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A review of recent advances in the synthesis of environmentally friendly, sustainable, and nontoxic bio-lubricants: Recommendations for the future implementations

Muhammad Ali Ijaz Malik [a], M.A. Kalam [a], M.A. Mujtaba [b], Fares Almomani [c,*]

[a] School of Civil and Environmental Engineering, FEIT, University of Technology Sydney, NSW 2007, Australia
[b] Department of Mechanical Engineering, University of Engineering and Technology (New Campus), Lahore 54890, Pakistan
[c] Department of Chemical Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

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ABSTRACT

Conventional petroleum-based lubricant resources are depleting rapidly, and their utilization severely threatens the environment. Environmental sustainability emphasizes the need for an alternative to petroleum resources. The lubricants play a significant role in machinery's adequate energy-saving performance. Therefore, the tribological aspects of machinery's maximum efficiency should be considered. The current study reviews the part of bio-lubricants towards environmental sustainability. This review has been conducted according to the PRISMA approach, where the sources of bio-lubricants, tribological performance, the role of additives and nanoparticles, benefits and disadvantages, production techniques, economic aspects, and future scope were explored and discussed. Bio-lubricants possess a better viscosity index, lubricity, biodegradability, and non-toxic and renewable nature than petroleum lubricants. However, lower thermo-oxidative stability and higher pour points due to moisture content require further improvements. Food security is another significant concern for bio-lubricants. Consequently, it emphasized the importance of algae-based bio-lubricant sources in reducing the threat to food security, water purification, and greenhouse gas mitigation. Further improvements and optimization of production methods are required to increase lubricant yield rates and promote sustainability. The importance of new (algae-based) bio lubricant substitutes with details of their physicochemical properties for a sustainable future is highlighted in this review research.

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* Corresponding author.
E-mail address: falmomani@qu.edu.qa (F. Almomani).

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1. Introduction

The world's population is growing at an alarming pace of 83.1 million per year, which is mainly responsible for the rise in demand for natural resources (Ijaz Malik et al., 2021). Petroleum fuels play a significant part in meeting the world's energy needs. Global primary energy consumption more than doubled, from 270.5 EJ in 1978 to 580 EJ in 2018 (Kober et al., 2020). European Union (EU) projects that 12% of global energy demand will be fulfilled by renewable sources in 2030 (Hájek et al., 2021). As per estimates, worldwide energy consumption by transport is projected to rise by an average of 1.8% per year from 2005 to 2025. Fossil fuels are a primary source for the transportation sector, approximately 97.6% of energy utilization in the transport sector meet through fossil fuel utilization. Scientists reported the depletion of fossil fuel reserves within 50 years as per their current utilization (Ijaz Malik et al., 2021). Moreover, the transportation sector utilizes global primary energy approximately 18% and is accountable for CO_2 emissions (23%) around the globe, which eventually marks global warming (Usman et al., 2022). However, the environmental concerns, depletion of fossil fuel resources, and hike in their prices alarm the researchers to explore the avenues to cope with such issues (Ağbulut et al., 2020a). The scientists after significant research came to know that most of the total energy extracted from petroleum sources is wasted as a result of friction between mating parts inside the engine and drag force faced by vehicles during movement (Vaitkunaite et al., 2022). Moreover, 17 to 19% of engine power approximately consume to overcome friction which greatly affects its performance (Ali et al., 2018). Lubricant oil is primarily responsible for the effective performance of mechanical systems by providing facilitation in sliding motion between mating parts (Chen et al., 2022). Lubricant oil mainly includes two components; one is base oil and the second is additive. The base oil served as a major component with 70 to 99% of lubricant formation (Dehghani Soufi et al., 2019). Additives mainly include dispersants, anti-wear characteristics, higher flashpoint, higher viscosity index, and higher pour point (Ahmad et al., 2022). The nano-additives have demonstrated significant potential sources to improve tribological performance because of their small size and ability to fill the valleys among mating parts (Uflyand et al., 2019). The substantial increase in lubricant oil spillage and inefficient lubricant oil recycling techniques mainly harm the ecosystem. As per estimates, 50% of lubricant oil dispose of into the environment and 95% of this disposed lubricant which put adverse impacts on human lives and the ecosystem (Xu et al., 2019). It is approximated that 1 million liters of drinking water are polluted by 1 kg of petroleum lubricants (Barthlott et al., 2020). Moreover, the biosphere receives 10 to 15 million tons of oleochemicals (of petroleum origin) each year, and about 40% originate from urban runoff, spills, condensation of exhaust from marine engines, refinery processes, and municipal and industrial waste. Bio-based lubricant oils are biodegradable, renewable, and nontoxic and the ecosystem remains unharmed during their spillage (Saxena et al., 2022). Bio-lubricants are classified as sustainable lubricants due to their carbon-neutral nature (Durango-Giraldo et al., 2021). It is expected that the bio-lubricant market will rise by 15 to 20% in the next two decades (Almasi et al., 2021). A bio lubricant can be produced from edible (palm, sunflower, coconut, olive, soybean, peanut oil, rapeseed, and linseed oil) or nonedible (plant, animal fats, and microalgae) sources (Almasi et al., 2021; Salih and Salimon, 2021). However, bio-lubricants possess certain undesirable properties like higher pourpoint, lower kinematic viscosity, and poor thermo-oxidative stability (Khan et al., 2022). The extracted biofuels from food crops are known to be first-generation biofuels, they possess limited ability to reduce climatic transformation, replace petroleum sources, and economic growth due to land issues, raw materials, food security and requirement of fertilizers for growth. The non-edible energy crops known to be second generation of biofuels with more potential to replace petroleum, fuels than previous generations due to comparatively less requirement of land, but still the need of production land is substantial. The issues with first and second generation can be sort out by algae and cyanobacteria sources owing to rapid growth of micro-organisms (Almomani et al., 2022, 2023). This source named as third generation of biofuels as they utilize sunlight and CO_2 for production of hydrocarbon based fuels (Jacob et al., 2021). Therefore, the aim of this review article is to focus on the significance of algae-based sources in the production of bio-lubricants. Algae can be built both naturally and synthetically, however, the optimum conditions and production techniques need to be discovered for higher yield rate of algae-based lubricants. In additions, microalgae are also the fastest-growing photosynthesizing organisms, and they have the ability to complete a full production cycle in a matter of days. Depending on the species and production method, the yearly oil production from microalgae between 20,000 to 80,000 L per acre, which is several times greater than that of the top oil-producing terrestrial crop (palm) (Demirbas and Demirbas, 2011). Additionally, compared to their terrestrial counterparts, the necessary land footprint is 10–340 times lower. According to some statistics, microalgae can produce up to 200 times more oil than even the most productive vegetable oils (Sadvakasova et al., 2023). In recent years, lubricants have mostly been extracted from vegetable oils (edible or nonedible) but food security is a major concern for bio-lubricants. However, the current study compares all sources of bio-lubricants with each other on the basis of their impact on engine performance and tribology along with the future recommendation to extract bio-lubricants from algae-based sources. The major source of algae is fresh and salty water which significantly surrounds the ground surface of the earth. One just needs to focus on extraction techniques in order to harness natural energy sources rather than source exploration. Improvements in production methods may increase yield rates and promote sustainability for algae-based lubricants. A current study comprehensively analyzes the prospects of bio-lubricants in the automotive sector by focusing on their production methods, physicochemical characteristics, SWOT, LCA, lubricant formulation with additives, and biodegradability.

2. Methodology

This review was conducted as per the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (the PRISMA approach) as presented in Fig. 1. This approach includes screening papers related to bio-lubricants from 2010 to 2022. It is the minimum set of items for documenting in meta-analyses and systematic reviews that is supported by evidence. Such analysis helps the authors to improve the quality of the review by sorting quality articles and ensuring transparency in this systematic review. The problem identified in this review was the "Role of bio-lubricants for the sustainable environment". For this, the recommendations for Meta-Analysis were followed (Lelis et al., 2021). Depending on the population, intervention, comparison, and outcome (PICO), the research questions were centered on: (i) What are the sources/base stocks for the bio-lubricants? (ii) What are the production techniques for the bio-lubricants (iii) What are the primary modes of action of bio-lubricants in the sustainability matrix? (iv) What is the impact of sources and additives on the physicochemical quality of bio-lubricants? (v) How to access the performance of bio-lubricants? (vi) What are the applications, present challenges, and prospects of bio-lubricants?

The exclusion/inclusion criterion was used for the eligibility of research papers to avoid potential bias sources. The review was carried out by screening the Research titles, abstract, and keywords and considering only studies with prospects of bio-lubricants for a green and sustainable environment. Topics focused on renewable sources for the bio-lubricants, production techniques, performance assessment, applications (automotive, cooling, wear debris removal), additives for bio-lubricants, and their life cycle assessments were considered. Two electronic databases: Science Direct and PubMed were used in the search. The search strings are dependent on keywords relevant to research queries that were set up to find relevant articles in databases through the application of Boolean operators (AND, OR, and NOT). The keywords used in the search strategy are bio-lubricant, lubricant additives, tribological assessment, sources of bio-lubricants, production techniques for bio-lubricants, bio-lubricant characteristics, and bio-lubricant applications. The

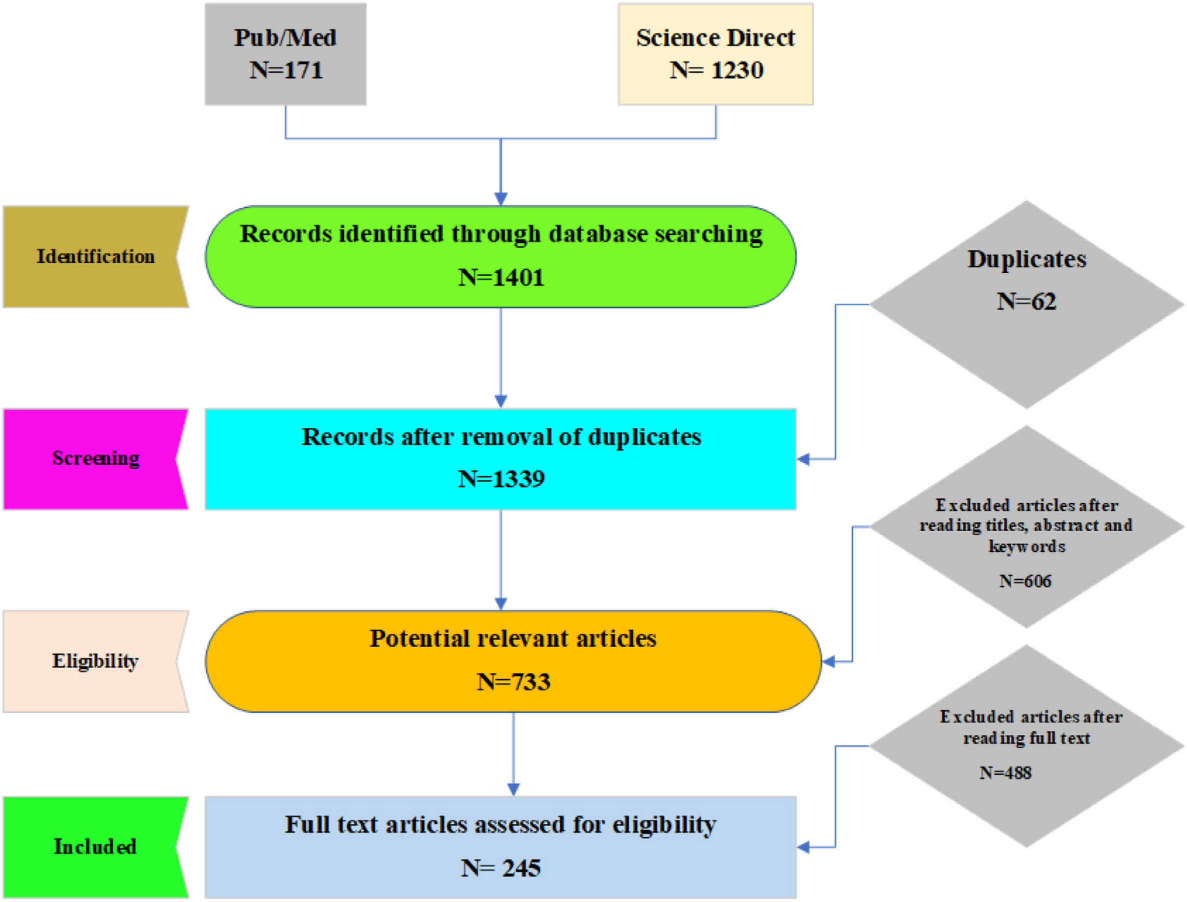


Fig. 1. PRISMA approach for review on bio-lubricants.

articles were imported to Mendeley after the selection procedure. The repetition in downloaded articles was automatically removed in Mendeley, and the remaining articles were passed to the identification, assortment, and extraction stage. The articles were further filtered based on reading abstracts, keywords, and titles to remove doubts that arose from the identification stage. 1230 relevant articles were found from science direct and 171 articles were found from PubMed. A total of 1401 research papers were found from searching databases. A total of 62 duplicates were removed from databases, and the remaining 1339 research papers were left. Then, the title, abstract, and keywords were examined to find their relevance to the research study, and 606 articles were excluded. But after reading the full text, 488 papers were rejected for the study. The remaining papers which fulfill the criteria were found to be 245. Fig. 1 also shows the PRISMA approach used for review of the bio-lubricants.

3. Significance of tribology

Tribology accounts for frictional losses, wear and lubrication to cope with such issues. Krishnamurthy et al. (2021) declared that 1/3rd of fuel energy was utilized in overcoming friction. They proposed that 18% of frictional energy in the automotive sector can be reduced in the next 5 to 10 years, and 61% of frictional energy can be reduced in the next 15 to 25 years with the tribological advancements. About 23% of global energy consumption compensates for wear and frictional losses. Out of 23% of energy losses, 20% of such energy consumes in overcoming friction and 3% in replacing worn machine parts (Holmberg and Erdemir, 2017). The frictional and wear losses can be decreased by up to 40% through the employment of advanced lubricants, which correspond to savings of 1 to 1.55% of the country's gross domestic product (GDP) (Guo et al., 2019). The applications of tribological advancements are not only responsible for economic benefits but also accountable for environmental benefits (CO_2 reduction) (Vigneshwaran et al., 2020). It is approximated that about 75 to 82% of overall energy loss in the vehicle, and 68 to 72% of energy losses in the engine. However, about 12 to 30% of fuel energy is consumed in vehicle propulsion and 3% of energy losses as frictional energy (Jason et al., 2020). Lubrication turned out to be the most important parameter for the reduction in energy losses. The unsaturated/saturated stretched fatty acid chains and polar group presence in bio lubricant made hydrodynamic

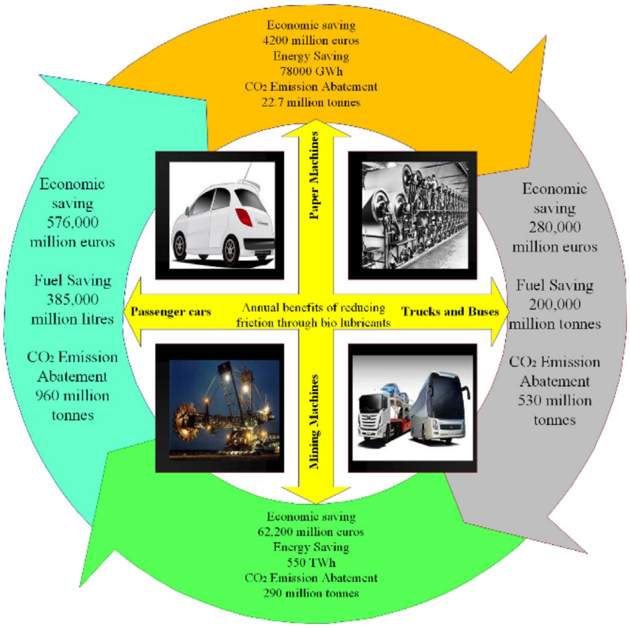


Fig. 2. Tribological benefits of biolubricants.

and boundary lubrication possible (Karmakar et al., 2017). Moreover, the development of lubricant additives and genetic modification of additives (fatty amides, amines, alcohols and propyl gallate) engineered specifically for bio lubricants with massive achievements (Singh et al., 2020b). In short, frictional energy losses in vehicles can be reduced by modification in the design of bearings and tires, advancements in tribology and lubricant additives.

4. Tribological benefits of bio lubricants

Fig. 2 displays the annual savings in terms of economy, fuel/electricity savings, and CO_2 emission abatement corresponding to passenger cars, trucks or buses, paper and mining missions. The facts indicate that a huge amount of money can be saved in the automotive sector through tribological advancements, and its significance cannot be denied. The fuel/electricity saving of approximately 385,000 million liters, 200,000 million liters, 78,000 GWh, and 550 TWh in passenger cars, buses or trucks, paper, and mining machines, respectively. Carbon dioxide is the primary source of global warming, and the advancements are focused on its abatement for environmental sustainability. The CO_2 emission reduction of approximately 960 million tons, 530 million tons, 22.7 million tons and 290 million tons in passenger cars, buses or trucks, paper and mining machines, respectively.

5. Lubricant base stocks

The processing of crude oil for the transformation into petroleum feedstocks also acts as a derivative of mineral oil base stocks by removing insoluble and volatile components (Owuna et al., 2020). Therefore, the base stocks for synthetic oil originate from fossil fuels after adequate chemical modification. The base stocks for biomass mainly include animal and plants source for bio-lubricant processing. However, the other lubricant sources comprise vegetable oils and agriculture-based residues and need to be studied in order to have better understanding of lubricant oil characteristics (Gupta and Verma, 2015; Afonso et al., 2023).

5.1. Bio lubricant base stocks

5.1.1. Vegetable oils

Conventional lubricants are generally extracted from crude oil. They are typically consisted of mineral oils and different kind of additives which increase their overall performance and efficiency. On the other hand, bio-lubricants are based on renewable resources such as vegetable oils, animal fats and plant-based feedstocks like synthetic esters etc. One of the major drawbacks of conventional lubricants is its non-biodegradable nature which results in soil and water contamination if they are not properly disposed of. They are also generally caused pollution and are harmful to the ecosystems. On the contrary, bio-lubricants are biodegradable and easily break down naturally and are eco-friendly. In addition, conventional lubricants possess detrimental chemicals and additives which are harmful to humans.

However, bio-lubricants are less toxic and generally safer for human health. Vegetable oils served to be an effective source for bio-lubricant production owing to their eco-friendly nature. Although vegetable-based lubricant oils do not match petroleum-based lubricant standards, they exhibit higher flash points, lower evaporative losses, higher viscosity index and better lubrication (Masripan et al., 2020). On the contrary, vegetable oils indicate unsaturated fatty acids, which make them unsuitable for lubricating applications by imparting poor oxidation and thermal properties. But chemical modification procedures (hydrogenation, transesterification, and epoxidation) can reduce the degree of unsaturation and make vegetable oils comparable to conventional lubricants with improved tribological characteristics (Shankar et al., 2021). The common feedstocks for bio-lubricants are enlisted below:

Sunflower oil is mainly extracted from Helianthus Annuus seeds. Oil is primarily a triglyceride which is usually comprised of oleic acid (monounsaturated), linoleic acid (polyunsaturated), palmitic acid and stearic acid (saturated). Sunflower oil exhibits higher viscosity in cold temperatures owing to higher levels of unsaturated fats (Vickers, 2017). Castor oil is extracted from the Ricinus plant (castor beans). The triglyceride of castor oil contains 90% of fatty acid chains as ricinolate (ricinoleic acid). Castor oil possesses low-temperature viscosity and higher-temperature lubricity, making it perfect for diesel, jet, and racing engines (Rac and Vencl, 2009; Molefe et al., 2019). Rapeseed oil is mainly cultivated for oil-rich seed (54% Erucic acid).

Canola oil plant is a subtype of rapeseed plant with high nutritional value and low erucic acid. Jatropha oil is extracted from the Jatropha Curcas plant, which can grow in all terrain with a higher seed production rate and is used in synthesizing lubricants owing to higher fatty acid content (Singh et al., 2017). Coconut oil possesses a higher degree of saturated fats responsible for slow oxidation. Coconut oil derivatives (fatty acids), can be utilized as a transformer oil and lubricant. As palm oil has a higher percentage of saturated fat (palmitic acid) and monounsaturated oleic acid as the main component, it lends itself to producing lubricants with a more extraordinary load-carrying ability (Zulkifli et al., 2013c; Li et al., 2020). However, palm oil lacks thermo-oxidative stability. With 51% linoleic acid and 23% monounsaturated oleic acid, soybean oil is typically used for cooking. Soybean oil's ability to increase flash points and prolong transformer life made it suitable for dielectric fluid (Vickers, 2017). Table 1 portrays the physicochemical attributes of distinct lubricant oil sources. It can be observed that lubricant oil extracted from chicken fat and manhua exhibits the highest oxidation stability; however, the lubricant oil derived from linseed oil possesses minor oxidation stability. The lubricant oil can be extracted from many sources, and the research is going towards finding novel sources. Algae is one of the novel sources of lubricant oil with competitive physicochemical properties with other sources.

5.1.2. Fatty acids

The primary constituent of fats and oils is fatty acids, which are esterified by glycerol. The chemical treatment of fatty acid carboxyl and unsaturated group residues provides the basis for oleochemical compounds (Zarli, 2020). The commercially accessible oils and fats are lipid mixes that primarily contain free fatty acids, monoacylglycerols, and diacylglycerols in varying ratios. They might also contain hydrocarbons, phospholipids, triterpene alcohols, sterol esters, and fat-soluble vitamins.

5.1.3. Microalgae

Microalgae possess a high photosynthetic potential and CO_2 retention. The primary industrial use of algal biomass is as a bio-lubricant source. The thousands of different species of algae with lipids, proteins, and carbohydrates in their composition (Kopp et al., 2017). The oil concentration varies from 10 to 50% depending on the microalgae condition and growth pace. The fact that a large agricultural field is not necessary for microalgae growth has worked in the microalgae's favor. The microalgae source is cheap as it can be produced by industrial effluents or in seawater (Kutluk and Kutluk, 2022). Higher surface protection against wear and a lower degree of friction are critical benefits of microalgal and yeast oils, which can be credited to an optimal combination of unsaturated and saturated fatty acids. Microalgal and yeast oils have a significantly reduced friction coefficient and metallic surface wear when compared to conventional mineral-based lubricants like PEG 200. The number of fatty acids in the feedstock has a major impact on its tribological characteristics, for example, the double bonds in the fatty acid chain make it extremely vulnerable to auto-oxidation when in contact with air.

Moreover, some limitations of using microbial oils as bio-lubricants, including oxidative and hydrolytic stability, can be further improved through chemical modifications in oil static sites, such as double bonds and acyl groups or by blending with some oils having different fatty acid profiles (Patel et al., 2021). Algal/ cyanobacterial biomass can be cultivated from industrial effluents and seawater more early in contrast with plants. The shorter cultivation time makes them desirable for an uninterrupted supply of raw material, and the ability to grow in seawater eliminates the requirement for fresh water. The pigments and carbohydrates are value-added by-products of algal biorefineries. The proportion of carbohydrates can be detached and utilized for bio-lubricant (C-BLUB) production to minimize production costs for primary products. Three factors including macronutrient starvation, salinity rise, and mild ozonation responsible for maximum microalgae/ cyanobacteria production (Borah et al., 2021). In open ponds or raceways (sea water, saline water, organic/inorganic growth medium, and industrial wastage), algal/cyanobacterial strains can outcompete bacteria by producing metabolites with an allelopathic impact (Borah et al., 2020). Algal biomass production linked with bioremediation can considerably decrease water and nutrient need. However, the production cost can be abridged by the continuous supply of raw materials. Simple stresses like nutrient starvation and ozonation for a brief passage of time can enhance

Table 1
Physicochemical properties of lubricant oil sources.

Lubricant oil sources	Density (kg/m^3)	$(KV)_{40\ °C}$ (mm^2/s)	Oxidation stability at 110 °C (h)	Cloud point (°C)	Viscosity Index	Pour point (°C)	Flash point (°C)	TAN (mgKOH/g)
Palm (Khan et al., 2022; Mobarak et al., 2014; Bahari et al., 2018)	875	5.72	4	13	39.8	12	165	0.24
Fish oil (Behçet et al., 2015; Papargyriou et al., 2019; Salih et al., 2021)	881	4.45	–	–	–	−5.8 to −3.6	177	0.53
Sunflower (Khan et al., 2022; Mobarak et al., 2014; Ramos et al., 2019)	878	4.45	0.9	3.42	202.87	−5 to −14	185	0.51
Chicken fat (Khan et al., 2022; Singh et al., 2019b; Aliana-Nasharuddin et al., 2020)	883	5.14	6.46	–	191	–	175	33.66
Coconut (Mobarak et al., 2014; Ramos et al., 2019; Appiah et al., 2022)	805	2.75	35.4	0	169	21	112	0.24
Cotton seed oil (Yaşar, 2020; Shaah et al., 2021; He et al., 2023)	897	4.19	1.88	–	197	−3	210	0.21
Corn (Gülüm and Bilgin, 2015; Di Lena et al., 2020; Pop et al., 2008)	878	4.42	1.3	–	237.5	−26	172	19.72–24.29
Soyabean (Khan et al., 2022; Bahari et al., 2018; Erhan and Asadauskas, 2000)	885	4.05	2.1	1	159.27	−2	176	0.98
Linseed (Mobarak et al., 2014; Otabor et al., 2019; Soltani et al., 2020)	890	3.74	0.2	−3.8	262.5	−15	178	8.92
Olive (Gryglewicz et al., 2003)	892	4.52	3.4	−13.5	–	–	179	–
Peanut (Mobarak et al., 2014)	882	4.92	2.1	5	–	–	177	–
Coconut (Khan et al., 2022; Atabani et al., 2013)	867	3.2	5.12	–	172.1	24	114	–
Rapeseed (Khan et al., 2022; Mobarak et al., 2014; Otabor et al., 2019)	880	4.45	7.5	−3.3	218.5	−15	62	9.75
Kusum (Shaah et al., 2021; Pali and Kumar, 2016)	875	4.34	6.5	–	–	–	152	21
Canola oil (Ge et al., 2017; Annisa and Widayat, 2018)	878	4.42	1.3	–	204	−66	172	–
Castor (Khan et al., 2022; Karmakar et al., 2010; Keera et al., 2018)	898	15.25	1.2	−13.5	88	−24	260	1.19
Manhua (Mobarak et al., 2014; Shaah et al., 2021)	895	4.77	8.2	–	–	–	210	36
Jatropha (Khan et al., 2022; Shaah et al., 2021; Gui et al., 2008)	878	4.82	2.3	2.75	204	−12	136	1.50
Hazelnut (Öztürk, 2015)	896	4.81	2.1	–	–	–	160	–
Neem (Mobarak et al., 2014; Shaah et al., 2021; Joshi et al., 2022)	885	5.20	7.2	14.5	−12	–	44	18
Karanja (Khan et al., 2022; Mobarak et al., 2014; Shaah et al., 2021)	918	4.80	6	9	172	−9	150	5.70
Algae (Khan et al., 2022; Rahman et al., 2021; Satputaley et al., 2017)	881	4.55	2.3	–	180	–	140	0.7737

the accumulation of carbohydrates in cells - the sonification technique used to extract lubricant oil from algae. Moreover, the physicochemical attributes of carbohydrates derived from cyanobacteria/algae exhibit compliance with mandatory attributes for bio-lubricants. Purba et al. (2022) Cultivated microalgae in wastewater to establish a correlation between the selected species for a specific type of wastewater. Desmodesmus maximus CN06 showed an excellent growth rate of 0.23/day, exhibited excellent nutrient removal efficiencies and highest Lipid productivity of 3.43 mg/L · day. The extracted fatty acids indicated a good potential to be applied for biodiesel and bio-lubricant production. Additionally, microalgae have a good potential to utilize CO_2 and sunlight to generate biomass for commercial applications (Khanra et al., 2022). In such applications, microalgae are considered a promising Carbon capture and utilization technology (Nguyen et al., 2023).

6. Physicochemical properties

The physicochemical properties significantly impact lubricant performance, therefore it is necessary to study these properties in detail. The physicochemical properties of bio lubricant are briefly explained below:

6.1. Viscosity and viscosity index

Bio lubricants mostly possess higher viscosity due to the higher chain length of the alcohol hydrocarbon chain in ester (carboxylic acid) bio-lubricants. However, the viscosity index (VI) explains the variation in viscosity due to temperature. As the VI is higher, the minor viscosity variation occurs over the comprehensive temperature range. The VI decreases by increasing the branches of carboxylic acid/alcohol while keeping a constant number of carbons. Ebtisam et al. (2017) investigated the impact of vacuum pressure on the viscosity index of lubricant oil during the transesterification of palm oil methyl esters with trimethylolpropane (TMP). The improvement in viscosity index from 171 to 214 was observed when vacuum pressure was reduced from 50 to 10 mmHg.

6.2. Flash point

Flash point (FP) is a minor temperature around which the vaporization of lubricant leads to an explosive air mixture. The FP exhibits an inversely proportional relation with flammability. The flashpoint assesses lubricant behavior under atmospheric temperature and indicates the lubricant volatility and fire tolerance. Bio-lubricants usually possess higher flashpoints (Balambica et al., 2022).

6.3. Carbon residue

The bio-lubricants possess lower carbon residue than base mineral oil because the bulk of mineral oils (paraffinic nature) account for higher residues. Carbon residue determines fuel decay and carbonaceous material formation that resultantly chokes the nozzle and hinders fuel injection.

6.4. Moisture content

Moisture content ascertains the amount of water in the lubricant sample and affects the physical properties of the lubricant, including viscosity, weight, conductivity and density. The oil's moisture content is equivalent to mass lost during heating. Bio-lubricant oils possess moisture content naturally, which is inevitable (Balambica et al., 2022). Therefore, to reduce moisture content in lubricant oil, the composition of base oil should be higher in bio-lubricants.

6.5. Pour point

A pour point is a minor temperature beneath which a lubricant fails to sustain flow ability and maintain liquid properties. The viscosity index and pour moment are related to bio-lubricants. Trimethylolpropane (TMP), one of the ternary alcohols used in bio-lubricants, exhibits a lower pour point and less resilience against thermos oxidation. Larger branched alcohols with lower pour points and improved oxidative stability, such as neopentyl polyols, have shown promise as a substitute for bio-lubricants.

6.6. Total acid number (TAN)

TAN is the amount of base expressed in milligrams of potassium hydroxide needed to neutralize the amount of acid in one gram of lubricant oil. If its value is too higher, then it indicates higher contamination, oxidation and acidic sludges.

7. Biodegradability

Biodegradability accounts biological degradation of organic materials by living organisms into basic elements like H_2O, CO_2, CH_4 and biomass. A lubricant dissolves almost 80% in 28 days as per CECL-33-A-93 standard and 60% after 28 days per OECD 301B standard. Therefore, it is deemed to be degradable. Ecotoxicity is assessed through Lethal Dose (LD50), mandatory to kill 50% of the population. A lubricant is found to be non-ecotoxic if it possesses LD50 higher than 1000 ppm (Cecilia et al., 2020). The literature shows that vegetable oils undergo biodegradability of approximately 70%–100% in 28 days, making them eco-friendly substitutes for mineral oils (Durango-Giraldo et al., 2021). ASTM D5864 standard is followed to determine lubricant biodegradability. As aromatic/polar compounds significantly improves biodegradability (see Table 2). Alkyl benzene possess longest timeframe for biodegradability as compared to other feedstocks as shown in Table 2. A biodegradability possess linear relationship with flash point of lubricant. Moreover, kinematic viscosity served as critical factor in biodegradability assessment. The biodegradability of base oil cannot be prolonged through additives, as affected by the application of non-biodegradable substances (Sulfur, phosphorus, nitrogen, and zinc). Different researchers examined palm oil biodegradability through OECD 301F (Afida et al., 2015; Durango-Giraldo et al., 2022). They found 60% biodegradability after 28 days, due to ester linkage in the ester group. Bio-lubricants possess biodegradable nature, which is in their favor over conventional lubricants.

Table 2
Biodegradability of lubricant feedstocks.

Feedstock types	Biodegradability loss in 21 days (%)
Non-edible vegetable oil	70–100
Polyethylene glycols	10–75
Alkyl benzenes	5–20
Diesters	55–95
Aromatic esters	0–90
Polyols	5–95
Mineral oils	15–75

8. Lubricant oil regeneration

Ecosystem sustainability and pollution control are the most common topics of current research in order to reduce adverse impacts of dumped petrochemical waste in environment. Regeneration of lubricant oil can significantly contribute in reducing these adverse effects on ecosystems through enhancing lubricant oil lifecycle and engine efficiency (Usman et al., 2021). The lubricant oil regeneration led the scientist to develop novel refining techniques. In this regard, many scientist presented their work in order to contribute in energy conservation. Usman et al. (2021) examined the tribological characteristics of regenerated lubricant oil and found that around 50% of lubricant oil properties can be recovered through regeneration. Moreover, brake power and brake specific fuel consumption can be improved by 4.4% and 7.84% respectively. Acid/clay technique is the most conventional method for lubricant oil regeneration. Although it produces significant acidic sludge but still it is most commonly used technique as compared to vacuum distillation, solvent extraction and hydrogenation. Modern technologies lubricant oil regeneration comprised of pyrolysis process, thin film evaporation, membrane technology, pyrolytic distillation method, other hybrid technologies like thin film evaporation with clay and solvent finishing, thermal de-asphalting with clay and solvent finishing (Parekh et al., 2021). Fresh lubricant oil possess higher kinematic viscosity than deteriorated lubricant oil due to thermal molecular breakdown when subjected to higher stress and fuel dilution (Hsu and Liu, 2011). A viscosity index determines thermal stability of lubricant oil, as fresh lubricants possess higher viscosity index than deteriorated lubricant oil. However, the lubricant oil can regain viscosity and viscosity index through regenerative techniques as compared to deteriorated lubricant (Epelle et al., 2017). Higher specific gravity (SG) depicts higher moisture content, distinct heavy components (oxides, sludges, soot) along with higher ash content and dissolved metal concentration. A lubricant oil when gets deteriorated, the SG becomes higher as compared to fresh lubricant. The removal of impurities from lubricant during its regeneration significantly reduce SG (Sadraddin and Haji, 2022). Fresh lubricant oil always possess higher flash point (FP) because of the presence of volatile compounds in deteriorated lubricants and fuel dilution. But the regeneration process can be effective in raising the FP of deteriorated lubricant for its reuse (Usman et al., 2020). Higher TBN value and lower TAN values depicts stability of lubricant oil as they provide resistance against lubricant oil degradation. A fresh lubricant possesses higher TBN and lower TAN as compared to deteriorated lubricant oil. These properties can also be improved through lubricant oil regeneration (Sadraddin and Haji, 2022). It can be concluded that regeneration not only allows lubricant oils to regain lubricity and tribological characteristics, but also allows lubricant oil to improve engine performance and efficiency.

9. Lubricant additives

The main objective of using additives in lubricant oil is to improve tribological parameters, prolong degradation rate and improve rheological aspects (Gulzar et al., 2016). The additives can modify chemical properties by reacting on the interface site to improve tribological parameters. In addition, the rheology of lubricant can be enhanced by modification in physical properties (Danilov et al., 2021). Corrosion inhibitors, detergents, and demulsifiers can prolong the degradation rate of fat. The corrosion inhibitor produces chemical changes at the interface working side to avoid rust—the detergent work as an antioxidant through chemical changes in the bulk working site. The dispersants function as anti-foam agents or demulsifiers without any change at the interfacial working site (Braun, 2017).

Engine oil covers most of the global lubricant market applications (Chowdary et al., 2021). The operating conditions of the engine are categorized into low and high loads. Boundary friction dominates in high-load conditions, whereas non-boundary conflict dominates in low-load conditions. Endurance tests are usually performed under these conditions to yield useful outcomes in terms of wear loss in respectively assigned parts and fuel consumption. Table 3 comprehensively explains the finding of previous researchers regarding the performance of bio lubricant additives. The engine oil should exhibit a viscosity index greater than 90 to ensure appropriate working (Abdul Raof et al., 2022). Rico et al. (2002) found the minor wear scar diameters (WSD) under 264 to 490 N loading conditions. However, 0.533 and 0.612 mm WSD were recorded for pure trimethylolpropane esters (TMPE) and polarity oil (PAO). They postulate that the lubricity of PAO can be further improved by highly polar TMPE. The reduced WSD of 0.5 mm indicates the role of TMPE as a wear reducer with 5% TMPE in polarity oil.

Authors observed that a 3 to 7% addition of TMPE in commercial oil (CO) is sufficient for lower WSD and coefficient of friction (COF) (Zulkifli et al., 2013a; Raof et al., 2022). For 3% TMPE in CO, 0.28 mm WSD was obtained compared to

Table 3
A comprehensive summary of bio lubricant additives performance.

Bio-lubricant sources	Findings
Palm-based TMPE + Molybdenum disulfide (MoS_2) nanoparticle + surfactant (oleic acid) (Gulzar et al., 2017)	1 wt% of MoS_2 and 1 wt% of surfactant in TMPE. The mean WSD at ISL for small GnP size is 2.48 mm, whereas, for large GnP size, it is 2.66 mm. WSD produced by pure TMPE was 2.68 mm.
Palm-based TMPE + GNP + Phosphate ester (PE) (Rashmi et al., 2017)	5% of PE and 0.1% of GNP gave a 16.2% reduction in WSD (0.34 mm for 392 N load)
Palm-based TMPE + Palm oil + nanoglass (Yunus et al., 2020)	0.5% nanoglass + 30% (98% Palm oil + 2% TMPE) + 70% CO achieved 33% of WSD (295 μm) reduction and improved 40% of COF (0.057)
Palm-based TMPE + PAO + graphene nanoplatelets (GNP) (Azman et al., 2016)	5% of TMPE in 95% of PAO and 0.05% GnP improves COF (0.0737) and WSD (0.42 mm) by 5 and 15%, respectively.
TMPE + Poly alpha olefin (PAO) (Rico et al., 2002)	5% of TMPE in PAO exhibits the best wear performance under load (264 to 490 N)
Palm-based TMPE + Commercial oil (CO) (Zulkifli et al., 2013a)	3% of TMPE reduces 30% of COF (0.05) and WSD (0.28 mm), and 7% of TMPE gives the least frictional torque of 0.02 Nm.
Calophyllum inophyllum-based TMPE + CO (Srinivas et al., 2020)	10% of TMPE in CO yields 391.36 and 467.62 μm of WSD for 392 and 589 N load, respectively. The formulation gave a small COF but failed at 785 N

0.36 mm in the case of CO and 0.78 mm in TMPE. COF directly impacts the efficiency and life of the machine and lubricant. They declared that 3% TMPE provided an adequate protection layer between mating parts, and 7% TMPE depicted the most negligible frictional torque of 0.02 Nm under 160 kg or 1569 N. But the higher concentration of TMPE in fatty acid may lead to the accumulation of corrosive acid during oxidation.

Kotturu et al. (2020) and Srinivas et al. (2020) assessed 396.11 and 391.36 μm WSD for 20% Calophyllum inophyllum-based TMPE under 392 N load, respectively. However, the COF was about 0.0727 to 0.0788. Srinivas et al. (2020) postulated that synthetic engine oil could not sustain a load higher than 785 N before the breakage of the protection layer. A 0.25% of graphene nanoparticles (GnP) in TMPE produced the lowest WSD (48 nm) for the 2.5 N load condition ascertained by Liñeira del Río et al. (2018). The smallest COF, of 0.105, was obtained at 0.5% of GnP in TMPE due to the thin protective graphene layer which covers rough surfaces. The higher concentration of GnP may increase agglomeration tendency, which may increase WSD. It was found in literature studies that adding 0.05% GnP and 5%TMPE in polarity oil exhibit an increment of 5% in COF (0.0737) and 15% in WSD (0.42 mm) (Azman et al., 2016).

Rashmi et al. (2017) also studied the effect of GnP in TMPE base oil on tribological properties. The WSD reduced by 16.2% for 0.1 wt% of GnP and 5% phosphate ester at 392 N load compared with pure TMPE. It proves that GnP creates a protective layer to resist oxidation attacks. Similarly, the COF reduced by 7%for 0.1 wt% of GnP and 5% of phosphate ester at 785 N load in comparison with pure TMPE. Gulzar et al. (2017) studied the impact of nanoparticle size [1% of molybdenum disulfide (MoS_2)] and surfactant (oleic acid) on wear protection in TMPE and compared the results with commercially available PAO. They noticed that surfactant improves the stabilization through adsorption onto nanoparticles. The Larger size nanoparticles of about 50 to 2000 nm demonstrated a lower agglomeration tendency than small nanoparticles (20–150 nm). The larger size GnP was observed to disperse well in oil compared to small size GnP particles without dispersant. The surfactant addition endorsed better suspension in different GnPs sizes. The TMPE to pure oil depicts an improved performance of 25, 14.28, and 37.5% than formulated PAO to pure oil in terms of weld point (WP), final non-seizure length (LNSL) and initial seizure load (ISL). The synthetic TMPE produced mean WSD at ISL 2.48 mm for small GnP sizes and 2.66 mm for large GnP sizes, compared to pure TMPE's 2.68 mm. Nanoparticles tend to cover mating surfaces and restore worn-out surfaces. GnP thus concurrently attends to and polishes the mating surfaces

9.1. Hydraulic fluid

Eco-friendly hydraulic fluid development also lies under the application area of TMPE in bio lubricant. Hydraulic fluids usually transmit power among moving machine parts, including tractors, automobiles, cranes, bulldozers, and construction equipment. Lab-scale Hydraulic Test Rig was developed to investigate hydraulic fluid formulation's wear characteristics and oxidative stability (Ugolini et al., 2023). The comparative analysis was made by investigating the performance of palm-oil-based TMPE under a temperature range of 80 to 100 °C for 800 h in the presence and absence of additives. They check variations in oil viscosity and acidity. The results showed that the Irgalube F10 A additives performed inferior to Irganox L135. After 800 h of exposure, TAN value for synthetic oil was 0.32 mg KOH/g, in contrast to 4.88 mg KOH/g for oil with no additives. The results depict that TMPE and Irganox L135 work well together as antioxidants. In a further investigation, the same authors carried wear and friction tests on a TMPE formulation including 1% Irganox L135 and discovered a decrease in COF from 0.08 to 0.06 in comparison with TMPE base oil without additives. The formed TMPE showed a high WSD in contrast to un-additive TMPE,.

9.2. Heat transfer fluid

Heat transfer fluid is used for heat transmission with oxidation resistance. Water has the natural ability for cooling and heat transfer, but it can corrode the surface as well temperature and pressure may limit its operations (Qazi, 2017). Therefore, using a waster as a cooling agent in machines is not viable. Heat transfer fluid specially designed in this regard has appropriate thermal conductivity, the heat of vaporization, and specific heat. Hear transfer exhibits a directly proportional relation with energy efficiency. Polyglycols, ester compounds, water–glycol fluids, and silicone-based greases or oils are the primary synthetic heat transfer fluids. TMPE has a somewhat higher thermal conductivity than hydrocarbons, which is mainly responsible for better heat transfer properties (Dong et al., 2022). In the Patent, published in 2012, Claeys et al. (2012) discuss the use of tryster as a heat transfer fluid in electric vehicles. Biomass and a mono-unsaturated fatty acid were used to create the ester. At 25 degrees Celsius, the coolant displays an electrical volume resistivity of 1010 Ω-cm, typically 1012 Ω-cm. At 20 °C, the current coolants typically exhibit specific heat of 2.00 kJ/kg · K, and at least 2.30 kJ/kg · K. Additionally, the current coolant composition often displays a thermal conductivity at 20 °C of 0.170 W/m · K., if not at least 0.200 W/m · K. The ester samples can be employed as a dielectric fluid since they possess electrical resistivities that are higher than those of water/glycol combinations.

9.3. Cutting fluid

Cutting fluids limit the excessive temperature increase during machine operations (Katna et al., 2020). Although mineral oils are cheaper, they perform poorly due to lower pour points, oxidation instability, and viscosity loss under higher temperatures. The usage of cutting fluid is hazardous due to its explosiveness in the presence of the oxidizing agent. The non-edible vegetable oils are biodegradable, eventually broken down and mineralized by bacteria into CO_2 and hydrogen (H_2). A safe reintroduction of biomaterial into the natural carbon cycle is ensured by biodegradability. In naturally occurring climatic circumstances, non-edible vegetable oils deteriorate more quickly than mineral oils (Katna et al., 2020).

9.4. Metalworking fluids

Fatty acid esters and TMPE are metal working fluids' most commonly used additives (MWF) (Mathiesen, 1998; Sani et al., 2023). MWF facilitate lubrication through thin layer among metal tools and workpiece mating surfaces. MWF also acts as a coolant for reducing heat among tools and workpieces to achieve better productivity and efficiency. However, low toxic and biodegradable lubricant and minimum quantity lubrication (MQL) is required for eco-friendly machining operations (Talib and Rahim, 2014; Sen et al., 2021). A machining process with the MQL technique can be evaluated through modified jatropha oil (MJO) and jatropha oil-based TMPE with additives like 0.05wt% hexagonal boron nitride (hBN) nanoparticles. MJO with 0.05 wt% hBN faced the minor cutting temperature (210 °C) and cutting force of 383 N compared with pure MJO and MWF. Moreover, the tool chip contact length on cutting inserts can be significantly reduced through additives in MJO. Abdul Sani et al. (2019) found that plant oil-based TMPE with mixable ionic liquids additives through MQL practice can replace the MWF. They can reduce 1 to 2% friction angle, 7 to 10% cutting temperature, 22 to 25% chip thickness, 2 to 3% friction coefficient, 4 to 5% specific cutting energy, 8 to 11% tool chip contact length and increase 25 to 29% shear angle in comparison with synthetic ester lubricant.

9.5. Minimum quantity lubrication (MQL)

MQL is an eco-friendly technique that sprays the least amount of compressed gas and lubricant to the cutting zone through the nozzle for lubrication and cooling purposes (Dong et al., 2021). Dong et al. (2021) investigated the performance of palm, peanut, castor, soybean and cottonseed oil through temperature achieved during MQL steel milling. They found the best cooling effect for palm and cottonseed oils due to short carbon chain lengths conducive to MQL milling.

9.6. Gear oil

Gear oil significantly reduces noise, corrosion, and heat transfer and improves efficiency in automotive and industrial applications (Arca et al., 2013; Ghosh et al., 2021). However, vegetable oils do not exhibit desired viscosity for the above-mentioned applications; therefore, lubricant oil usually heats in inert conditions (thermal polymerization) to generate molecular weight products (Arca et al., 2013). The lubricant can be developed from crude or waste through hydrothermal liquefaction for viscous applications.

10. Driving forces of engine oil development

The lubricant oil should be prepared to meet fuel economy and emission standards.

10.1. Emission standards

The world is imposing strict emission standards to prevent the ecosystem from pollutants. Each country follows standards to regulate emissions and impose a strict tax on the polluting agency. America, Europe, and China are the top-of-line countries in adopting strict emission standards. Since the transportation sector is mostly to blame for the deterioration of the environment, this unfavorable climate change is primarily caused by emissions from automobiles, forcing the entire globe to implement robust rules for minimizing exhaust emissions from vehicles (Ijaz Malik et al., 2021). The policy pacts for emission control include the UN framework convention held in 1992, the Doha Amendment in 2012, the Kyoto protocol held in 1998, the Copenhagen Accord held in 2009, and the Paris Agreement in 2015 (Rodman Oprešnik et al., 2018). As per estimates, the transportation sector contributes between 60 and 80 percent of all hazardous environmental emissions and provides 95% of the energy utilized in automobiles globally (Kuczyński et al., 2019). The main reasons for emissions are incomplete combustion, acidic contaminants, and excessive temperature. Therefore, the lubricant originating from bio-sources can be useful in reducing carbon emissions and its cooling impact inside the engine can also be beneficial in reducing NOx emissions.

10.2. Global fuel economy standards

The United States Department of Transportation (USDOT) announced new vehicle fuel economy standards for 2024 to 2026. The standards include achieving 49 miles per gallon for the vehicles in 2026 and this fuel consumption is 33% less than in 2021. These standards are set to reduce carbon emissions by 2.5 billion metric tons for the year 2026 (Bui and Yang, 2022). From 41.9 miles per gallon in 2015 to 92 miles per gallon by 2030, the EU has mandated an average fuel efficiency across manufacturer fleets of around 57 U.S. mpg by 2021 (Forbes, 2019). China is also imposing strict standards for fuel economy like other global countries. As per Chinese standards, the average target set for 2025 is 4 liters per hundred kilometers (9.41 miles per gallon). This is a 20% reduction from the previous target of 5L/100 km (11.76 miles per gallon) in 2020 (Transportation I.C.o.C., 2019). In 2019, Japan projected fuel efficiency standards for passenger vehicles in 2030. This standard includes 25.4 km per liter by the year 2030 with an improvement of 32.4% as compared to 2016 (Transportation I.C.o.C., 2019). Lubricant oil plays a significant role in the fuel economy of the engine as it considers like blood in the engine which is not only responsible for wear and friction reduction but also responsible for cooling between mating parts and removal of wear debris among mating components. The viscosity of lubricant oil plays a keen role in its performance in the engine, if the viscosity is too high then the engine will serve force for pumping it and ultimately results in power loss and if its viscosity is too low then the lubricant oil is unable to sustain itself among mating parts and results contact between them which will lead to wear and tear.

11. Tribological performance

Tribology allows the analysis of three main streams (friction, wear, and lubrication). Vegetable oils possess an ester structure that plays a keen part in lubrication. The fatty acid contains both polar and non-polar ends. The polar end was responsible for the layer on the metal surface, and the non-polar end was responsible for COF reduction. Tribological tests, mainly four-ball and pin-on-disk tests, usually ascertain the tribological performance (WSD, COF, wear scar volume (WSV)) of bio-lubricants. Four ball tests evaluated lubricant behavior under extreme pressure and wear scars. However, the WSD and COF are temperature, speed, and load-dependent and sometimes it becomes difficult to compare them through tests. Therefore, the testing conditions and chemical composition of lubricant oil should be accounted for in each application. Table 4 reviews different bio lubricant sources and test methods to compare their performance.

Bahari et al. (2018) compared the lubricant sample with soybean and palm oil and found that palm oil showed a lower COF of 0.105 than soyabean oil (0.112). The smaller COF can be credited to the linear chain alignment of saturated fatty acid and the formation of a protective layer on the surface in the case of palm oil. However, soyabean oil contains unsaturated fatty acids that usually contain double bonds that do not cover the surface through a protective layer and are responsible for higher COF. It was found that the amount of palm oil methyl ester in lubricant oil of more than 5% causes corrosion and oxidation. The study also stated that the characteristics of bio-lubricants are significantly influenced by moisture, oxidation, and temperature (Cao et al., 2020). Erhan et al. (2006) studied the tribo-performance of palm oil-based TMP ester under various lubrication regimes (boundary, hydrodynamic and elastic hydrodynamic) on four balls testing machines. The results indicated tribological performance improvement in WSD and COF in TMP ester-based lubricant. Maleque et al. (1998) used three lubricant samples in diesel engines to compare their performance. Three lubricant samples were neat mineral oil, neat pongamia oil and blend of mineral and pongamia oil. The least brake specific fuel consumption (BSFC) and maximum brake thermal efficiency (BTE) were achieved for neat Pongamia oil under medium and higher loading conditions owing to lower viscosity. Moreover, the Pongamia reduced frictional losses and emissions of metal traces compared to other lubricant samples.

Bhale et al. (2008) evaluated the potential of non-edible vegetable oil in the automotive sector as an alternative to conventional lubricants. They concluded that lubricants derived from non-edible vegetable sources are biodegradable and renewable and do not disturb the food security of any country. Moreover, their renewable nature reduces their operating costs. Vegetable oils possess more advantages than conventional lubricants in terms of lower evaporative losses,

Table 4
Review of bio lubricant sources and their tribological performance.

Bio lubricants	Standard	Test method	Tribological conditions	Results	References
Palm oil	(SAE20W50)	High-frequency reciprocating rig (Ball on the flat), steel-to-steel pair contacts.	Sliding speed of 500 rpm, Contact load of 60 to 120 MPa and temperature of 80 °C	Less corrosion, less COF, good oxidation properties, Strong lubricant film stability	Haseeb et al. (2010), Fazal et al. (2012, 2011), Masjuki and Maleque (1997), Anastopoulos et al. (2001), Maleque et al. (2000), Mahmud et al. (2019)
Soyabean oil	–	Four ball tribo tester	Sliding speed of 1200 rpm, Contact load of 1.7 GPa and temperature of 100 °C	Less COF, better lubricity, and non-toxicity	Bahari et al. (2018), Adhvaryu et al. (2005), Asadauskas et al. (1997)
Castor oil and palm oil	(SAE20W40)	Pin on disk tribo wear tribometer Four ball wear testers	Sliding speed of 0.13 m/s, Contact load of 3.685 GPa and temperature of 100 °C	Less COF, Higher viscosity index, Lower volatility, higher antioxidant concentration	Zulkifli et al. (2013c), Arumugam and Sriram (2012), Wu et al. (2014)
Jatropha oil	–	Pin on disk machine	Sliding speed of 1000 rpm, Contact load varies from 50 to 150 N and temperature of 40 °C	Less wear and COF	Bekal and Bhat (2012), Mushtaq and Hanief (2021)
Coconut oil	(SAE20W50)	Four ball tester	Sliding speed of 1.4 to 5.6 m/s, Contact load 2 MPa and temperature of 90 °C	Lower COF, better lubricity, and higher anti-wear properties	Jayadas et al. (2007), Thottackkad et al. (2012)
Waste palm oil	(SAE40)	Four ball tester (Ip-239)	Sliding speed of 1.4 to 5 m/s, Contact load 100 N and temperature of 27 °C	Lower COF and higher viscosity	Kalam et al. (2011), Noorawzi and Samion (2016)
Palm oil with TMP ester	(SAE40)	High-frequency reciprocating machine	Sliding speed of 1770 rpm, Contact load 100 N and temperature of 27 °C	Good anti-wear properties (Lower COF and WSD)	Erhan et al. (2006)
Pongamia oil	(SAE20W40)	4-stroke single, cylinder, water-cooled CI engine	Sliding speed varies from 300 to 1500 rpm, Contact load of 200 N, Temperature varied from 100 to 200 °C	Higher BTE, lower frictional losses and emission	Maleque et al. (1998), Singh et al. (2019a)
Chemically modified rapeseed oil	(SAE20W40)	High-frequency reciprocating tribometer test rig	Sliding speed varies from 600 to 2200 rpm, Contact load varies from 100 to 300 N and Temperature of 60 °C	Higher oxidative stability, Improved pour point, lower COF	Jaina and Suhanea (2013), Guglea et al. (2022)

higher viscosity index, higher flash point, and lubricity. Jaina and Suhanea (2013) employed a high-frequency reciprocating Tribometer test rig to ascertain the tribo-performance of bio-lubricants and commercially available synthetic lubricants in the cylinder liner and piston ring of diesel engines. They concluded that bio-lubricants possess good thermal stability, oxidative resistance, improved pour point (flowability at a lower temperature), lower COF and better wear characteristics than conventional lubricants. Owing to the development of a stable polymeric coating on metal surface during boundary lubrication, they discovered a 23% lower COF in the case of chemically modified bio-lubricants. However, the inclusion of anti-wear additives, responsible for a 12% higher wear rate was seen in bio-lubricants than in commercially available synthetic lubricants. Arumugam and Sriram (2013) used neat soyabean oil, epoxidized soyabean oil, and hydrogenated soyabean oil as base oil and evaluated their operational efficiency to develop engine bio-lubricants. The results indicated that epoxidized soyabean oil and hydrogenated soya beans possess lower viscosity than engine oils. The viscosity analysis provides the optimum proportion of the bio-lubricant, including neat soyabean oil, epoxidized soyabean oil, and hydrogenated soyabean oil.

12. Impact of nano-particles

The tribological advancements highlight the effectiveness of nanoparticles for improved tribo-performance in terms of wear and friction (Ağbulut et al., 2020b). Many researchers employed inorganic and organic nanoparticles as additives in bio-lubricants for improved performance (Xin et al., 2021). The tribo-performance of nano-based lubricants significantly depends upon the nanoparticle size. The smaller nanoparticle size can support the lubricant to penetrate among intersecting surfaces in order to reduce wear and friction between them (Luo et al., 2014a). The mechanical characteristics of nanoparticles can be ascertained by their size, which greatly affects the tribological performance of nano-based lubricants. Therefore it is necessary to discuss the tribological impact of nano-particles on lubricant oil. Hardness exhibits an inverse relation with particle size for nano-particle heights greater than 100 mm. Therefore, the hardness of nano-based oils should not be higher because exceeding specific limits will result in indentation and scratching (Abd Elhaseeb et al., 2023).

The root means square roughness of the lubricated surface is a critical parameter in the selection of nanoparticle size. Lower lubrication is required for bigger particles because they get a deposit on the surface (Rabaso et al., 2014). Apart from size, the nano-particle shape is also a key indicator of tribological performance. The nano-particles possess five distinct shapes, i.e. onion, granular, tubular, spherical and sheet (Xie et al., 2016). The spherical shape of nano-particle is mainly preferred because nanoparticles have large surface energy owing to a higher surface volume ratio. In addition, the spherical-shaped particles possess homogeneous surface energy in all directions, like the ball bearing mechanism, and equilibrium can easily be achieved when particle agglomerate with each other's (Yu et al., 2011). The dispersion stability of nanoparticles is another key indicator of tribological performance because agglomeration greatly impacts sedimentation rate and ability to prevent wear and friction. The dispersion stability directly affects the sedimentation and clogging; if dispersion stability is less, there will be more clogging and sedimentation (Wu et al., 2018b).

The dispersion stability can be improved through surfactants and surface modification techniques (Kałuzny et al., 2020). The nanoparticle concentration is the third indicator of effective tribological performance and stable suspension. Therefore, the optimal concentration of nanoparticles is required to decrease wear and friction (Cecilia et al., 2020). The optimal concentration depends on dispersion duration, test condition, dispersion method and nature of nanoparticles, while counter surface roughness and type of base oil do not affect the tribological characteristics of nanoparticles (Luo et al., 2014b). The mechanisms which affect the tribological performance of nano-particles are the mending effect, polishing effect, rolling effect and protective layer effect (Singh et al., 2020a). In the rolling or ball-bearing effect, the nanoparticles usually convert sliding friction to rolling friction through three-body rolling effects among mating surfaces. In the mending effect, the nano-particles usually deposit in grooves and valleys between mating surfaces. In the polishing effect, the large asperities transformed into smooth surfaces. In the protective layer formation mechanism, the protective film developed between mating surfaces to prevent direct contact.

Cui et al. (2019) employed graphene nanoparticles by volume of 3% in palm oil along with a stabilizer (alkylphenol polyoxyethylene ether-10). They found that a blend of palm oil with graphene nano-particles produces 34.3% lower COF (0.295) than neat palm oil for similar conditions. The graphene adhered between mating surfaces and formed protective layers against wear and friction in the friction test. Razak et al. (2019) used dispersed nano clay in palm oil and observed that 0.04% nanoclay in the palm could reduce COF by 16% with 0.692 mm WSD compared to 1.020 mm WSD in the case of mineral oil. Gulzar et al. (2015) used palm oil methyl esters transesterified with TMP and two nanoparticles (CuO and MoS_2) to assess sliding wear. They used oleic acid (1%) as a surfactant and CuO and MoS_2 (1%). The MoS_2 blended lubricant oil produces 29% less sliding than palm oil, and MoS_2 blended oil possesses higher stability than CuO blended lubricant oil. The CuO blended lubricant oil produced 20% lower wear than palm oil. Zulkifli et al. (2013b) assessed the impact of TiO_2 particle addition into palm oil-based TMP esters. They observed 15 and 11% lower COF and WSD in case of TiO_2 blended lubricant oil.

Popoola et al. (2021a) used a different proportion of CuO nanoparticles (0, 0.75 and 1.50 wt%) in lubricant oil and evaluated their tribological properties through ball-on-disk tribometer under three loading conditions (2, 5 and 8 N) and three distinct speeds (150, 200 and 250 rpm). The output parameters were flash temperature, COF and wore rate. The lowest COF of 0.048 was achieved at 250 rpm speed, 0.75% concentration and 5 N load. The lowest wear rate of 0.012 was achieved at 200 rpm speed, 0.75% concentration and 5 N load. The highest flash temperature of 0.035 was reached at 250 rpm speed, 0.75% concentration and 5 N load. The optimized conditions for minimum wear rate, COF, and maximum flash temperatures were 1.1061 wt% concentration, 217.6768 rpm speed, and 5.0909 N load. They also performed scanning electron microscopy (SEM) on aluminum alloy disk specimens to comprehend the lubrication mechanism in piston ring cylinder assembly. As observed from Fig. 3(a) that higher concentration of nanoparticles aids in mending the surface through a protective layer. The tendency for wear crack was seen higher for a lower concentration of nanoparticles (0.75%wt). For higher concentrations of nanoparticles (1.50 wt%), the mending effect started to improve by filling crevices between mating surfaces and enhancing the ability to protect against wear. The tiny nanoparticles produced stable dispersion, such that particles penetrated mating surfaces and filled wear scars as aligned with previous research (Gulzar, 2018).

Baskar et al. (2017) examined the journal bearings in terms of their tribological performance for SAE20W40 synthetic lubricant and chemically modified rapeseed oil (CMRO) as bio lubricant dispersed with CuO, WS_2 and TiO_2 nanoparticles as an anti-wear additive (see Fig. 3(b)). The journal bearing test rig was used to measure COF, wear rate and oil film thickness under 10 kN load and 3000 rpm speed. The best results were obtained for CuO additives lubricant oil in terms of 27% lower COF and 47% lower wear rate than synthetic lubricant.

The presence of contaminants, moisture, temperature, pressure, and rough metal surfaces is inevitable in most lubricant applications. They can boost oxidation presence, resulting in higher friction, wear rate and early corrosion (Salih and Salimon, 2021; Ağbulut et al., 2021). Therefore, lubricants should possess higher oxidative stability. Moreover, the antioxidants can be used as additives to prolong the oxidation time of lubricant. The impact of zinc diethyldithiocarbamate (ZDDC) and zinc dialkyl dithiophosphate (ZDDP) on the oxidative stability of palm oil was assessed by Azhari et al. (2017). However, the main disadvantage of ZDDP is that it can produce ash during combustion and may poison emissions control catalysts. To mitigate the hazardous impact of ZDDP, the Hexagonal Boron Nitride powder can be used as an alternative to ZDDP due to its chemically inert nature, high load-bearing capacity, higher thermal stability along with lower coefficient of friction (Çelik et al., 2013).

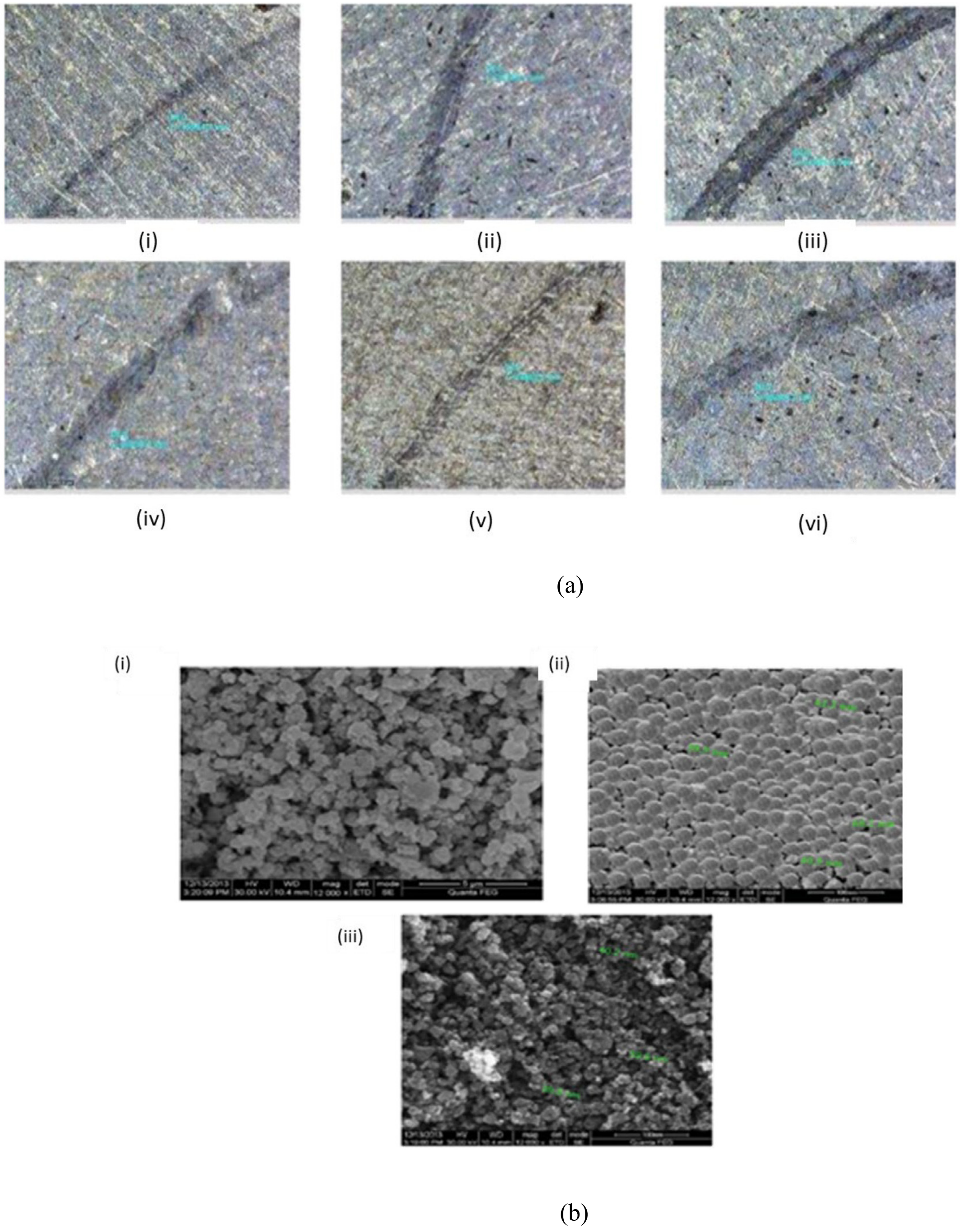


Fig. 3. (a) SEM micrographs of disk specimens assessed with the formulated bio-lubricants (i). 0.75 wt% CuO (2 N) (ii). 0.75 wt% CuO (5 N) (iii). 0.75 wt% CuO (8 N) (iv). 1.50 wt% CuO (2 N) (v). 1.50 wt% CuO (5 N) (Vi). 1.50 wt% CuO (8 N) (Popoola et al., 2021a) and (b) SEM image of nano CuO; (i) SEM image of nano WS_2; (ii) SEM image of nano TiO_2 (Baskar et al., 2017).

The tests were carried out in compliance with ASTM D2272 standard, and it was found that the oxidation time for ZDDP (2 wt%) was 128 min, which was more than that ascertained with palm oil (32 min) and ZDDC (62 min) due to presence of sulphides in ZDDP that delayed the radical chain formation. Sen et al. (2020) used 50 nm dispersed alumina nanoparticles in palm oil for 0.3 and 1.5% concentration in 0.3% v/v polysorbate 80 (surfactant). They observed a 200% rise in thermal conductivity with a 0.9% concentration of Al_2O_3. The stability of Al_2O_3 could be reduced at higher concentrations which is dangerous for the thermal characteristics of lubricant oil. Table 5 presents the impact of different nano additives on

Table 5
Impact of nano-additives on synthetic and bio-lubricants.

Nano additives	Synthetic lubricant	Bio-lubricant
TiO_2	COF (30%) - 1% wt TiO_2 in SAE 5W-30 - pin-on-disk tribometer (Rashed and Nabhan, 2018) COF (48%) - 0.25% wt TiO_2 in SAE 5W-30 - pin-on-ring test (Ali et al., 2016)	COF (10%) - 0.1% wt TiO_2 in pongamia oil - pin-on-disk tribometer (Singh et al., 2018)
CuO	COF (53.98%) - 1% wt CuO in engine oil (HD 50) - pin-on-disk tribometer (Namer et al., 2019)	COF (41.42.%) - 1% wt CuO in castor oil - pin-on-disk tribometer (Noori et al., 2019)
MoS_2	COF (50%) - 1% wt MoS_2 in molding oil - piston skirt liner tribometer (Awang et al., 2019)	COF (76.02%) - 1% wt MoS_2 in castor oil - pin on the disk tribometer (Noori et al., 2019) COF (57.89%) - 0.1 to 1.25% wt MoS_2 in sun flower oil - pin on the disk tribometer (Namer et al., 2019)
ZnO	COF (22%) - 0.6% wt ZnO in engine oil (10W-40) - pin on disk tribometer (Elagouz et al., 2020)	COF (14.74%) - 0.1 to 2% wt ZnO in castor oil - pin on disk tribometer (Bhaumik et al., 2018)
Al_2O_3	COF (24.22%) - Al_2O_3 in engine oil (SAE 5W-30) - piston ring assembly (Ali, 2018) COF (59.17%) - 1% wt Al_2O_3 in engine oil (SAE 20W-40) - pin-on-disk tribometer (Thakre et al., 2016)	COF (27.76%) - 0.08% wt Al_2O_3 in polanga oil - four ball tribometer (Singh et al., 2019c)
SiO_2	COF (36.84%) - 1% wt SiO_2 in engine oil (SAE 15W-50) - pin-on-disk tribometer (Rashed and Nabhan, 2018)	COF (50.85%) - 0.25 to 1.25% wt SiO_2 in coconut oil - pin-on-disk tribometer (Ghaednia et al., 2015)

synthetic and bio bio-lubricant performance. A green synthesized silica nano additive added to biodiesel blend showed a great influence on engine speed, engine load, and performance (Bitire and Jen, 2023).

Table 6 depicts the comprehensive review of lubricant formulations with different nano-particle concentrations to check the lubricant oil stability. The tungsten disulfide in polyaphaolefin (PAO) base oil produced the most stable lubricant oil with a stability time of 4320 h. However, the amalgam of Zirconia and silicon dioxide with 20# machine oil exhibit the least stable lubricant with a time of 12 h. Different dispersion techniques of nanoscale ionic material (NIM), silanization, dispersant, surface-induced-atom-transfer-radical polymerization (SI-ATRP) and solid surface method (SSM). When silicon dioxide (SiO_2) blended with Glyceryl Oleate (GMO) through the silanization technique produced stable composition with a stability time of 3600 h.

13. Production techniques

Bio lubricants can be categorized as per their chemical conformation in synthetic and natural oils. Natural oils usually originate from animal fats and vegetable oils, while synthetic oils are comprised of natural oil as base oil, and further modifications can be made according to requirements. The modification can be made through microorganisms, polyglycols, ester synthesis, perfluoroalkyl ethers, and polyalcohols in natural oil (de Sousa et al., 2022). The main sources of bio lubricant are seeds, animal fats, and vegetable oils, which go through a distillation and extraction process for conversion into oils (Cecilia et al., 2020). However, the bio lubricant can be synthesized through the aforementioned modifications, and possess lubricity, wear resistance, corrosion resistance, and oxidative stability greater than mineral oils (Uppar et al., 2022). However, synthetic oil has some limitations, including increased cost during chemical modification, higher volatility, higher toxicity, reduced frictional tolerance, and mismatch between esters and mineral oils in contrast to neat vegetable oils. Chan et al. (2018) Bio lubricants possess a wide range of applications owing to their low cost and higher biodegradability than mineral oils (Emmanuel et al., 2009). The consumption of natural oils to synthesize bio-lubricants is inconsistent due to food security issues, crop prices, and social imbalance. Synthetic esters are developed by chemical treatment of plant-based oil and animal fats. The main focus of today's research is to optimize the physicochemical attributes of bio-lubricants through different chemical modifications or catalytic processes. The unsaturated oils usually modify through a chemical process as their double bonds are susceptible to reaction with atmospheric oxygen.

13.1. Epoxidation

The molecules with a higher degree of unsaturation are more susceptible to hydrolytic degradation (Salimon et al., 2012a). Moser and Erhan suggested an auto-oxidation process that may occur through the reaction between oxygen and free radicals to produce peroxy radicals. This peroxy radical then reacts with lipid molecules to form hydroperoxide and other free radicals, and thereby oxidation process may propagate (Salimon et al., 2012b). The modification in the alkene group and the addition of alkyl side chains improve thermo-oxidative stability and other physicochemical attributes (Cecilia et al., 2020). Epoxidation is the key process to modify C–C double bonds through alkyl hydroperoxides, dioxiranes, peroxy acids, peracids as foundations to produce bio-lubricants with better acidity, improved pour points, higher adsorption on the metal surface, higher viscosity index, better lubricity and higher thermo-oxidative stability (Salimon and Salih, 2009). After epoxidation, it is necessary to modify physicochemical properties especially pour point, further through acyloxylation, hydroaminomethylation, hydroformylation, interaction, alkylation, cooligomerization, acylation,

Table 6
Review of lubricant formulations with distinct nano-particles.

Particle		Size (mm)	Base oil	Dispersion technique	Stability time	Observation
Carbon	Nanotube	100	PAO	Dispersant	24 h (Nunn et al., 2015)	Carbon nanoparticles are added to lubricants owing to their excellent mechanical, thermal, electrical, and chemical properties.
	Graphene	N/A	PEG400	NIM	720 h (Yang et al., 2017)	
Sulfide	WS_2	7	PAO	SSM	4320 h (Jiang et al., 2016)	Tungsten disulfide possesses excellent lubricious properties with a COF of around 0.3. Molybdenum disulfide possess high temperature applications, under higher load and speed owing to its ability to maintain its basic structure.
	MoS_2	3	PAG	SSM	336 h (Wu et al., 2018a)	
Oxides	TiO_2	2	Liquid paraffin	SSM	720 h (Li et al., 2006b)	TiO_2 is added to lubricants due to its exceptional catalytic and semiconducting characteristics. Moreover, it is non-toxic, chemically stable, and biocompatible. Nano TiO_2 particles are good oxidizing agents with large surface area and higher photo-catalytic activities.
		15	PAO spectrasyn 4	SI-ATRP	1344 h (Wright et al., 2016)	
		25	Liquid paraffin	Silanization+ Dispersant	3600 h (Bogunovic et al., 2015)	
	SiO_2	12	PAO	NIM	48 h (Kim and Archer, 2011)	Silicon dioxide possess boiling and melting points of 2950 °C and 1713 °C, respectively with the density of 2.648 g/cm^3. Moreover, it is insoluble in water and acid, but soluble in hydrofluoric acid.
		23	PAO	SI-ATRP	1440 h (Chen et al., 2019)	
		25	GMO	Silanization	3600 h (Li et al., 2006a)	
		60	PAO100	Silanization	1440 h (Sui et al., 2015)	
		100	RO base oil	Silanization	192 h (López et al., 2015)	
		110	PAO	Silanization	1440 h (Sui et al., 2018)	
		200	PAO	Silanization	2880 h (Sui et al., 2016)	
	ZrO_2/SiO_2	100	20# machine oil	Other	12 h (Li et al., 2011)	ZrO_2 form a protective layer on mating surfaces through van der Waals forces and functions as nano-bearings among mating parts in order to protect them.
	Al_2O_3/SiO_2	70	Liquid paraffin	Silanization	2160 h (Jiao et al., 2011)	The lubricity can be improved owing to mending and ball bearing effect of Al_2O_3 nanoparticles producing a self-protective film among mating surfaces. Moreover, its blends with SiO_2 imparts excellent tribological attributes.
	ZnO/Al_2O_3	50	20# machine oil	SSM	672 h (Chen et al., 2012)	ZnO imparts anti wear characteristics to lubricant and its blends with alumina tri-oxide form stable lubricant formulation.
	Al_2O_3	80	20# machine oil	SSM	480 h (Luo et al., 2014a)	The lubricity can be improved owing to mending and ball bearing effect of Al_2O_3 nanoparticles producing a self-protective film among mating surfaces.

esterification and amino alkylation (Karmakar et al., 2017). Many researchers reported that modification processes significantly improve lubricity, thermo-oxidative stability, COF, pour point and viscosity index (Erhan et al., 2008; Salih et al., 2011; Salimon et al., 2010; Hwang and Erhan, 2006; Ahn et al., 2012). Both acetylation and esterification reactions were conducted through homogeneous acid catalysts (H_2SO_4) blended with alcohols (Hwang and Erhan, 2006; Kulkarni et al., 2013; Salimon et al., 2011). The reaction medium's corrosion potential leads to solid acid catalysts' formation through sulfated-SnO_2 and cationic exchange resins (Somidi et al., 2014).

13.2. Esterification/transesterification

Transesterification reactions include the replacement of glycerol moieties of the triacylglyceride with long/ branched chain alcohol. However, the esterification process includes a reaction between free fatty acid of natural oil and long-chain alcohol, ultimately forming respective esters (Salih et al., 2011). Both transesterification and esterification reactions can take place in the presence of acidic or basic catalysts. The properties of acids and alcohols significantly affect synthetic esters' physicochemical properties. Synthetic esters possess better properties in terms of higher flash points, higher pour points, lower volatility, and higher thermo-oxidative stability than their respective esters or natural oils (McNutt, 2016). The esters are prone to thermal degradation and hydrolysis. But thermal characteristics can be amended by substituting longer alkyl/branched chains such as trimethylolethane (TME), trimethylolpropane (TMP), 2-ethyl hexanol, neopentylglycol (NPG), pentaerythritol (PE), trimethylolethane (TMH) (Cecilia et al., 2020). Transesterification mainly occurs under acidic conditions, but this is a slow process and is intermittently used. The base-catalyzed reaction is approximately four thousand times faster and entails low temperature and reaction time in comparison with acid-catalyzed (Cecilia et al., 2020). The mineral acids like H_3PO_4, HCl and H_2SO_4 are mainly used as catalysts. Despite better conversion ability, there are several disadvantages related to corrosion, purification, and separation of obtained bio-lubricants. Considering the weaknesses, the ion exchange resins or oxides like WO_3, Nb_2O_5, ZrO_2, Ta_2O_5, Al_2O_3, TiO_2 and zeolites show the potential to replace conventional mineral oils (Saboya et al., 2017a,b; Marx, 2016; Go et al., 2016; García-Sancho et al., 2017; Kuzminska et al., 2015). However, the 98% yielding can be achieved through base catalysts like alkaline earth oxides, carbonates, alkoxides and hydroxides compared with solid acid catalysts (Schwab et al., 1987; Kim et al., 2004).

13.3. Estolide formation

The branched/oligomeric esters (estolides) are synthesized when the unsaturated site of one fatty acid gets attached to the carboxylic acid of other fatty acids through carbocation (nucleophilic attack) during the presence of acid catalyst (H_2SO_4) and oxidant ($HClO_4$). Estolides have more resistance against hydrolytic degradation as compared to triglycerides. The physicochemical attributes of bio lubricant depend on the hydrocarbon chain length and estolide number as specified by estolides formed from 2-ethyl hexanol, oleic acid, and lauric acid (Brimberg and Kamal-Eldin, 2003; García-Zapateiro et al., 2013). The estolides possess higher lubricity, viscosity index, thermo-oxidative stability, and lower pour point (Salimon and Salih, 2009). Further, the estolides esters have higher biodegradability than commercially available estolides, which can only be used as a blend with vegetable oils with modified physicochemical properties (Cermak et al., 2006, 2013).

13.4. Selective hydrogenation

The degree of unsaturation exhibits an antagonistic impact on thermo-oxidative stability of bio-lubricant. However, the degree of unsaturation can be reduced through hydrogenation through Ru, Ni, Pt or Pd-based catalysts at higher temperatures (250–300 °C) and higher pressure (25–35 MPa) (Hassiotis et al., 2014; Sánchez et al., 2015). The hydrogenation (chemical modification) results from isomerization in cis and trans acid, as well as the decreased fluid ability of the lubricant. Therefore, hydrogenation is more suitable for solid lubricants or waxes. Thus, hydrogenation is not considered effective in improving physicochemical properties (Salimon et al., 2010).

13.5. Microwave technology

Microwave heating transforms electrical energy to radiation by increasing the internal energy of reactant molecules, and this technology is mainly used to enhance transesterification. Significant energy saving can be achieved through microwave technology as it helps in reducing reaction time by 60% in comparison with conventional heating (convection/conduction) (Mohamad Aziz et al., 2021). Microwave heating is most suitable for drying polar compounds. The moisture presence aligns the OH bond and constantly varies the magnetic field to generate molecular friction and heat. Microwave heating is unsuitable for heating non-polar compounds and requires modification, such as polar species addition into a reactive mixture. The researchers have already studied the impact of adding the passive heating element and ionic liquid to heat non-polar substances (hexane, chloroform, toluene) (Kappe, 2008; Hoogenboom et al., 2009). Dipolar and polar ionization are two mechanisms to generate heat from microwave irradiation. The polar molecules in the reactive mixture are engaged in dipole–dipole interaction, as free ions are impacted by ionic polarization as oriented in the electric field. The applied electric field varies continuously as the ion field tries to re-align itself, which is responsible for heat energy loss through dielectric loss and molecular friction (Lidström et al., 2001). Sufficient energy is required for reactant molecules for effective collisions, and this sufficient energy is usually achieved from optimum temperature. The higher temperature provides higher reactant solubility and product conversion (Chuah et al., 2015). Methanol is generally used as a catalyst to drive the reaction in the forward direction with the generation of more methyl ester in less reaction time. The molar ratio of methanol to oil is usually kept between 6:1 to 60:1, with a conversion efficiency of 71.4 to 98.9%. A higher proportion of methanol is used for highly viscous oil to augment oil solubility in methanol (Chuah et al., 2015). The temperature measurement is a significant limitation in microwave oven by a thermocouple (k-type) due to arc formation when the interaction between microwave and metallic probe occur (Farag and Chaouki, 2015). This arc/spark can also be produced from metal scrap or chipped paint inside the surface. The hot spot usually occurs for materials whose dielectric loss increments with overheating or temperature.

13.6. Microwave and supercritical/ subcritical

The microwave-assisted subcritical or supercritical process is a catalytic-free process that does not need any pre-treatment or purification steps, as it is free from wastewater. This process is easy for trans-esterifying bio-based resources (Mohamad Aziz et al., 2021). However, the higher temperature and pressure required for both subcritical and supercritical reactions consume higher energy. Water is utilized in sub-critical conditions (2 MPa and 488 K) as a solvent to enhance oil extraction of jatrpha curcas oil seed through increasing porosity and weakening sample structure (Go et al., 2014). Lipid hydrolysis becomes more feasible as transesterification of fatty acid methyl ester (FAME) occurs at lower activation energy under 250 °C and 13 MPa. Parekh et al. (2021) used acetic acid and methanol solvent and found that the transesterification process takes place in 105 min with a 65.1% yield rate. A molar ratio of 1:42 was used for the transesterification of methyl acetate and rapeseed oil in another study of the non-catalytic synthesis of FAME under supercritical conditions. The yield rate was 97% in 45 min at 320 °C and 20 MPa (Saka and Isayama, 2009).

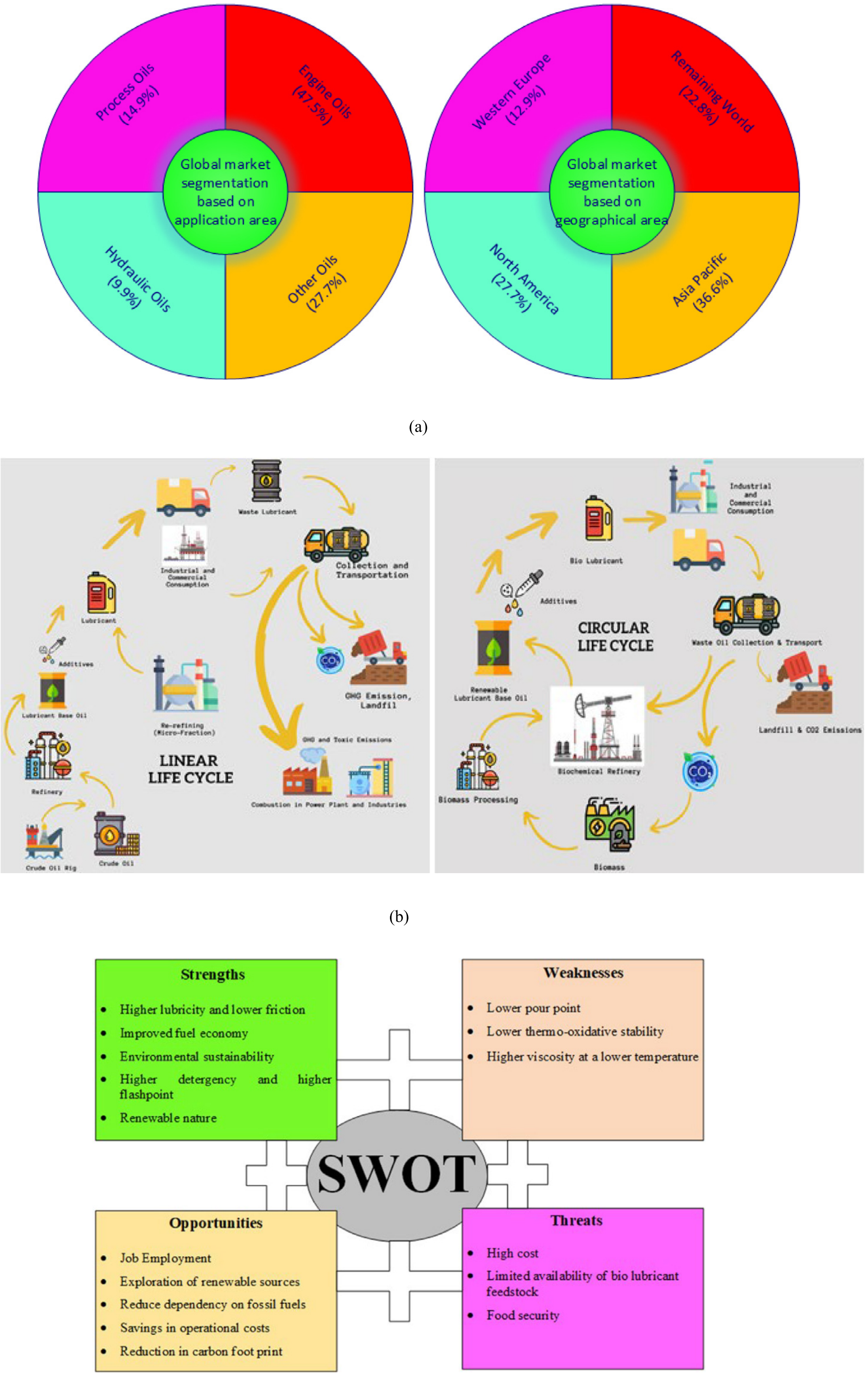
14. Advantages and disadvantages

For holistic view of biolubricant performance, its advantages and disadvantages need to be discussed. It will open new avenues for future research in order to minimize disadvantages and utilization of biolubricants at a large scale. Vegetable oil has excellent lubricity, a higher viscosity index, and biodegradability is less toxic and renewable. But then, vegetable oil has less oxidative stability, higher pour point, higher biological deterioration (bacterial) and aqueous decomposition (Negi et al., 2021). Bio lubricants possess 2 to 4 times higher lubricity than petroleum-based lubricants, resulting in reduced friction and energy saving from 5 to 15%. Bio lubricants have a higher viscosity index and can be used in high-temperature applications, mostly above 250 °C. Bio lubricants produce lower emissions owing to higher boiling temperature ranges of esters (Bilal et al., 2013). Bio lubricants depict higher safety standards regarding lower volatility, oil mist, emissions, stable viscosity, and higher flash points. Bio lubricants create lower dermatological issues due to better compatibility with skin. Bio lubricants possess higher biodegradability and eco-friendly characteristics, reducing their disposal costs. Bio lubricants are non-toxic and have minimum corrosion tendency interlinked with energy savings. On the contrary, bio-lubricants possess a bad smell due to contaminants, are viscous at a lower temperature, and have lower thermo-oxidative stability at higher temperatures and lower pour points (Bilal et al., 2013). The limited availability of bio-lubricant base stock and higher production costs are significant challenges linked with bio-lubricant production. The numerous factors involved in the determination of bio lubricant cost. These factors comprised processing technology, plant capacity, feedstock quality, net energy balance in the purification process, storage and base stock prices etc. (Haas, 2005). The feedstock cost determines 75% of the total bio-lubricant cost (Miao and Wu, 2006). The lower pour point and lower thermos-oxidative stability are primarily responsible for bio-lubricant performance setbacks (Zhang et al., 2020).

15. Lubricant oil market share

The development of new product is not only enough if it is not marketize appropriately. It is necessary to have holistic view of market before product development in order to examine its adoptability. In this section, a trend of lubricant in market from last few decades is examined. The market analysis can give a brief idea for the characteristics of successful biolubricant. The lubricant market has faced drastic changes during the last few decades. The global lubricant demand has been 35 million tons per year since 1991. However, the global lubricant demand in 2004 was evaluated as 37.4 million tons, with 10% process oil, 53% in the automotive sector, 5% marine oils, and 32% industrial lubricants (Nagendramma and Kaul, 2012). In 2005, the global lubricant demand slightly increased to 37.9 million tons. In 2007, a sudden hike in lubricant demand was observed globally, with 41.8 million tons and a 0.8% growth rate. In 2012, a growth rate of 2% was observed. As a result, the bio-lubricant market is anticipated to expand to $2.4 billion in 2025 at a rate of 4.1%, as the global demand for lubricants is anticipated to reach $68.54 billion in 2022 (Unugul et al., 2020). There are a total of 1700 lubricant manufacturers worldwide, out of which three hundred are in Europe. The primary business of these manufacturers is to explore, extract and refine crude petroleum products.

About 1200 lubricant manufacturers concentrate on engine, hydraulic and gear oils. Around 2% of lubricant manufacturers meet 60% of global lubricant demand (Mang and Dresel, 2007), the manufacturers working currently on the market eco-friendly, biodegradable bio-lubricants in the US, Asia and Europe. High-performance multi-grade hydraulic fluid is one of more than thirty useful formulations based on soybeans based on lubricants, greases, and metalworking fluids (Mobarak et al., 2014). Bio lubricants rapidly replace mineral oil products (engine oils, hydraulic fluids, compressor oils, process oils, transformer fluids, turbine oils) in global markets. Fig. 4(a) depicts the segmentation of global markets based on application areas like engine oils, process oils, hydraulic oils, etc. and segmentation based on geographical area, Asia pacific, north America, western Europe, and the remaining world. It has been found the main application of lubricants includes engine oil, and Asia/Pacific is the biggest market for lubricants.



(a)

(b)

(c)

Fig. 4. (a) Segmentation of the global market based on the (i) application area and (ii) geographical area, (b) Life cycle assessment of (i) conventional lubricants and (ii) bio-lubricants and (c) SWOT analysis of bio lubricant impact in society.

16. Life cycle assessment

Despite of many advantages of bio-lubricants in terms of environmental sustainability, the economic cost linked with bio-lubricants is higher owing to food security issues. But the bio-lubricants are based on a circular economy, as they can be recycled and regenerated again with zero carbon footprint. Lifecycle assessment (LCA) for both bio-lubricants and petroleum-based lubricants in terms of environmental sustainability and economy highlights conventional and bio-lubricants in terms of economy and environment, laying stress on awareness about the potential in this sector. LCA can be conducted in four stages. The first is scope determination, the second is inventory lifecycle, the third is the assessment of lifecycle impact, and the fourth is result interpretation. The lifecycle phases for conventional lubricants involve crude oil source exploration, crude oil extraction, crude oil refining, lubricant production, use and disposal into the environment. While the life cycle phases for bio-lubricants comprised farming, milling, refining of bio sources, lubricant production, use, and disposal to the environment (Baumann and Tillman, 2004). The main issue with bio-lubricants consumption is their production cost which is approximately 10 to 20 times higher than conventional lubricants. Comparable results can be achieved by adopting consistent metrics to benefit all stakeholders and, ultimately, the environment. These metrics would help analyze the ecological footprint and financial indicators necessary for development, planning and decision-making (Damjanović et al., 2016). It has been stated by the living planet report 2010 global footprint network that we need approximately 1.5 planets to fulfill the annual requirements of humanity and that 50% of global biocapacity lies within ten countries. Fig. 4(b) assesses the lifecycle for both conventional and bio lubricants. The bio lubricant production and utilization are based on a circular economy because its disposal at the landfill site and CO_2 emission can be further utilized in synthesizing the raw materials. But conventional lubricants' waste disposal cannot be reutilized in the formation of lubricant raw material, and their life cycle is based on the linear economy. The primary difference between linear and circular economy is that linear economy emphasizes profit irrespective of the lifecycle. However, the circular economy targets towards sustainability of sources.

17. SWOT analysis

SWOT analysis accounts for the strengths, weaknesses, opportunities, and threats from the happening of a particular event. Fig. 4(c) displays the SWOT analysis for adopting biotechnology in the lubricant sector to ensure environmental sustainability. Bio-lubricants' strengths are higher lubricity, lower friction, improved fuel economy, environmental sustainability, higher detergency, higher Flashpoint, and renewable nature. The opportunities associated with bio-lubricants are job employment, exploration of renewable sources, reduced dependency on fossil fuels, savings in operational costs, and reduction in carbon footprint. The adverse impacts (weaknesses) of bio-lubricants are lower pour point, lower thermo-oxidative stability, and higher viscosity at a lower temperature. The threats involved in adopting bio-lubricants are higher feedstock costs, limited availability, and food security issues.

18. Future prospects

Modernization and expansion of the manufacturing sector satisfy the rising need for lubricants worldwide. Due to its relatively low labor costs and political stability, the Asia-Pacific region, driven by China, will continue to be the critical driver of growth in the lubricant markets (Mobarak et al., 2014). The main concern in 1950 regarding lubricant was maintaining appropriate viscosity without any acid components in the base oil. Base oils were demoted to the status of solvents or carriers for additions in the 1960s. However, in the 1970s, synthetic fluids with a consistent chemical structure outperformed mineral base oils in terms of performance.

The quasi-synthetic hydro-cracked lubricants were launched in Europe at low prices with properties similar to synthetic lubricants in the 1980s. In the 1990s, the environmental, health and safety standards influenced base oil development and the need to develop lubricants that could match these standards. Future research explores new avenues for developing bio-lubricant production techniques to lower production and operational costs. The production cost could also be reduced by exploring cheaper feedstocks that do not threaten food security. The new generation additives can also be developed, which ensure biodegradability and environmental protection. To ensure appropriate lubricant developments, it is mandatory to understand the methodological concept of biodegradability. This concept does not mean that biodegradability provides complete environmental protection because intermediate products are also involved in the decomposition cycle. But technology is advanced to a great extent. It can develop such lubricants and additives, which would perform far better than mineral oils in terms of zero carbon footprint, thermo-oxidative stability, viscosity, and volatility.

19. Conclusions

The petroleum reserves are depleting rapidly because of their increasing demand in driving the economy of any country. Moreover, petroleum products serve as severe environmental threats because of their emissions. Therefore, the trend is shifting towards bio-lubricants that are renewable in nature and eco-friendly. This paper reviews the bio lubricant role comprehensively towards a sustainable environment. The findings of the paper are stated below:

A current review study entails lifecycle assessment, SWOT analysis, effective production techniques, lubricant oil feedstocks, market analysis, tribological performance and characteristics of biolubricants along with its comparison with conventional lubricants.

Although bio-lubricants possess a higher viscosity index, lubricity, biodegradability, and non-toxic and renewable nature compared to petroleum lubricants, they also exhibit higher pour point, lower thermo-oxidative stability, and moisture content. Moreover, food security also serves as a severe concern for bio-lubricants. These issues highlight the need to develop such additives that may prolong thermo-oxidative stability and reduce pour point and moisture for its smooth operations. Further, lubricant oil sources that do not threaten food security should be considered. The algae-based lubricant is one such example. The algae can be obtained from industrial effluents and seawater, readily available sources.

Future research should be focused on such additives and nanoparticles that would further enhance lubricity, thermo-oxidative stability, increase flash point, lower evaporation rate, higher biodegradability, and better wear protection. The production cost of bio-lubricant seems higher than that of petroleum products. Therefore, cheaper feedstocks should be considered to achieve an economic breakthrough. Moreover, such production techniques need to be developed that will play their role in minimizing cost. Mechano-chemical treatments, microwaves, or ultrasounds can significantly improve bio-lubricant yields under mild conditions. Most recently, enzymatic catalysis processes have produced bio-lubricants (algae-based) at low reaction temperatures with higher yield rates. Therefore, research needs to be done on algae-based bio-lubricants preparation along with their genetic modifications and performance in engines.

CRediT authorship contribution statement

Muhammad Ali Ijaz Malik: Conceptualization, Project administration, Supervision, Investigation, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **M.A. Kalam:** Investigation, Methodology, Writing – original draft, Writing – review & editing. **M.A. Mujtaba:** Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Fares Almomani:** Conceptualization, Project administration, Supervision, Investigation, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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