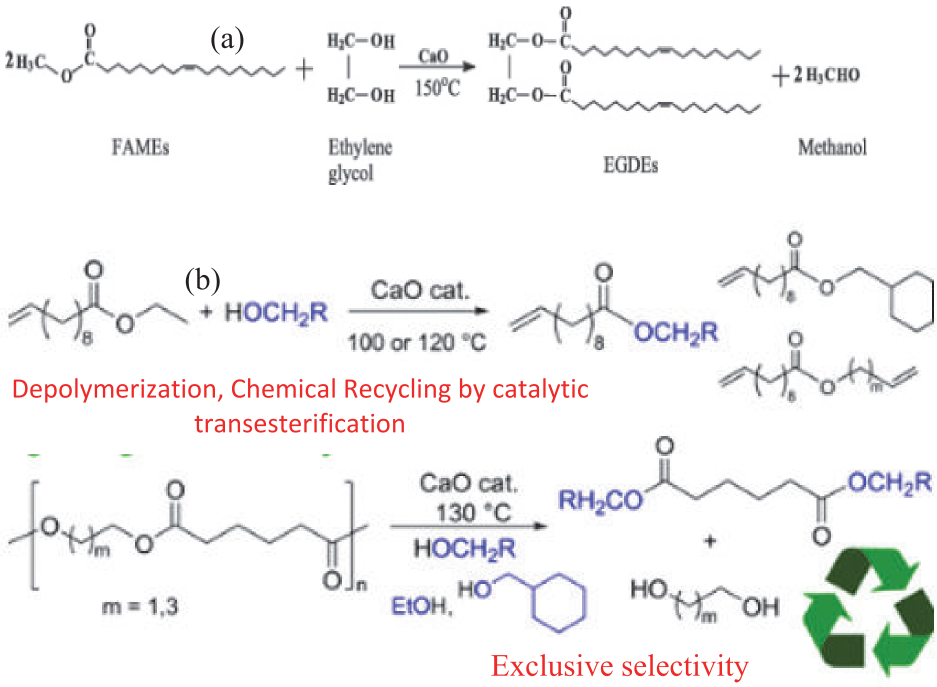

Fig. 6 Synthesis of EGDEs from FAMEs using CaO as a base-strength catalyst [58], (a); and utilization of 2-ethyl-1-butanol, 1-hexanol, 3-buten-1-ol (b) [63]

before movement stops [68]. Pour point (PP) is a crucial feature for machinery that works with cold fluids or operates in a cold environment. As a result of wax formation, very viscous oils may become too viscous to flow at low temperatures. The pour point will be higher than the cloud point in this situation [45].

v. **Acid value:** High levels of acidic chemicals in a bio-lubricant can cause varnish and sludge to accumulate, which can clog oil filters and cause machine parts to corrode. A bio-lubricant's total acid value is a gauge of its acid content. Any bio-lubricant's acid concentration could vary depending on whether an additive package, acidic pollution, and oxidation contaminants are present [17, 69].

vi. **Cloud point:** The cloud point (CP) is the degree upon which bio-lubricant begins to show signs of wax production [16, 17]. It is the temperature at which clouds first appears. The wax crystals that are produced can clog filters and apertures, leaving deposits on surfaces like heat exchangers, and they can also make bio lubricating oil more viscous.

Legend: $C_{8.0}$ = caprillic; $C_{10.0}$ = capric, $C_{18.1}$ = oleic; $C_{12.0}$ = lauric; $C_{14.0}$ = miristic; $C_{18.0}$ = stearic; $C_{18.2}$ = linoleic; $C_{18.3}$ = linolenic; $C_{16.0}$ = palmitic $C_{20.0}$ = arachidic; $C_{22.0}$ = behenic; $C_{24.0}$ = lignoceric

Legend: Can = canola; COR/CRN = corn; SUN/SUR = sunflower, COT = cottonseed; EPR = evening primrose; FC) + linseed; SOY/SYB = soybean; OEV = extra virgin olive; POR = olive pomace; ORF = olive; PEA = Peanut; RIO/RBO = rice bran, COC = Coconut oil.

On the impact of the content of saturated and unsaturated fatty acids in bio-lubricants during lubrication. Zulhanafi et al. [26], on their study, observed that PMO with a good amount of saturated fatty acids has outstanding tribological properties when exposed to a range of temperatures and rotational speeds. However, in extreme pressure (EP) circumstances, no discernible effect was seen. Additionally, the physical wear condition was examined and addressed.

5 Tribological performance of bio-lubricants

Some investigations had been conducted on different bio-lubricants under application of different NPs as additives, with recommended results as presented in Table 4. Thottackkad et al., [70], conducted tribological investigation using CuO NPs combined with coconut oil. According to the findings, the CuO nanoparticle concentration that produced the lowest wear rate and friction coefficient was 0.34 mass%. The viscosity and fire point increased when the nano-additive was applied, while the surface roughness reduced [70]. On analysis conducted by Alves et al., [71] employing zinc oxide (ZnO) and copper oxide (CuO) as lubricant additives. The outcome found that both zinc oxide and copper oxide NPs were rendered inactive as an anti-wear addition for soybean and sunflower oil due to the rise in friction coefficient and the presence of abrasive wear on the worn surface. In another study by Arumugam and Sriram argued on the performance of microparticle addition [72], TiO_2 NPs were added to chemically changed rapeseed. Comparing the TiO_2 microparticles, TiO_2 NPs visibly observed to enhanced the lubricant lubrication performance [72, 73]. Under nanoscale TiO_2 of 6.9% and micro TiO_2, the COF of rapeseed oil blended additives yielded reduction by 15.2% and 6.9%, respectively [72].

Rani et al. [74], performed through experiment on biolubricant behavior under additives of TiO_2, CeO_2, and ZrO_2 NPs, using rice bran oil as base lubricant. The result revealed that 0.5 mass% CeO_2 and 0.3 mass% TiO_2 respectively yielded the greatest COF and wear reduction. This was affirmed by Suthar et al. [75] through analysis on Al_2O_3 NPs mixed with jojoba oil with concentration of 0.1 mass%, thus minimal friction and wear was achieved compared the base lubricant. Again, Rajubhai et al., [76] carried out tribological investigation utilizing CuO blended with Pongamia oil. The result observed that 0.075 mass% of CuO was the optimal concentration to the based lubricant used with excellent wear and friction reduction. Again, copper and h-BN NPs were added to epoxidized olive oil during tribological investigatory work by Kerni et al. [30]. The outcome observed that certain lubricant properties like

Table 3 Percentage composition of fatty acids in some vegetable oils

Oil tested	**Saturated fatty acid**														
Veg. oil	$C_{8.0}$	$C_{10.0}$	$C_{12.0}$	$C_{14.0}$	$C_{16.0}$	$C_{17.0}$	$C_{18.0}$	$C_{18.1}$	$C_{18.2}$	$C_{18.3}$	$C_{20.0}$	$C_{22.0}$	$C_{24.0}$	Total	Ref.
CAN	-	-	-	0,06	3,75	0,04	1,87	-	-	-	0,64	0,35	0,27	6,98	[70, 71]
CRN	-	-	-	-	10,34	0,07	2,04				0,44	0,31	0,26	13,46	[70, 71]
COR	-	-	-	-	10,47	0,08	2,02				0,39	0,76	0,15	13,87	[70, 71]
SUN	-	-	-	0,06	5,70	0,04	4,79				0,30	1,16	0,31	12,36	[70, 71]
SUR	-	-	-	0,05	5,76	0,05	4,76	-	-	-	0,30	0,78	0,22	11,95	[70, 71]
COT	-	-	-	0,77	21,87	0,08	2,27	-	-	-	0,26	0,36	0,09	25,73	[70, 71]
EPR	-	-	-	0,45	5,47	0,07	1,83	-	-	-	0,30	0,31	0,01	25,75	[70, 71]
FCO	-	-	-	0,05	4,81	0,05	3,03	-	-	-	0,20	-	0,21	8,11	[70, 71]
SOY	-	-	-	0,06	9,90	0,10	3,94	-	-	-	0,41	0,48	0,21	8,15	[70, 71]
SYB	-	-	-	0,06	9,63	0,11	4,38	-	-	-	0,35	0,67	0,24	15,10	[70, 71]
OEV	-	-	-	-	8,70	0,17	3,47	-	-	-	0,46	0,13	0,05	15,12	[70, 71]
OPR	-	-	-	0,02	9,31	0,09	3,20	-	-	-	0,55	0,25	0,11	12,98	[70, 71]
ORF	-	-	-	0,03	9,40	0,14	2,59	-	-	-	0,50	0,15	0,06	13,53	[70, 71]
PEA	-	-	-	0,03	9,40	0,12	2,65	-	-	-	1,38	3,14	1,66	15,28	[70, 71]
RBO	-	-	-	0,21	16,90	-	1,76	-	-	-	0,61	0,77	0,41	20,68	[70, 71]
RIO	-	-	-	0,29	14,24		2,13	-	-	-	0,75	0,33	0,48	18,22	[70, 71]
PKL	3,43	3,23	46,14	16,17	8,65	-	2,27	-	-	-	0,15	-	0,30	80,34	[70, 71]
COC	0,8	0,7	49	8	8	-	2	6	2	-	-	-	-	79	[72]
Moringa	-	-	-	-	5,50	-	5,70	73,20	1,00	-	-	-	-	84,140	
Calabash	-	-	-	-	12,11	-	8,49	17,86	60,15	0,12	-	-	-	97,173	

Table 4 Summary of tribological qualities of some bio-lubricants and their application

Bio-lubricant	Application	Quality/performance	Ref
Pongamia oil	Anti-corrosive coating and Power transformer applications,	At medium loads, minimal frictional losses, low emissions, low specific fuel consumption, and good break thermal efficiency.	[82, 87]
Jatropha oil	Biodiesel	High VI, little weight loss from wear or progressive weight reduction, and little friction	[18, 62]
Rapeseed oil	hydraulic fluids, Power transformer applications, greases	improved cold flow characteristics, improved oxidation stability, and low coefficient of friction	[87, 88]
Palm oil	metal working fluids (MWFs)	High viscosity, low coefficient of friction, and less corrosive	[24, 89]
Sunflower oil	biodiesel fuel, Hydraulic oils, engine oils, paints, detergents	High VI, higher flash point than some standard oils, greater lubricity, reduced evaporating loss, lower frictional coefficient, and non-toxic	[26, 90]
Coconut oil	Engine oils	Better lubricity, low coefficient of friction, and high anti-wear	[27]
Canola oi	Transmission fluids, transmission fluid, hydraulic fluids, penetrating oils	High VI, higher flash point than some standard oils, greater lubricity, reduced evaporative loss, lower frictional coefficient, and non-toxic	[30]
Linseed oil	Stains, vanishes, paint	High VI, higher flash point than some standard oils, greater lubricity, reduced evaporative loss, lower frictional coefficient, and non-toxic	[23, 72]
Castor oil	Greases, gear lubricants	Low volatility, high levels of antioxidants, and low deposit formation	[83]

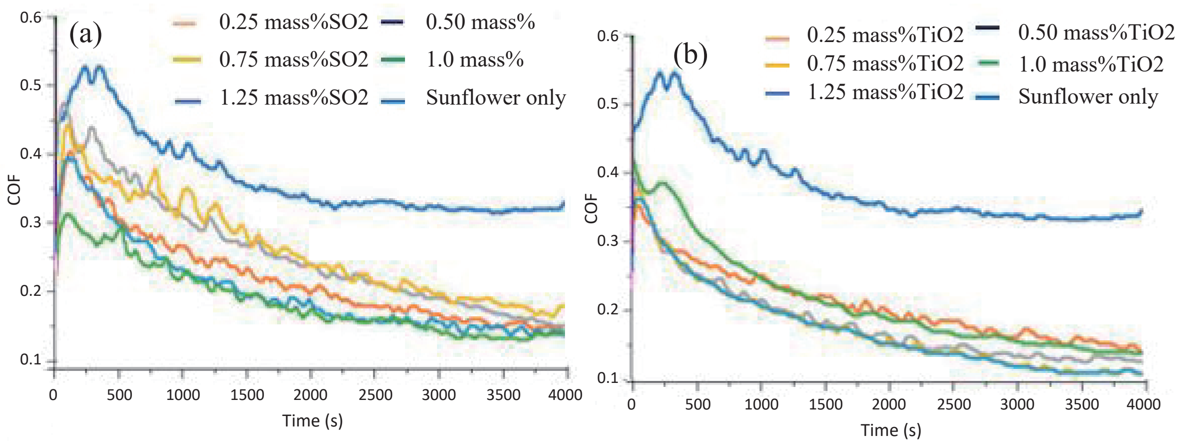

Fig. 7 COF against time for sunflower lubricant blended; SiO_2 (a); and TiO_2 (b) NPs; reproduced with permission from Ref. [27] Copyright (2020) MDPI

wear volume and COF improved after adding 0.5 mass% nano-additives.

Kumar et al. [31], investigated tribological performance of CuO NPs in canola oil using 0.1 mass%, which yielded the lowest friction coefficient and lowest specific wear rate. Brassica and palm oils were combined with CuO and TiO_2 NPs with idea of knowing their tribological behaviors and was conducted by Rajaganapathy et al. [33]. When compared to other nano-lubricants created, palm oil containing 0.5 mass% CuO NPs had the lowest COF and specific wear rate. Similarly, Singh [77], observed that minimum friction coefficient and wear rate for castor oil mixed with TiO_2 NPs occurs at 0.2 mass%. In the study carried out by Zaid et al. [78] using TiO_2 NPs, improved the lubricating properties of jojoba oil. The outcome revealed that the COF and wear scar were lowered under 0.3 mass% TiO_2 NPs were added to jojoba oil.

When lubricant additives of silicon dioxide (SiO_2) and titanium dioxide (TiO_2) NPs were studied by Cortes et al [27], for their effects on the tribological and rheological properties of sunflower oil as in Fig. 7. The outcomes showed that the type and concentration of the NPs utilized affect the rheological properties. The friction coefficient and wear volume loss were respectively reduced by 93.7% and 70.1%; and 77.7% and 74.1% by TiO_2 and SiO_2 NPs [27]. The lubricants curve behaviors are demonstrated in Fig. 7. Halloysite nano-clay was tested by Sneha et al. [79] as anti-wear additive in base rice bran oil and turmeric oil. When compared to other nano-clay concentrations, the tribological results of rice bran oil with 0.1 mass% halloysite nano-clay revealed the lowest friction coefficient and wear scar diameter (WSD) (0.072, 0.531 mm). The WSD was decreased to 0.491 mm by the addition of 1.5 mass% turmeric oil as an anti-oxidant ingredient in rice bran oil with halloysite nano clay [79].

Supporting the performance of NPs in reducing friction and wear, Zhou et al., [80] revealed that COF substantially reduced through application of FeS NPs with excellent wear protection when used under dry sliding condition.

Hassan et al., [81], conducted investigation on the performance of base bio lubricant blended with mineral oil. The analysis made use of bio-lubricants of bleached and deodorized palm olein blends, and it was tested for compliance with the ASTM D4172-B Standard utilizing a four-ball tribo-tester. The sample of E60/RB40 blend had the lowest friction coefficient at 0.057, compared to plain RBD palm olein at 0.072 and mineral oil at 0.081. The E60/RB40 mixture had the lowest diametric wear scar, measuring 408.46 m, compared to neat RBD palm olein's 660.8 m and mineral oil's 546.46 m. The investigation concluded that the chosen vegetable oil (RBD palm olein in its pure form and blends with mineral oil) performed effectively owing to good compatibility.

6 Mechanism of bio-lubricants during operation

As stated above, enhancement of physiochemical and tribological performance of bio-lubricant is through modification and inclusion of suitable additives. For good compatibility and performance of NPs in bio-lubricant, most of them were discovered to be of hydrophobic potential, with ability to repel oxidative agent. The investigatory study on lubricating strength of Eichhornia crassipes NPs (EC-NPs) further revealed that reduction in the size of EC into nanoscale changes from hydrophobic to amphiphilic (hydrophobic tail and hydrophilic head) form [82, 83] as a result of increase in surface area, thus illustrated in Fig. 8 (a). Also, the diffusion behavior of the FeS NPs on the sliding material surfaces was conducted by Zhou et al., [80], illustrating the sulfur (S) atom diffusion resulting in friction reduction, thus illustrated in Fig. 8 (b), while Fig. 8 (c) illustrated the defending mechanism of additives in bio-lubricant during operations. The behavior of various additives during operations are demonstrated in Fig. 8 (c), owing to the degradation effect.

Rust and corrosion are both electrochemical processes that result in the oxidative deterioration of metallic materials. The corrosion process that most characterizes lubrication systems is galvanic corrosion [39]. In a nutshell, the mechanism is as follows. An oxide layer typically covers metal surfaces. The oxide is removed by the tribological process, exposing metal surfaces. Between metal and metal oxide, there is a difference in electrical potential. Galvanic cells are created when a conductive liquid occurs between the surfaces [39]. The metal atom increases its oxidation number, releasing electrons to form metal ions (this process is the oxidation of metal). An oxygen molecule in the system is reduced by the metal's released electron (see

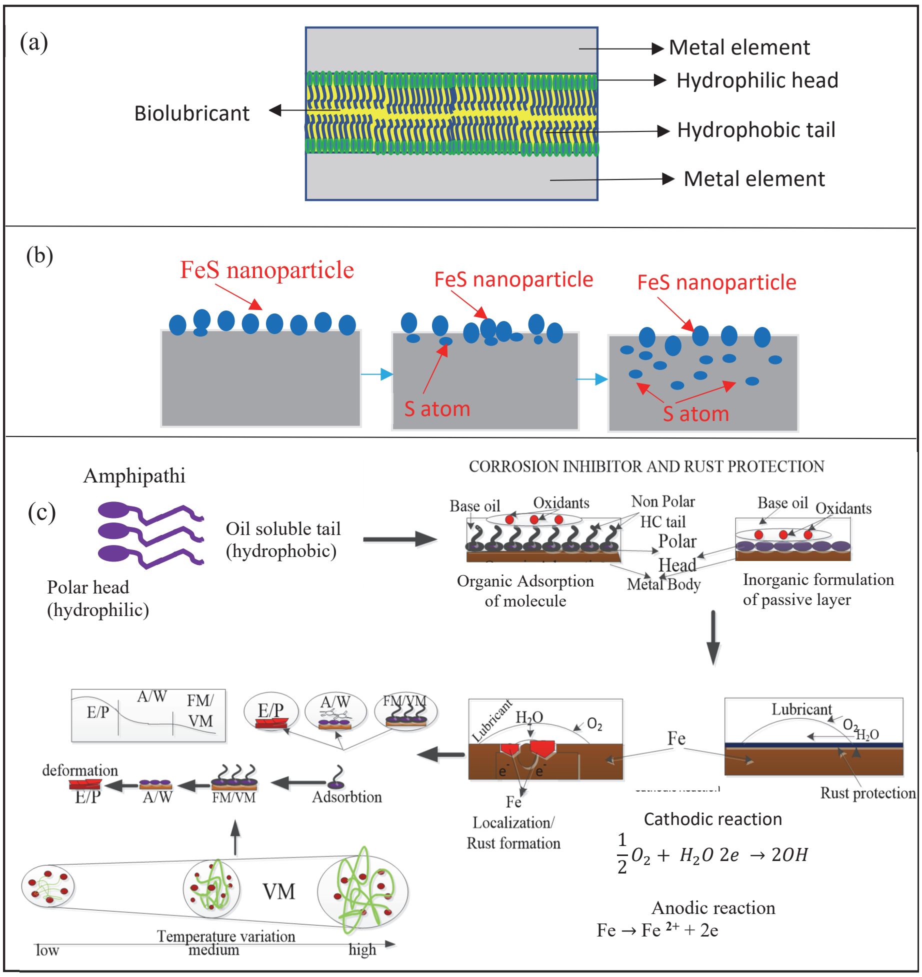

Fig. 8 Arrangement of amphipathic additives inside bio-lubricant (a); diffusion of sulfur (S) atom of FeS NPs (b) and defensive operation of organic/inorganic additive in bio-lubricant against oxidation and rust (c). Note: Extreme pressure additive (EP); anti-wear additive (AW); viscosity modifier (VM); friction modifier (FM).

Fig. 8 (b)). Base lubricants fluids are insulators, however various additions can make the lubricant more electrically conductive. Ionization of metal by acidic chemicals that develop without oxygen is another factor in corrosion. Both corrosion mechanisms are capable of occurring when the equipment is stationary or working. On metal surfaces, corrosion inhibitors offer a layer of protection [39, 84]. The protective layers, which are comparable to FMs, could either be organic (yielding protective organic layer/adsorption type) or inorganic (reaction type, passive layers) (see Figs. 8 (b) and (c)). Films that prevent corrosion do not require mechanical resilience, in contrast to friction modifiers (FMs).

At this point, NPs used as bio-lubricant additives for lubrication lessen wear and friction while increasing the load capacity of mechanical parts [85, 86]. According to Opia et al., [87], affirmed that the fast penetration of NPs of bio-lubricant contribute significantly on the friction and wear reduction during lubrication, as well as load carrying capacity. Particularly, deposited particles on worn or pits/valleys aid to minimizing friction and wear by assisting in the formation of an efficient and workable tribo-film that can separate direct contact. Opia et al., [88], again argued that machine orientation influences the behavior and performance of bio lubricant during operation. The use of high frequency reciprocating rig (HFRR) and unidirectional mode were used during the investigation. The result revealed that under unidirectional, high accumulation of NPs were observed leading to lubricant starvation within the sliding zone, resulting in higher COF and wear compared HFRR mode [88]. Studies of lubrication mechanisms will be essential in understanding the tribological characteristics of the nano-lubricants. Among the lubricating mechanisms of NPs already foreseen are the ball bearing effect, creation of protective layers, mending effect, and polishing effect. Most of these processes fall into one of two types. NPs improve lubrication directly in the first group (ball bearing effect/formation of protective layers), and surface enhancement which comes from polishing/mending as the second group.

6.1 Rolling effect

The added additive size, structure, type, and concentrations contribute in the rolling effect effectiveness [89]. Normal spherical or quasi-spherical NPs roll between the contact surface like ball bearings, converting sliding friction to a combination of sliding and rolling friction [90, 91], as seen in Fig. 9 (a). The ball-bearing mechanism has been the subject of numerous investigations. After analyzing carbon-coated copper NPs, Singh et al., [92] concluded that the ball-bearing mechanism is responsible for tribological enhancement. By using a ball-on-disk tribometer, Shaari et al., [93], examined the tribology characteristics of TiO_2 nano-lubricants. According to their research, these nano-lubricants demonstrated the ball-bearing effect between the ball under four ball tribo-tester, thus examined the wear nature using SEM micrograph. Also, revealed that 0.1% TiO_2 nano-additives yielded the best COF and wear scar diameter. The outcome on the rolling mechanism on wear reduction under bio-lubricant was supported by Abere [94], on bio-lubricant tribological improvement using Polyvit NPs made of alumina (Al_2O_3), graphite and silica (SiO_2). The performance of Al_2O_3 in rapeseed lubricant toward friction reduction was not improved but recorded enhanced result under wear rate reduction. The study shows that COF increased with inclusion of NPs both in rapeseed and mineral oil but revealed reduction on wear rate when tested rapeseed blended NPs. The COF and wear rate were 0.0833 and 38.96 (m^3/m); 0.0995 and 84.64 (m^3/m); 0.0893 and 37.03 (m^3/m); 0.1078 and 119.60 (m^3/m) for base rapeseed oil, base mineral oil, rapeseed blended and mineral blended, respectively.

6.2 Protective effect/film formation operation

The production of protective films, also known as tribo-film, is another bio-lubricant mechanism towards good tribological performance via friction and wear reduction [22, 68]. Tribo-films and materials that are close to the surface control the tribological behaviors of interacting surfaces as illustrated in Fig. 9 (b). This film is produced as a result of the reaction between the treated material and the additives in the working machine [95, 96]. Such films' production is a complex phenomenon that has led to extensive investigation into how they are made and what goes into them. By producing a physical protective layer of distorted NPs depositing on the surfaces, Rapoport et al. discovered that dispersing IF-WS2 NPs in lubricating oil enhanced tribological capabilities [97]. In addition, Menkiti et al., [98], Fuyan et al., [99]. observed that shearing action caused chemical reaction products to deposit on rubbed surfaces, resulting in the formation of a tribo-chemical coating.

6.3 Mending effect

The mending or self-repairing effect that NPs can produce is defined by the deposition of NPs on interacting surfaces to make up for mass loss [91]. The deposited NPs reduce surface

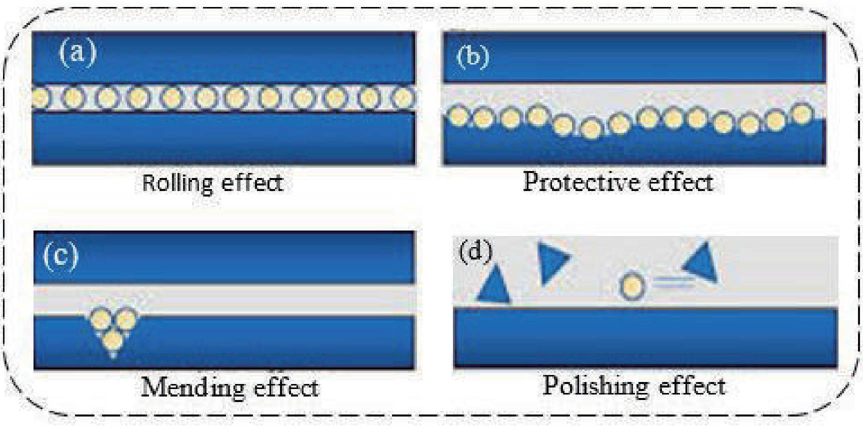

Fig. 9 Different lubrication mechanism towards machine elements protection

abrasion by depositing on the worn surface. Scars and grooves on friction surfaces can be filled [100] by NPs suspended in lubricant as shown in Fig. 9 (c). The mechanism of mending towards reduction on friction and wear by the NPs as a way of enhancing the tribological performance is shown in Fig. 5. Lubricants that contained NPs filled in microgrooves on the metal surface (the "mending effect").

6.4 Polishing effect

The polishing or smoothing out procedure is another technique. The ability of NPs to "smooth out" or fill in the valleys between asperities has been predicted [90], and empirically shown in Fig. 9 (d). This "artificial smoothing" technique will enhance tribological properties because it reduces surface roughness [39, 101]. Less friction and hence less wear would result from a smoother surface. This is mostly by polishing rough metal surfaces (the "polishing effect") when they came into contact with the metal. Both mending and polishing techniques have the potential to lessen surface roughness, which would reduce wear and friction.

7 Benefits of bio-lubricants and market availability

Lubricants from vegetable source can be naturally used. They have several advantages and disadvantages as will be seen in the challenges which make the product lack some values in the market. As mentioned above, vegetable oils offer outstanding lubricity, which is significantly better than that of mineral oils. Furthermore, vegetable oils have a high VI. For instance, vegetable oils frequently have a VI of 223, but most mineral oils typically have a VI of 90–100. Vegetable oils have high flash points, which is another significant characteristic. Vegetable oils typically have a flash point of 326°C, while common mineral oils have a flash temperature of 200°C. Other benefits from the use of vegetable lubricants are summarized in Table 5.

The global market for bio lubricants is expected to be influenced by the expanding opportunities for sustainable solutions, such as green buildings and sustainable lubrication. The international market for bio lubricants is anticipated to reach US$ 2.6 billion under a CAGR of 5.2% over the forecast timeline of 2020–2027, based on recent report by Global Industry Analyst Inc [102]. The demand for bio lubricants is still high, especially in Europe where it is encouraged by national and global branding regulations, subsidization, and tax benefits [102]. The economy analyst claims that unless governments provide incentives or laws for their use, bio lubricants are not going to take off in Asia. With more funding awarded by the government for the improvement and establishment of additional bio lubricant facilities for usage in the automotive and industrial sectors, Malaysia appears to be moving in this trend [103].

Due to the rapidly expanding markets for the end-user industries of polyol esters, the global demand of TMPE is anticipated to increase significantly over the next few years [104], and that the upgraded lubricant is anticipated to reach US$256.5 million, growing at a compound annual growth rate (CAGR) of 7% from US$182.8 million in 2016. Upon a CAGR of 6.7% in 2016, Salih and Salimon, [105], stated that the market is expected to reach 64.5 kilotons globally by 2021. Among them, the ester-based transformer oil market is anticipated to develop at a CAGR of 1.8% from 2021 to 2027, reaching USD 94 million by the end of the year. Due to the intense rise in fire incidents involving transformers powered by mineral oil and the fact that mineral oil is not biodegradable, bio-based, naphthenic transformer oil will become more and more popular over the coming years. Over the upcoming few years, the development of fire-resistant transformer oils, and other related lubricants are estimated to witness new growth prospects for the ester market [106].

Again, Fortune Business Insights, 2022 [107], revealed that global metalworking market is anticipated to reach USD 11.6 billion by 2029, with a CAGR of 4.3% over the estimated period of 2020–2027, notwithstanding the detrimental effects of the COVID–19 epidemic on the bio lubricant business. Although it still has a small market share compared to metalworking fluid based on mineral oil, the bio lubricant market is shifting toward bio-based metalworking fluid made from synthetic esters and plant oils. This is based on the strict regulations of related organizations, including the Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), National Institute of Occupational Safety and Health (NIOSH), and Canadian Centre of Occupational Safety and Health, are the reason for this market's forecast (OSH).

8 Challenges from the use of vegetable lubricants

Although, as indicated, some vegetable lubricants have good tribological characteristics (section 1 and 3). However, the inherent qualities of the vegetable lubricants rather than their composition with additional additives are what limit their functionality. Because of a number of variables owing

Table 5 Key benefits of bio-lubricant type in lubrication

Property	Performance contribution	Ref.
Good lubricity	Controlled friction losses with good fuel economy	[85]
Low volatility	Enhanced reduction of exhaust emissions	[59]
Good viscosity index	Applied for a wide range of temperature	[110]
Excellent boiling temperatures	Reduced emissions during operation	[111]
Higher detergency	Eliminating the requirement of detergent additives	[59]
Rapid biodegradation	Minimized toxic contaminants and environmental danger	[112]
Good compatibility	Better cleanliness with less harm at work environment	[113]

to their food competition, bio-based lubricants currently only make up a small portion of the market. The most obvious reasons would be that crude vegetable oils have poor low-temperature characteristics and limited oxidative stability. According to various research on pour points, vegetable oils would first become cloudy, then precipitate, and finally solidify at a temperature point of 10°C, preventing them from flowing in low temperature conditions [108]. This resulted from the development of macro-crystalline. Some important factors from massive availability of vegetable lubricant for industrial production are as follows.

i. Hydrolytic properties and Poor low temperature: Vegetable lubricants are obviously more prone to hydrolytic breakdown when they contain a high ester group content [109]. As a result, it was important to stay away from pollutants during preparations, like water that was an emulsion. Yet again, vegetable lubricants fall short in their efforts to thwart corrosion, especially when moisture is present. The hydrogen atom is easily removed from the molecular structure when there is oxygen and moisture present, which leads to the breakdown of esters into acid and olefin. The reason for cloudiness, poor flowability, and precipitation is low temperature [110]. According to studies on their low temperature feature, the majority of vegetable lubricants demonstrate the characteristics as indicated [17, 32, 67].

ii. Thermal stability and Weak oxidation: In contrast to oxidation stability, which refers to a lubricant's resistance to chemical breakdown at high temperatures in the presence of oxygen, thermal stability is the resistance to molecular breakdown at high temperatures in the absence of oxygen. This argument states that in order for lubricants to withstand usage-related circumstances, they need to be updated from their insufficient oxidation stability. Again, since polyunsaturated oils make up the majority of vegetable lubricants, low oxidation stability is an issue. As a result of issues with double bonds from fatty acids and alcoholic components, as well as high linoleic concentrations, vegetable oil's oxidation and thermal stability are decreased. To solve these problems, the right additives must be used while making bio-lubricant. Since base stock makes up 90% of the total lubricant, the poor oxidation nature of vegetable lubricants becomes a major concern when lubricant formulation is done. This is when features like high biodegradability, low volatility, low acid content, high solvency, etc. are analyzed for the best response to additives and working systems [32].

iii. Competition and cost confrontations: Food and energy are in competition with one another (for biofuel and lubricant products), especially when it comes to edible vegetable oil. Some countries are currently totally dependent on foreign countries for their supply of edible and inedible vegetable oils. For instance, India's industrial sector used 16.6 million tons of vegetable lubricants annually, the most of which were imported, which increased the cost of the good on the market [111]. As the world moves toward a sustainable economy, demand for vegetable lubricants is rising dramatically. The price of bio lubricants is 30–40% more expensive than the price of conventional lubricants, according to research [112]. To solve the problem, the government should engage in vast farming practices that will result in the production of a sizable quantity of vegetable oil in a range of forms.

9 Future prospects on bio-lubricant application

The present growth of the recovery in manufacturing and other industrial activities because of the continuous fast modernization and the rising car ownership rates, could contribute to increasing the demand for lubricants globally. Additionally, these patterns will encourage growth in all continents of the world. During the first ten years of the new millennium, the trend toward better compatibility and increased performance continued [85]. Appropriate viscosity and the absence of acidic components were the two criteria for base oils that were most significant throughout the 1950s [90]. Base oils were demoted to the status of solvents or carriers for additions in the 1960s. In comparison to mineral base oils, a number of synthetic fluids with fundamental chemical structures demonstrated greater performance in the 1970s [90]. Western Europe saw the introduction of inexpensive, nearly synthetic hydro-cracked oils in the 1980s [90]; these oils roughly matched the characteristics of synthetic hydrocarbons. Base oil development in the 1990s was impacted by environmental, health, and safety standards as well as performance requirements for lubricants. Because of their quick biodegradability, these oils became more chemically pure, and their oleochemical derivatives enjoyed a revival. Due to the development of advanced machines that words for a long period of time, the present quality trends in lubricants show a major change toward viscosity grades and product specifications. As a result of these factors, formulation of a nano-bio-lubricant with good solution stability, a more effective surfactant, and the capacity to overcome agglomeration challenges [113] is required.

In the area of viscosity, low carbon-forming tendency, stability, oxidation stability, volatility need, and reaction to additives, bio-lubricants perform better than mineral lubricants, as was already said. The lubricant business faces a challenge in supplying adequate performing lubricants for particular applications, even though they were only accomplished under light loading [34, 110]. One example of the industry's response to the demand for lubricated automotive equipment that would lessen environmental burden by reducing emissions and to achieve biodegradability and non-toxicity is the development of new-generation heavy-duty lubricants [114]. Modern vehicle engine oils are formulated using bio-lubricants, which are now widely acknowledged to have a variety of inherent performance advantages over traditional petroleum-based oils. Additionally, more investigation is required to determine the ideal machine orientation for a particular formulation as affirmed by Opia et al. [88], during investigations on different working orientations, thus observed various performances from a particular formulation. The research concluded that performance of the designed lubricant is significantly influenced by the machine orientation.

10 Conclusion

The advantages of bio-lubricant over its competitors were explored in this present research, including its promise for sustainability. Despite the fact that vegetable oil-based lubricants are widely used due to their excellent lubricating qualities, including their eco-friendliness and biodegradability, their need for food might increase costs and limit their availability on a big scale. From the perspective of satisfying the lubricating need, bio-lubricant modification seemed an intriguing alternative. From the literature, it can be concluded that bio-lubricants can compete with synthetic and mineral oils, which are often used for lubrication, and, more importantly, can be used to get the fundamental qualities needed for a variety of engineering applications. In this regard, it is anticipated that the need for bio-lubricants in turbomachinery, hydraulic oils, engine oils, gear oils, and cutting fluids would only rise in the near future. The study indicated that bio-lubricants exhibit all the necessary physiochemical characteristics for effective lubrication in the domain of working operations for superior tribological performance. Additionally, the study showed that bio-lubricants exhibit every conceivable mechanism with outstanding outcomes, indicating strong compatibility with additives.

However, problems with agglomeration during lubricating operations, possibly due to inappropriate concentration or improper mixing technique, necessitating good formulation knowledge. The main difficulties and areas for additional research in the field of bio-lubricants might be to maintain and create bio-lubricant base stocks from a particular variety of biomass residue that has been studied. This is because the qualities and content of thermochemically formed bio-oil or bio-crude are greatly influenced by the biomass feedstock. In order to provide service in other engineering applications where bio-lubricant use is lacking, particularly in heavy machinery, more advancement on bio-lubricant still needs to be done in terms of research as to solve the confrontations associated with bio-lubricants lubrication.

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