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Original Research Article

A Review of the Preparation, Enhancement and Properties of Plant Oil-Based Biolubricant

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ABSRTACT

The employment of lubricants derived from fossil fuels has rapidly lost preference in favour of its equivalent, known as biolubricants. This shift results from the harmful environmental implications and non-biodegradability of items obtained from fossil fuels. They contaminate the land, water, and air, harming both plant and human life. Thus, the requirement for substitutes. Biolubricants are not as widely used as those derived from fossil fuels despite their biodegradability and sustainability. The use of biolubricants can only surpass that of fossil fuels if research and development are encouraged. The need for biolubricants surged in tandem with the introduction of environmental rules aimed at curbing environmental damage. Because they are renewable, eco-friendly, and biodegradable, vegetable oils have the potential to be used as base fluids in biolubricants. They have superior physicochemical qualities, such as enhanced friction coefficient, greater viscosity index, and excellent lubricity, when produced properly. They have higher physicochemical qualities (high flash points, pour points, greater viscosity index, friction coefficient, and better skin compatibility) when handled properly. Even though using an untreated vegetable oil lubricant has certain disadvantages, such as poor oxidative stability and poor low temperature performance, these characteristics have been enhanced by the application of various chemical modification techniques, including epoxidation, hydrogenation, transesterification, and formation of estolides. An overview of the most recent developments in novel chemical modification techniques that have produced biolubricants with enhanced physicochemical qualities is given in this article.

Key words: Chemical modification, Transesterification, Epoxidation, Additives, Biodegradability

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Introduction

A lubricant is a material that reduces heat generated during motion and helps reduce friction between two surfaces in contact. Lubricants reduce wear, clear debris, disperse heat, and boost performance. [1,2] Lubricity is the process via which a machine's friction property is decreased, and it helps a machine mechanism operate more effectively. Good viscosity index, hydraulic stability, excellent oxidative resistance, low freezing and boiling temperatures, and resistance to corrosion are some of the qualities of lubricants. Although they are often liquid, lubricants can also be solid or semi-solid. It is made up of different base fluids and additives and is significant in tribology. [3, 4]

The classification of lubricants is determined by the characteristics of the base fluid, which is the primary component of the lubricant. Using various lubricants in industrial applications has important environmental consequences, especially as industries move towards more environmentally friendly methods. The selection of lubricants has an impact on both ecological health and operational efficiency, with a rising focus on non-toxic and biodegradable options.

According to Robert et al.[5] lubricants are categorised into three types: refined petroleum stocks, synthetic stocks, and plant oils. Each type of oil has a distinct purpose and set of performance parameters. Petroleum-based lubricants, which constitute approximately 95% of the world's lubricant use,[6,7] are obtained from petroleum oil which are neither biodegradable nor renewable. They have long-chain hydrocarbon structures and are resistant to oxidation and viscosity, which makes them ideal for a range of industrial uses.[8] But their potential for bioaccumulation and environmental toxicity has subjected them to more scrutiny.[9] They are non-biodegradable and non-renewable. These factors, along with others, contribute to the uncertain and negative outlook for petroleum-based lubricants, both currently and in the future.[10,11] Therefore, there is a demand for a sustainable and renewable alternative, such as biolubricants which provide a sustainable substitute that has a smaller negative impact on the environment due to their improved biodegradability and decreased spill pollution.[12] This review article specifically examines the many alterations that have been applied to improve the effectiveness of biolubricants.

Biolubricant

They are lubricants derived from biodegradable and sustainable sources, such as animal fat and plant oils. They are preferred over petroleum-based lubricants because of their inherent characteristics, such as being natural, biodegradable, and renewable. Biolubricants exhibit superior lubricity, enhanced anti-wear characteristics, improved load-carrying capacity, prolonged equipment lifespan, elevated viscosity, and reduced emission of metal residues into the atmosphere.[13,14] The biolubricant's viscosity index makes it suitable for use in settings that are at or above 250ºC.[15] They possess elevated fire and flash thresholds yet exhibit reduced volatility and minimal vapour discharges. Biolubricants are environmentally non-polluting. The non-polluting nature of the substance allows for its disposal at a significant

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expense. Despite the numerous benefits of biolubricants, there are still significant obstacles that can be effectively addressed.

Categories of Biolubricants

Biolubricants, which come from a variety of biological sources, are more environmentally friendly than conventional lubricants. They fall into many categories according to where they come from and how they are made; they include waste materials, animal fats, and plant oils. There are various categories of biolubricants which include organic oils, biologically engineered lubricants, and synthetic esters.

Biologically engineered lubricants

Lubricants that have been genetically modified are derived from biologically engineered oil-rich plants. This approach is an excellent tool for enhancing crops to generate a broader array of useful goods that cater to both human health advantages and industrial applications. This technique facilitates the augmentation of oil concentration in oil-rich plants to satisfy the growing need for environmentally friendly lubricants.

Organic oils

This encompasses oils that are derived from animals and plants, particularly oil-rich crops. Plant or vegetable oils are the main source of biolubricant, as they are sustainable and renewable supplies of environmentally friendly oils. They mostly include triacylglyceride, also referred to as triglycerides. These are composed of glycerol molecules bonded to saturated or unsaturated fatty acids through ester bonds.[16] The fatty acids found in plant oil triglycerides have the same lengths, ranging from 14 to 22 carbons, and differ in their amounts of unsaturation. There are two types of plant oils, the edible (walnut oil, soybean oil etc.) and the non-edible (milk bush, Jatropha caucus, etc.). Even though they make excellent bio-lubricants, edible oils are widely utilised in food, particularly in developing nations. Conversely, non-food oils which are the non-edible ones are now underutilised in the chemical industries to make soaps, detergents, cosmetics, and other products. This suggests that non-edible plant oils have a lot of potential for usage as lubricants. They might thus make excellent choices for lubricants in the future.

The chemical component of Plant oil

The main component of plant oils are different fatty acids, which have a great impact on their special qualities and uses. Saturated, monounsaturated, and polyunsaturated fatty acids are the three main types of fatty acids present in plant oils, and each one contributes unique qualities. Saturated fatty acids, mostly includes coconut and palm oils, these fatty acids help to extend shelf life and increase stability [17] Monounsaturated fatty acids are rich in oleic acid, which has been linked to heart health advantages,[18] are oils like olive and canola. While polyunsaturated fatty acids are rich in linoleic and linolenic acids, which are necessary for many metabolic activities, such as soybean and walnut oils respectively.[18] The suitability of plant oils for use in ecologically friendly lubricants (as base stock or additives) is determined by their level of unsaturation, which can be measured by the iodine value. Higher iodine concentrations are indicative of increased unsaturation levels within each triglyceride. Higher levels of unsaturation in the oil result in increased manufacturing of lubricant from plant oil. These oils are classified as drying oils (when iodine value is > 130), semi-drying oils (when iodine value is between 100 and 130), or non-drying oils (when the iodine value is < 100).[19] The triglyceride's structure the beneficial characteristics found in lubricants and the inherent limitations of vegetable oil are both inherent in the composition of plant oil triglycerides. The presence of a lengthy polar fatty acid chain results in the formation of a robust lubricant coating, which effectively reduces friction and wear by interchanging with metal surfaces.[20] Figure 1 depicts the molecular structure of a triglyceride while table 1 displays the fatty acid contents of specific plant seed oils.

Benefits of Plant Oils

Numerous advantages are provided by plant oils in the fields of industry, health, and the environment. Their varied uses and formulations make a substantial contribution to technical progress, health enhancement, and sustainability. Plant oils serve as a sustainable substitute for non-biodegradable petroleum resources. The use of plant oil enhances fuel efficiency owing to their low volatility, resulting in reduced exhaust emissions. Fatty acids derived from these sources are essential components of the human diet and contribute to environmental conservation due to their natural origin and renewable nature. Plant oils are environmentally clean because they are non-toxic and can easily break down naturally. The high viscosity index of synthetic oil makes it useful in applications that use higher temperature, unlike mineral oils.[1,37] Plant oils have many benefits, but their production and usage need to be carefully controlled to prevent any negative effects, like competing land uses and differing health effects depending on the type of oil. The increase in plant oil production has led to an increase in demand, which has garnered significant attention and prompted more land to be used for plantations. This phenomenon is frequently linked to the clearing of forests and the decline of biodiversity and ecological functioning. Simultaneously, the increase in plant oil production has resulted in job creation, increased income, and a decrease in poverty among farmers.

Limitations of plant oils as a foundation stock for biolubricants

Although plant oils have numerous advantages compared to mineral oils, their limited oxidative stability and inadequate cold resistance characteristics can make them less effective in lubricating applications than traditional mineral oils.[38] As seen in, the requirement for chemicals to improve their qualities might complicate formulas and raise prices. Furthermore, its oxidation resistance is restricted due to the unsaturated fatty acids.[3,14] Plant oil-based lubricants have a restricted application due to their comparatively higher production cost for commercial use as compared to mineral lubricants.

Inadequate cold resistance

Plant oils have been limited as lubricant base stock because of their low temperature. At a temperature of -20ºC, the low temperature might result in cloud formation, reduced fluidity, precipitation, and solidification. The low-temperature property of plant oils is attributed to the saturated fatty acid composition in their chemical structure, as stated.[39,40] Erhan et al.[41] and Nor et al.[42] attributed the poor temperature property of plant oil to the presence of polyunsaturated fatty acid. However, most researchers concur that the low-temperature performance of oils is primarily influenced by the composition of saturated fatty acids. The reason for this is because the carbon atoms in unsaturated fatty acid chains have a slower tendency to form bundles compared to saturated fatty acids at low temperatures, resulting in a transformation into a crystalline structure. The pour point temperature is determined to assess the low-temperature characteristics of vegetable oils.[43] Researchers have employed diverse modification techniques on various fatty acids found in plant oils to achieve biolubricant characteristics that are well-suited for industrial use. Fadzel et al.[44] carried out a study on the esterification process of palm-stearin saturated fatty acids with pentaerythritol to generate a tetraester compound based on palm-stearin fatty acids. The tetraester achieved a yield of 69%. The palm stearin saturated fatty acid-based tetraester exhibited flash and pour points of 44ºC, oxidative stability of 243ºC, and a viscosity index of 140.

The manufacture of biolubricant base stocks involved the transesterification of methyl ester oils derived from chemically enhanced Karanja oil and conventional mahua oil triesters with polyols, specifically Trimethylolpropane (TMP). The characteristics of the final product were compared to those of 2T engine oil. The biolubricant derived from Mahua oil and Karanja oil exhibited a lower fire point and flash point, resembling the characteristics of lubricants derived from mineral oils with a greater viscosity index.[45] The lubricity qualities of pentaerythritol ester (PE) and trimethylolpropane (TMP) derived from palm oil's methyl ester were examined as a base for lubricants.[46] PE and TMP esters have a greater ability to sustain loads under high pressure compared to minerals. Talib et al.[47] conducted a comparison between crude Jatropha oil and synthetic ester, examining the varying components of refined and chemically enhanced Jatropha oil. The researchers found that the altered Jatropha oil exhibited superior performance compared to the unrefined Jatropha oil. This was attributed to the formation of a thin coating that can withstand higher temperatures and reduce tool wear during machining.

Table 1: Fatty acid compositions of some plant oils

Plant Oils	Saturated Fatty acids	Oleic acid	Linoleic acid	Linolenic acid	References
Coconut	81.2 - 94%	5 - 10%	1 – 2.5%	0.2 – 2.5%	[21]
Olive	12.5 – 20.9%	54.5 – 80.2%	4.9 – 21.2%	0.7 – 1.5%	[22]
Walnut	5.0 – 17.0%	10.0 – 20.0%	55.0 – 70.0%	10.0 -18.0%	[23]
Peony seed	6.2 -12.4%	20.5 – 45.1%	16.5 – 33.6%	28.1 – 46.9%	[24,25]
Corn	15.0 – 16.0%	27.6 – 34.6%	48.6 – 55.3%	0.6 – 14.9%	[26]
Soybean	6.0 – 24.0%	15.0 – 36.0%	42.8 – 56.1%	2.0 – 14.0%	[27]
Rape seed	6.46 – 9.43%	56.0 – 72.0%	13.80 – 24.6%	4.3 – 11.3%	[28]
Peanut	9.9 – 13.8%	37.0 – 55.6%	25.3 – 39.7%	0.40 – 3.2%	[29]
Cotton seed	27.5 – 33.7%	16.5 – 27.0%	43.2 – 54.0%	0.13 - 0.3%	[30,31]
Palm	49.7 – 57.5%	37.3 – 40.8%	9.1 – 11.0%	0.01 -0.25%	[32]
Sunflower seed	9.0 – 13.0%	16.4 – 27.6%	60.2 – 72.1%	0.07 – 1.80%	[33,34]
Sesame	12.4 – 14.4%	36.7 – 42.9%	43.2 – 48.6%	0.2 – 0.95%	[35,36]

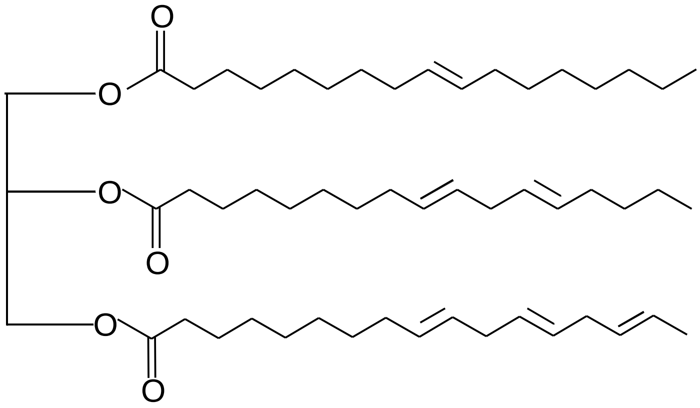


Figure 1: Structure of a plant oil triglyceride

Poor resistance to oxidation

Oxidation is the chemical process in which vegetable oils undergo a reaction that leads to increased viscosity, acidity, volatility, and corrosion. The limited usage of vegetable oils in lubricant synthesis is due to the low oxidative stability produced by the presence of carbon-carbon double bonds in fatty acids such as oleic, linoleic, and linolenic acids. Oils with a high level of saturation typically have limited capacity to flow at low temperatures, but they possess a high level of resistance to oxidation. Vegetable oils undergo oxidation based on the level of unsaturated fatty acids present. Plant oils with a greater level of unsaturation, such as sunflower (87.3%), soybean (84.4%), safflower (90.3%), and canola (88.5%), are more prone to oxidation.[48] Therefore, these oils require enhancement.

Synthetic esters

Synthetic esters are formulated through the chemical alteration of plant oils or animal fats. These esters are formulated through the reaction between an alcohol and a carboxylic acid. There is a wide range of synthetic esters that are currently available for commercial use, thanks to the diverse chemical properties of these building blocks. Due to their physicochemical qualities, synthetic esters are commonly chosen for usage in demanding settings that require high-performance lubricants. Jet engines employ the use of synthetic esters because of their exceptional ability to work at high temperatures and flow smoothly at low temperatures.[49] They provide the benefit of superior lubricity, enhanced viscosity indexes, elevated flash points, lowered pour points, decreased volatility, low temperature performance, exceptional oxidation resistance, and outstanding thermal stability. Previous research has mostly concentrated on improving the physicochemical characteristics of natural oil-based biolubricants and synthetic esters by employing different chemical modification techniques. The investigation has verified that synthetic esters, such as Dioctyl Sebacate generated from castor oil, are highly preferred for cold temperature operations due to their viscosity indexes exceeding 200 and low pour points.

Improving the performance of biolubricants

Chemical modification can help improve the performance of plant oil-based biolubricants, addressing the main problem they face. This augmentation enables the biolubricant to achieve a desired degree of performance. Despite the numerous setbacks associated with performance enhancements through various chemical modifications, specific chemical techniques have been devised to enhance the low oxidative and thermal stability of plant oils. These techniques include oxidation (epoxidation), esterification, transesterification, formation of estolides, selective hydrogenation, branched fatty acid, and Nanomaterials, among others (as illustrated in figure 2 and summarised in Table 2). While the procedures improve the physicochemical characteristics of lubricants derived from plant oils, they nevertheless have a range of downsides as outlined in Table 2.[50]

Modification of plant oils by epoxidation

Epoxidation is the chemical conversion of a carbon-carbon double bond into oxirane (epoxides) using various reagents such as H_2O_2, hypochlorous acid, and organic peracids. The susceptibility of unsaturated molecules to hydrolytic breakdown highlights the significant role of double bonds in the oxidation process.[51,52,53] Epoxidising the alkene groups improves the thermo-oxidative stability and other physicochemical aspects of the oil. [54] Epoxidation is a highly promising method for creating biolubricants that are suitable for use in high-temperature applications. Epoxidised soybean oil has been scientifically validated as a promising option for biolubricant applications at elevated temperatures.[55] The epoxidation process has been used to modify the C=C bonds in vegetable oils, resulting in the production of biolubricants. These biolubricants have shown improved properties such as improved oxidative stability and acidity, enhanced low-temperature properties, and greater metal adsorption. As a result, they exhibit increased lubricity, improved viscosity, a better viscosity index, and increased pour point, as shown in Table 3.[56] The epoxidation of C=C typically takes place via alkyl hydroperoxides utilising dioxirane peroxyacids or peracids.[57] Careful control of temperature, reaction ratios, and reaction time are necessary to achieve the best conditions for the epoxidation of vegetable oils, resulting in high-yield and selective epoxides. Empirical studies reveal that certain parameters have a substantial impact on the epoxidation process of the epoxidised molecule (figure 3).[4]

efficiency. Studies with cardoon seed oil and Terminalia catappa seed oil[58] have shown that an ideal reaction temperature of about 40–45 °C is advised. Varghese and Gopalakrishnan[59] have demonstrated that optimising the molar ratio of double bonds to hydrogen peroxide (DB:H_2O_2) to 1:1.5 can maximise epoxide yield while reducing adverse reactions. Furthermore, Gunawan et al. found that a molar ratio of 1:4:5 (formic acid to hydrogen peroxide) was useful in obtaining a relative conversion to oxirane of 78%.

Table 2: Benefits and the downsides of performance-enhanced plant oil-based biolubricant

Chemical modification	**Description**	**Merits**	**Drawbacks**
Esterification/ transesterification	Here, transformation of an ester into a higher stability ester takes place	low- temperature property, oxidative and thermal stability are improved.	feedstock with higher oxidative stability and high reaction temperature is required
Epoxidation	An oxygen atom is added through a C=C double bond	Thermo-oxidative stability and lubricity are enhanced at low reaction temperature	Pour point value increases while the viscosity index decreases
Selective hydrogenation	H_2 molecule is introduced leading to thermochemical cleavage of the ester	unsaturation degree is reduced while oxidation stability is enhanced	isomerization reaction takes place with high reaction temperature
Formation of estolide	Two different or identical molecules of acid are involved.	use of various molecules of plant oil is approved the thermal oxidative stability is improved with low reaction temperature	high production cost

Table 3: Physical and chemical properties of some chemically enhanced plant oils by epoxidation[50]

Plant oil	**Pour point**	**Viscosity at 100°C (cst)**	**Viscosity at 40°C (cst)**	**Viscosity index**
Soybean oil	-9	7.55	28.86	244
soybean epoxides /alcohol	-17	16.30 – 20.90	194.6 – 23.4	86 – 113
Olive oil	-3	8.24	39.52	190
Olive epoxides/ Formic acid	-27 to -12	-	-	95 – 213
Jatropha epoxides/ Formic acid	0	10.20	145.15	138
Jatropha oil	-6	7.80	35.4	206
Sunflower oil	-12	8.64	40.05	206
Sunflower epoxides/ acid	-9	8.77	43.69	180
Castor oil	-26	19.72	220.8	221
Castor epoxides/ acid	< -38	16.5	94.15	187

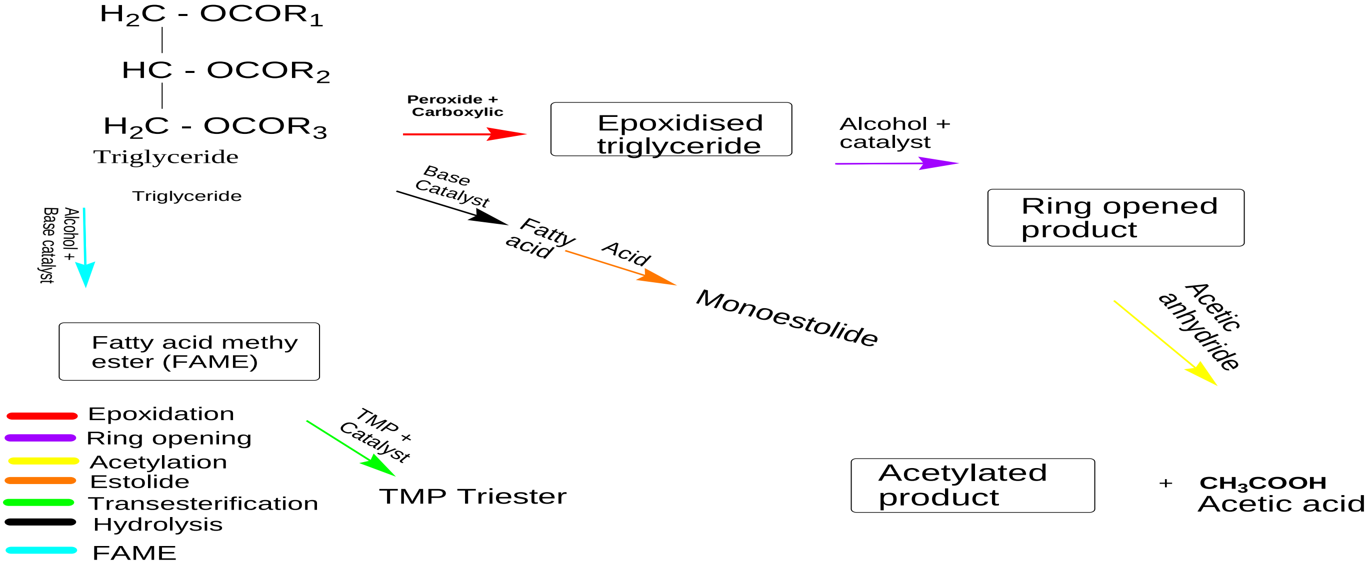


Figure 2: Performance enhancement of plant oil

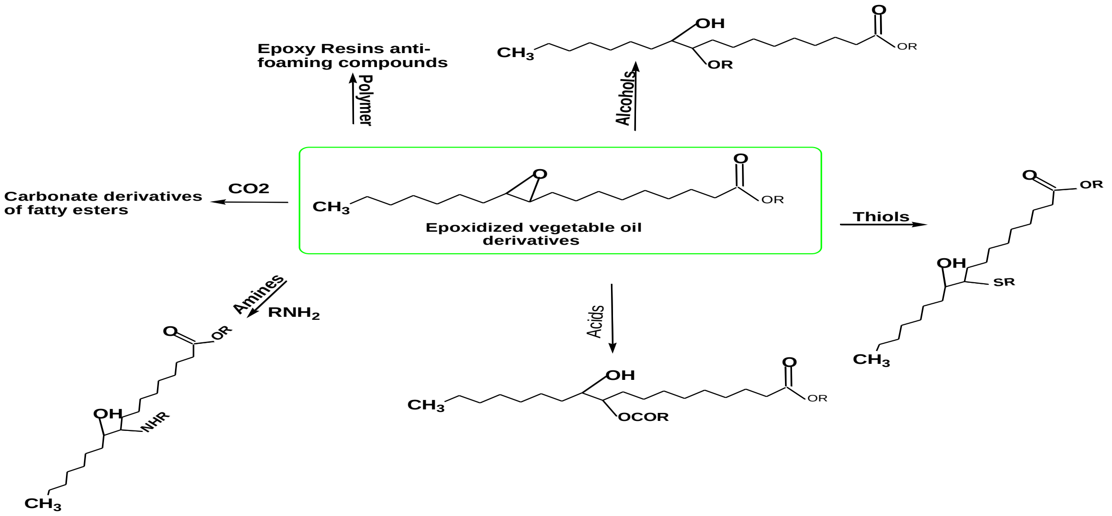


Figure 3: Biolubricant produced with different physicochemical properties using epoxidised plant oil as starting materials

The epoxidised product requires additional adjustments due to its persistently inadequate thermal characteristics. Consequently, acylation, esterification processes, amino alkylation acyloxylation, and hydroformylation are performed to improve the inadequate physicochemical featur

Table 4 displays the epoxidation of several vegetable oils conducted by multiple researchers, along with the corresponding reaction conditions and resulting yields. The usual approach to epoxidation was found to be in-situ epoxidation, with or without the use of a catalyst. This approach is more practical and cost-effective for carrying out epoxidation on a wide scale.[60] Despite the effectiveness of the approach, issues often arise during the epoxidation process because of factors including catalyst, temperature, and duration. Elevated temperatures promote increased conversion to the epoxide, but epoxidation at temperatures exceeding 60ºC might result in the opening of the epoxide ring and the formation of polyols. In addition, an increased concentration of hydrogen peroxide (2.5 mol) results in a greater conversion to oxirane, but it is accompanied by diminished oxidative stability. For hydrogen peroxide with a reduced concentration, the conversion rate will be modest, but the oxirane ring will remain stable. When comparing the effectiveness of catalysts, a liquid inorganic acid catalyst, specifically H_2SO_4, is more efficient than other catalysts like HCl, HNO_3, and H_3PO_4. Research has revealed that increasing the concentration of acid and raising the temperature often decrease the time required for the reaction to achieve optimal oxirane conversion.[61] While too much hydrogen peroxide might cause undesirable ring-opening reactions, higher concentrations of formic acid enhance epoxide yields. [59,62]

Egbuna et al.[63] developed a novel chemically enhanced palm kernel oil using the epoxidation-esterification method. A molar ratio of 1:1.5 of ethylenic to H_2O_2, a catalyst of 2.5wt% H_2SO_4, and a stirring speed of 1200rpm were employed at different temperatures (35, 45, 55, 65, and 75ºC) and durations. It was noted that the rate of conversion to oxirane increased proportionally with the duration of the reaction. However, the rate of oxirane conversion decreased as the reaction time increased further. The inconsistency in the time increase was caused by the opening of the oxirane ring, which sped up the process of epoxidation. The highest values for changing the palm kernel methyl ester to oxirane were achieved within 6, 5, and 4 hours at temperatures of 55, 65, and 75 degrees Celsius, respectively. This observation is consistent with the findings of other researchers[81,83] about the epoxidation of linoleic acid in J. curcas, Palm kernel oil, and Terminalia catappa L. methyl ester, respectively. The epoxidation process involves turning the double bond in the methyl ester into epoxy groups, which enhances the oxidative stability.

Modification by Transesterification

Plant oils can be modified due to their distinct functional groups. They can undergo changes in the ester groups of a triacylglyceride. An alternative method for enhancing the characteristics of biolubricants derived from plant oil is to fully alter the configuration of the triglyceride to create polyols ester. The hydrogen that is connected to the β-carbon of the triglyceride configuration is eliminated by transesterification process[84] resulting in the ester acquiring an increased level of thermal stability. This procedure can be catalysed either chemically or enzymatically. Esterification involves the reaction of alcohols such as methanol or ethanol with the free fatty acids present in plant oils to form methyl esters and water (Figure 4a). Simultaneously, transesterification involves reacting the fatty acid present in the triglyceride with three molecules of methanol to produce fatty acid methyl esters (FAME) and a byproduct (glycerol).[85] In addition, esters are prone to thermal degradation or hydrolysis. To enhance their thermal properties, alcohol substitution is carried out using branched or longer alkyl chains such as neopentylglycol, pentaerythriotol, 2-ethylhexanol, Trimethylolpropane, trimethylolethane, and trimethylolhexane to produce trimethylol esters of some specified plant oils (as shown in Figure 4b).[41,86,87,88] The type of plant oil utilised affects the fatty acid profile of biolubricant. Sunflower oil, for example, produces biolubricant that satisfies international standards and exhibits desirable characteristics including density and viscosity.[89] Also, the fatty acid profile is influenced by the catalyst of choice and the conditions of the reaction. For instance, distinct biolubricant yields and quality might result from altering methanol concentrations during transesterification.[90]

Transesterification with TMP enhances the thermo-oxidative stability of biolubricant derived from vegetable oil by improving its physicochemical qualities. The company manufactures lubricants for marine engines, gear oils, grease formulas, and hydraulic fluids for compressor oil.[88] Esterification and transesterification processes are typically facilitated by mineral acids such as H_2SO_4, HCl, or P-toluene sulfonic acid. These also have certain disadvantages related to the segregation of products and the caustic nature of the acid. Solid acid catalysts, which can be sulfated to increase their action, are used to replace mineral acid catalysts in the execution of transesterification reactions so as to overcome these limitations. While CaO is an alkaline catalyst used to achieve full conversion in transesterification reactions, both the regeneration phase and catalyst activation require elevated temperatures. Solid acid catalysts include cationic exchange resin, Zeolites, and oxides like Nb_2O_5, ZrO_2, Al_2O_3, Ta_2O_5, and WO_3.[91] Acid catalysts have lower reaction rates compared to their base counterparts. [92]

The selection of acids and alcohols employed in transesterification processes directly influences the properties of the resulting ester from a physicochemical standpoint. Table 4 demonstrates that synthetic esters possess superior physicochemical characteristics in comparison to their corresponding triglycerides. Yunus et al.[93] carried out transesterification using trimethylolpropane at temperatures ranging from 80 to 340 degrees Celsius, with a heating rate of 6 degrees Celsius per minute, to produce palm kernel and palm oil polyol esters. Furthermore, he developed the best possible synthesis procedure for trimethylolpropane transesterification and palm oil methyl esters, which led to the development of a biolubricant based on palm oil trimethylolpropane esters.[94] Zulkifili et al. [95] conducted research on the tribological characteristics of paraffin oil and trimethylolpropane ester of palm oil when combined with additives (TiO_2 nanoparticles). The friction and wear experiment were conducted with the aid of four ball tribometers. The experiment was carried out with loads of 40.00, 80.00, 120.00, and 160.00kg at a speed of 1200rpm and a temperature of 25ºC. The experiment ran for a duration of 10 minutes. According to the findings, the addition of TiO_2 nanoparticles to the trimethylolpropane ester resulted in a more significant decrease in friction.

Jung et al.[96] conducted non-catalytic transesterification of six different plant oils namely: coconut, olive, avocardo, soybean and canola oils, which resulted in the conversion of the oils into biodiesel yield of over 90% at 380ºC in 1 min. Jieyu et al.[83] documented the oxidative stability index of fatty acid methyl esters derived from five distinct oils using a two-stage transesterification process with a base catalyst. Ho et al.[97] found that the transesterification (two-stage) methods used to produce biolubricant from palm kernel oil result in the elimination of the β-hydrogen atom in the structure of the oil, resulting in the creation of an ester that exhibits excellent thermal and oxidative stability. This approach involves the substitution of volatile hydrogen with a more stable trimethylolpropane. During the initial phase, the glycerol backbone is eliminated. On the other hand, a successful TMP is used instead of glycerol in the second phase, resulting in the production of Trimethylolpropane triester with exceptional characteristics and performance. Trimethylolpropane-enhanced plant oils have outstanding qualities compared to their original plant oil sources, as demonstrated in Table 5.[98]

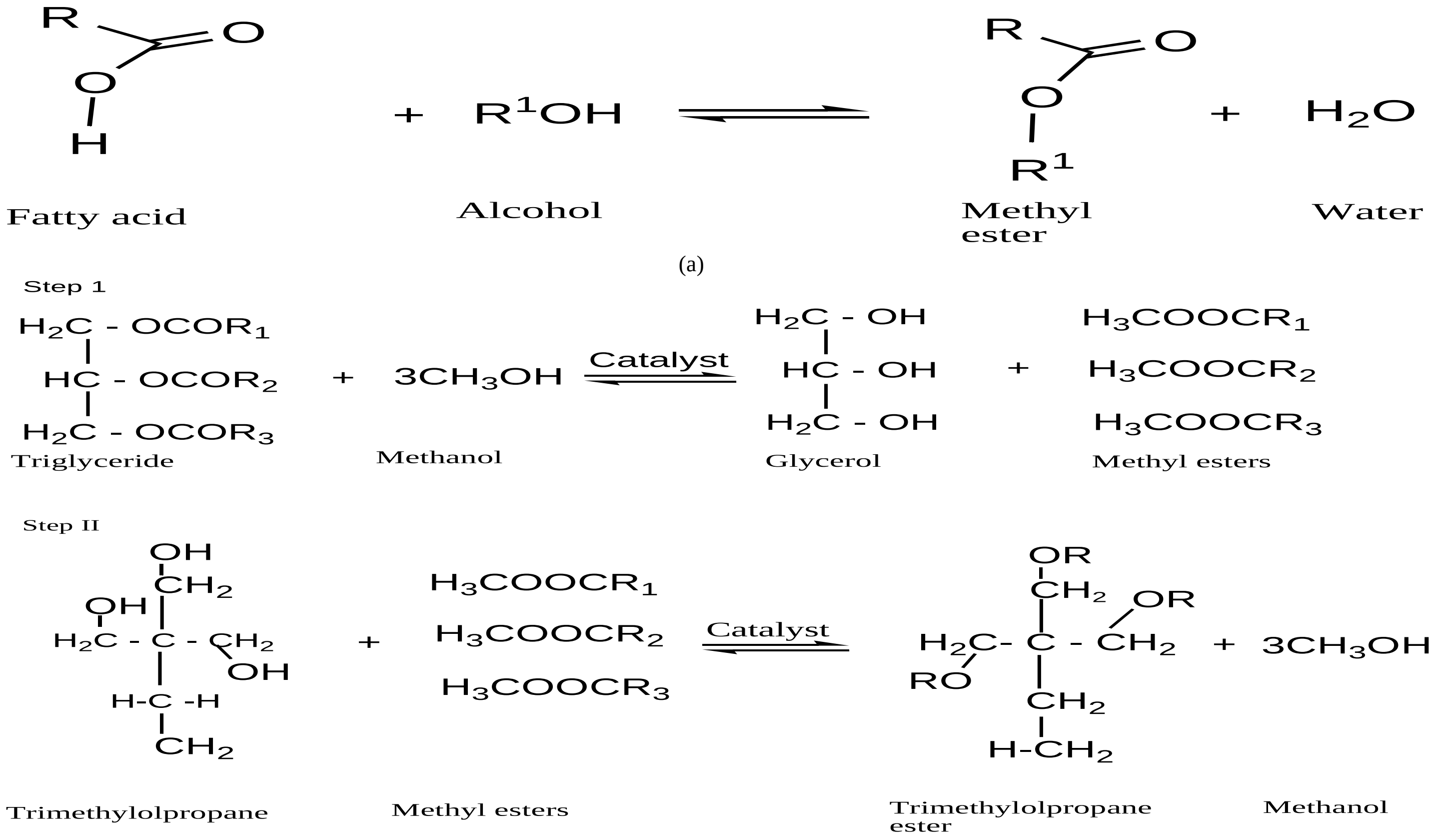
Table 4: Epoxidation of plant oil, reaction conditions and yield by different researchers

Plant oil	**Time**	**Temp. (ºC)**	**Conversion (%)**	**Acid**	**Amount of %H_2O_2**	**Amount of acid**	**Catalyst/ Solvent**	**Ref.**
Palm-kernel oil	4h	75	87%	CH_3COOH	15g	7g	Toluene	[63]
Tung oil	4h	50	47%	Glacier CH_3COOH	30%	-	Sulphuric acid	[64]
Sunflower oil	5h	50 – 60	82%	CH_3COOH and HCOOH (0.5:1)	-	-	Sulphuric acid	[65]
Jatropha methyl ester	6h	70	88.9%	CH_3COOH	-	-	Acidic ion exchange resin (16%)	[66]
Linseed oil	1h 15min	50	94%	CH_3COOH	50%	-	Acidic ion exchange resin (2.1g)	[67]
Tilapia oil methyl ester	16h	Room temperature	95.0%	HCOOH	30 (100mL)	14mL	Toluene	[68]
Soybean oil	4h	60ºC	-	CH_3COOH (98%)	34% (84.15g)	15.85g	sulphuric acid (3 w %)	[69]
Sunflower oil	9h	50ºC	-	Glacial CH_3COOH	30% (10mL)	10mL	Sulphuric acid / CH_2Cl_2 (5mL)	[70]
Grape seed oil	1h	90ºC	90%	CH_3COOH	50%	-	Sulphuric acid	[71]
Jatropha curcas	5h	50ºC	-	HCOOH (85%)	30% (40g)	2.5g	-	[72]
Jatropha oil	5h	65ºC	-	HCOOH acid	50%	-	-	[73]
Linseed oil	24h	55ºC	58%	-	35% (25g)	-	Candida Antarctica lipase B / Toluene (150g)	[74
Oleic acid	12h	40ºC	-	HCOOH (88%)	30% (8.0mL)	14mL	-	75
Palm Olein	2h	65ºC	97.1%	HCOOH (99%)	30% (4.0mL)	9.0mL	-	76
Cotton seed	4h	60ºC	77%	CH_3COOH	50% (2.0mol)	0.5mol	H_2SO_4 (2%)	77

Cotton seed	2h	60ºC	66%	HCOOH	50% (2.0mol)	-	H_2SO_4 (2%)	61
Canola oil	5h	65ºC	90%	CH_3COOH	30% (1.5mol)	0.5mol	Acidic ion exchange resin (22%)	
Canola oil	8h	Room temp.	89.2%	HCOOH (85%)	30%	-	Toluene (50mL)	79
Soybean oil	1h30min	45ºC	-	Glacial CH_3COOH	30% (0.5mol) (45mL)	5mol (286mL)	H_2SO_4 (1.7mL)	80

Table 5: Physico-chemical compositions of plant oils and their corresponding lubricants via transesterification

Lubricant	Viscosity at 40ºC (cst)	Viscosity index	Viscosity at 100ºC (cst)	Flash point (ºC)	Pour point (ºC)
Soybean oil	28.86	245	7.55	327	-9
Soybean oil/ alcohol	10.3 – 432.7	45 – 196	3.0 – 34.4	-	-
Rapeseed oil	45.60	180	10.07	254	-12
Rapeseed oil/ alcohol	7.8 – 38.2	204 – 224	2.7 – 8.4	-	-31.3 to -18
Sunflower oil	40.05	206	8.65	254	-12
Sunflower oil/ octanol	7.83	226	2.74	-	-3
Castor oil	220.6	220	19.62	250	-27
Castor oil/ trimethylolpropane	20.94	127	4.47	-	-
Palm oil	52.4	186	10.20	-	-5
Palm oil/ trimethylolpropane	47.9	176	9.00	355	-2
Jatropha oil	35.4	205	7.90	186	-6
Jatropha oil/ trimethylolpropane	43.9	180	8.71	325	-6
Olive oil	38.62	190	8.24	318	-3
Olive oil/ trimethylolpropane	63.07	190	12.00	-	-24



(a)

(b)

Figure 4: (a) Esterification reaction (b) Transesterification reaction

Hydrogenation

Hydrogenation is the process of adding hydrogen molecules (H_2) to unsaturated compounds. One important step in improving stability and changing the makeup of fatty acids in plant oils is hydrogenation. The iodine number, which indicates the degree of hydrogenation attained, is highly impacted by variations in catalyst activation and hydrogen gas introduction techniques.[99] The thermo-oxidative stability of biolubricants is influenced by their level of unsaturation. To enhance this stability, the unsaturated -C=C- bond can be saturated through a hydrogenation reaction. Palladium, nickel, platinum, and ruthenium-based catalysts are commonly used to carry out this reaction, resulting in improved stability of the biolubricant[100,101] Ni/SiO2 catalysts modified with cerium oxide (CeO2) have demonstrated enhanced activity and selectivity in hydrogenation, specifically amplifying the generation of C18:1 and C18:0 fatty acids. With over 90% conversion under mild circumstances, palladium (Pd) catalysts supported on graphene have shown good selectivity for stearic acid (C18:0) without producing trans fatty acids.[102] The process of hydrogenating double bonds (C=C) was not recommended for improving the properties of the biolubricant due to its high temperature (250 - 300°C) and pressure (25 – 35Mpa) requirements. This process often leads to isomerisation and a decrease in the fluidity of the lubricant, resulting in the formation of solid lubricants or waxes.[103] Figure 5 depicts the process of hydrogenation, while table 6 represents hydogenation of plant oils by various researchers.

Formation of Estolides

The estolides are branching esters that result from the connection between the unsaturated point of one fatty acid and the carboxylic acid of another fatty acid by a carbocation. They are created by utilising H_2SO_4 and $HClO_4$ to create oligomeric esters. Mineral acids or enzymes are frequently used as catalysts in the esterification of hydroxy fatty acids with free fatty acids to produce estolides.[113] Another method is the Ultrasound-Assisted Technique which greatly shortens reaction times from hours to less than three hours, which improves the environment for oleic acid-based estolide synthesis.[114,115] Estolides, which are branched esters, exhibit greater resistance to hydrolytic breakdown compared to triglycerides. The biolubricant qualities are influenced by the hydrogen chain length and the number of estolide. This information is based on the estolides that were generated from lauric acid and 2-ethylhexanol oleic acid, as reported in references.[116,117] In general, the estolides esters produced are more suitable as biodegradable lubricants when compared to the current commercial estolides. These commercial estolides are typically employed by blending them with vegetable oils that have varying properties.[118] In addition, the estolide generated exhibits superior viscosity index, thermo-oxidative stability, reduced pour point, and enhanced lubricity. Melo et al.[113] report that castor oil can experience simultaneous trans- and interesterification, resulting in estolides with improved viscosity and stability. Estolides are a good choice for bio-lubricants because of their enhanced hydrolytic and oxidative stability. For example, compared to standard oils, estolides made from used cooking oil demonstrated superior viscosity and pour point.[119] Table 7 displays the estolides derived from plant oils together with their corresponding physical and chemical features.[118,120]

Table 6: Hydrogenation of plant oils by various researchers

Oil	Catalyst loading	Temp.	Pressure	Particle size	Reaction time	Ref.
Soybean	Ruthenium nanoparticle	79.85^0C	1.5Mpa	1.13-17.22nm	12h	[104]
Canola and sunflower	Pd/ SiO_2 (1wt%)	110^0C	5atm	6.8nm pores	1h	[105]
Sunflower (ethyl esters)	Pd/SiO_2 (0.3-1.5wt%)	40^0C	10bar	0.10-0.004mm	-	[106]
Soybean	Pvp-stabilised pt and pd colloids	35^0C	Atmospheric pressure	1.5-3.1nm	90min	[107]
Rapeseed oil	Cu/SiO_2 (8-9wt%)		20 or 6bar of H_2	-	-	[108]
Edible plant oil	Nickel catalyst	150- 160^0C		-		[109]
Sunflower seed	Three-phase catalytic membrane	74^0C	5bar H_2 pressure	5nm pores	-	[110]
Palm olein	PVP-stabilised pt colloids	35^0C	Atmospheric pressure	1.4- 2.9nm	1h30min	[111]
Soybean oil and Sunflower seed oil	Nickel (0.33wt%)	195-200^0C	1.5MPa	-	3h	[112]

Table 7: Estolides from plant oils and their physical and chemical properties

Lubricants	Pour point (cst)	Viscosity at 40ºC (cst)	Viscosity at 100ºC (cst)	Viscosity index
Castor oil	-27	220.6	19.72	220
Ester (Castor oil/ 2- ethyl/hexanol/ lauric acid	-	51.4	9.99	183
Sunflower oil	-12	40.05	8.65	206
Esters (sunflower oil)	-	102.4 – 424.3	17.7 – 42.5	152 – 184
Olive oil	-3	39.62	8.24	190
Ester (Olive oil / 2- ethylhexanol)	-32 to-24	271.8 – 518.6	33.5 – 60.2	167 -198

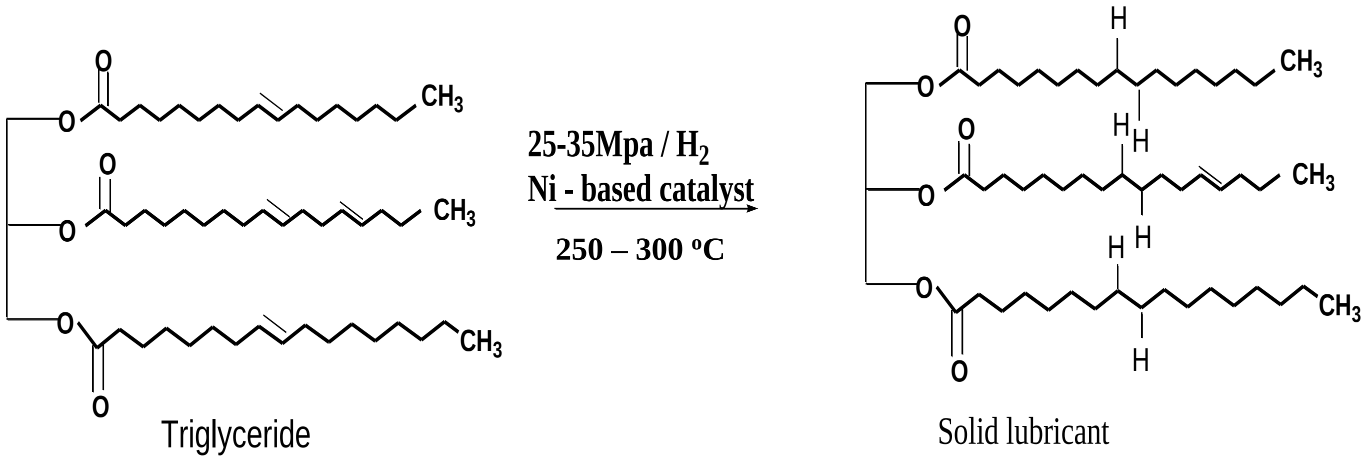


Figure 5: Hydrogenation reaction of a triglyceride

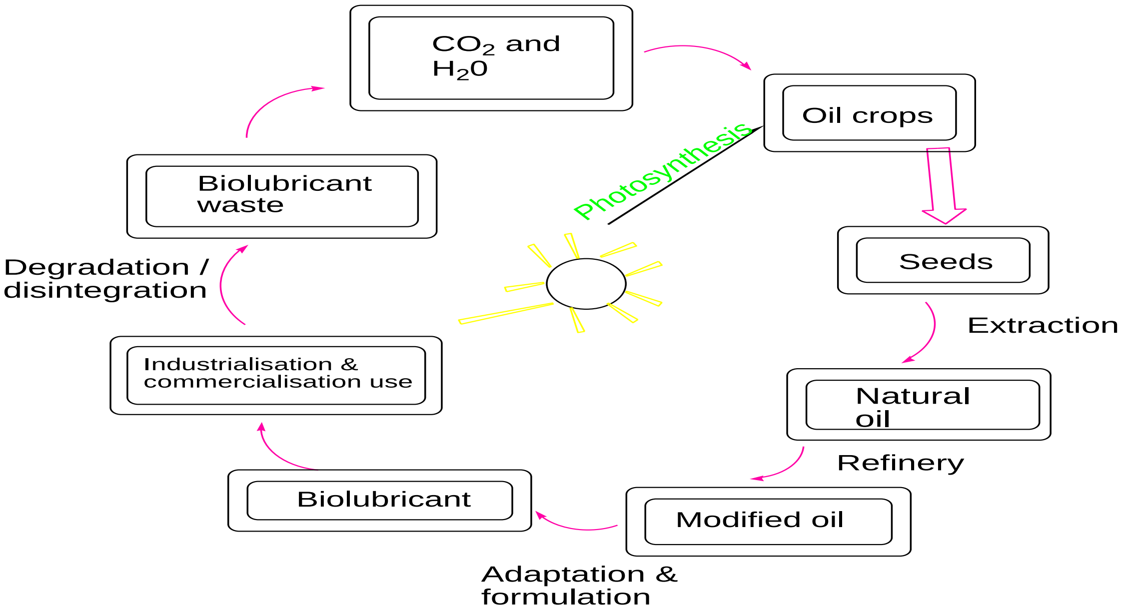


Figure 6: Biolubricant's Life cycle

Additives

They are supplementary compounds incorporated into other products to enhance their performance in specific activities. Hence, surpass the limitations of lubricants and boost their effectiveness, it is crucial to employ additives. Attempts have been made to create eco-friendly additives. [121,122,123] Additives are recognised for their ability to increase the qualities of base oils. Microbial oils have demonstrated a better ability to reduce friction, especially those that are high in carboxylic acids.

Environmentally acceptable lubricants (EALs) can benefit from the superior wear protection that yeast-derived additives offer.[124] The application of marine microalgae rich in lipids, including Coelastrella sp., has shown notable improvements in wear rates and friction. According to Khan et al., [125] adding 1% of EVA to a biolubricant based on Coelastrella decreased wear by 95% and friction by 60%. In bio-lubricants, multi-wall carbon nanotubes (MWCNTs) and organic polymers have been shown to reduce wear by 37.9% and friction by up to 67.8%.[126] When employed as an extreme pressure and antiwear additive, cardanol—a substance produced from the processing of cashew nuts—has demonstrated a 65% reduction in wear scar diameter.[127] Additionally successful in improving lubrication in lithium greases, especially at high temperatures, are bio-based ionic liquids derived from ricinoleic acid and choline. Table 8 shows some additives and their uses.

Table 8: Some additives and their uses [128,129]

Types of Additives	Uses	Common additives
Corrosion inhibitor	This helps in decreasing the corrosion rate of metals by protecting it surface from moisture, and the attack of other aggressive substances.	Sulphurised terpenes
Anti-wear and extreme pressure	They are useful for boundary lubrications	Ethyl stearate, cetyl chloride
Antioxidant	This helps to improve oxidation resistance.	Diphenylamine

Rust inhibitor	It helps to prevents the corrosion of ferrous materials	Amine phosphates
Friction modifier	By lowering wear and friction, friction modifiers (FMs) greatly improve the tribological characteristics of materials in a variety of industrial applications.	Ethers
Pour point	It controls crystal formation which helps fluidity	Polyalkyl methyl acrylates
Viscosity index enhancer	Thickening efficiency is enhanced as temperature increases	Polyisobutylene
Emulsifier	It prevents the formation of water-in-oil emulsion	Naphthenic acids

Characteristics of biolubricants from a physicochemical standpoint

Plant oil-based lubricants must exhibit specific characteristics to be suitable for industrial use, such as pour point, viscosity and viscosity index, flash point, oxidative stability, and fire point.

Viscosity and viscosity index

They are two important properties related to the flow of fluids. An optimal biolubricant must possess a suitable viscosity index that accurately shows the variation in kinematic viscosity in response to temperature fluctuations. The viscosity index measures the lubricant's quality. It is also used to characterise lubricating fluids in the automobile industry. The rheometer is used to measure the kinematic viscosity of biolubricant, and the viscosity index are then computed using the American Society for Testing and Materials (ASTM) method.[130] Viscosity is the measure of how effectively the biolubricant lowers friction and wear. As the temperature increases, its viscosity drops. The kinematic viscosity range of 3.8 to 20cst at 100ºC is suitable for engine oils, since it closely aligns with the kinematic viscosity of biolubricants. On the other hand, a kinematic viscosity of 35.2cst is appropriate for gear oil.[131]

For efficient lubrication and equipment longevity, the relationship between viscosity index (VI) and lubricant performance in high-temperature applications is crucial. A lower viscosity index suggests significant variations in kinematic viscosity due to temperature fluctuations. Conversely, a higher VI means that a lubricant is more likely to retain its viscosity over temperature variations, which is crucial in high-temperature environments.[132] The performance of lubricants, like castor oil, is impacted by temperature-related changes in their viscosity. For example, due to its low viscosity index, castor oil performs badly at higher temperatures despite having a low coefficient of friction (CoF) at 40°C.[133]

According to research on synthetic esters, lubricants with a high viscosity index, such as those made from trimesic acid, exhibit superior resistance to high temperatures and lower carbon deposition, hence improving performance under harsh circumstances.[134] The importance of base oil composition in high-temperature applications is highlighted by the reduced deposit formation and increased operational efficiency of lubricants formulated with pyromellitate and polyol esters. [135] Conversely, although lubricants with a high viscosity index tend to exhibit superior performance in thermal stress situations, certain formulations may still encounter difficulties, such as oxidative stability and shear thinning. Consequently, continuous investigation into novel additives and base oils is required to maximise efficacy in high-temperature conditions.

Pour point

The pour point, which represents the lowest temperature at which a lubricant can flow, is an important metric for determining the viscosity of lubricants. Comprehending this correlation is crucial for enhancing lubricant efficiency across diverse uses. Lubricant viscosity is directly influenced by the pour point, especially at low temperatures. A lubricant's pour point affects how well it performs in extremely hot conditions, including how well it flows and lubricates. Better performance in colder weather is indicated by a lower pour point, whereas hot temperatures necessitate the use of lubricants that retain stability and viscosity. According to Sousa et al.,[36] mineral oils, for example, show shear-thinning behaviour below their crystallisation temperature, which is also the pour point. Particularly esters, synthetic lubricants have a consistent rise in viscosity with decreasing temperatures, peaking near the pour point.[136]

The pour point values are typically obtained using the ASTM method.[137] This method determines the rheological properties of fluids at low temperatures. Pour points and their effect on viscosity may now be predicted using sophisticated techniques like Quantitative Structure-Property Relationship (QSPR) models and molecular dynamics simulations. These models demonstrate the relationship between lubricant characteristics and molecular structure.[138] To calculate pour points and viscosity indices, a variety of methods have been used, including IR spectroscopy, to enable real-time quality control of lubricants.[139] Although the pour point is a crucial measure of lubricant performance, viscosity is also greatly influenced by other elements, including molecular structure and ambient circumstances.

To maintain fluidity and avoid solidification, which can result in equipment failure, lubricants with a pour point below -50°C are crucial for use in extremely cold environments.[50,140] Pour point depressants, including terpolymers, have been developed to improve lubricants' low-temperature performance and enable them to function well over a larger temperature range. Biolubricants have reduced pour points compared to mineral oil, which means they provide excellent lubrication when starting in cold temperatures.

Ignition point

The precise temperature at which a substance ignites and starts to burn is known as the ignition point (flash point). Typically, it is determined using a Tag closed tester, following the ASTM standard.[141] Ignition point is a useful measure for assessing the combustibility and evaporation tendency of various substances. To ensure safety during operations and minimise evaporation at the highest working temperature, lubricants need to have a high ignition point. It is a useful parameter for characterising biolubricants that are often not employed as fuel.[142] Producers of biolubricants use the ignition point to determine whether the product is adulterated. If a lubricant has a low ignition point, it will be suspected of being contaminated by volatile substances.[143] The utility of a biolubricant is restricted by its low ignition points at elevated temperatures. The source and synthesis techniques of biolubricants have a considerable impact on their ignition point. In general, biolubricants have greater ignition points than traditional lubricants, which increases application safety. The Trimethylolpropane ester derived from cottonseed oil exhibits a good thermal stability for engine applications, with an ignition point of 202°C, as reported by Khan et al.[144] Propylene Glycol Ester from SBEO: Sukirno et al.[145] demonstrated the feasibility of this biolubricant for high-temperature conditions by achieving an ignition point of 252°C. Used Biolubricant for Cooking Oil: This biolubricant, which was created using zeolite catalyst derived from nature, has an exceptionally high flash point of 278°C, indicating superior thermal qualities. [146] These results imply that biolubricants are feasible substitutes since they can be modified to satisfy thermal stability standards.

Oxidative stability

This refers to the ability of a substance to resist oxidation, which is the chemical reaction that occurs when a substance reacts with oxygen. The chemical process that occurs when biolubricant and oxygen mix is called oxidation. Oxidation stability, on the other hand, measures the biolubricant's capacity to resist or endure oxidation. The oxidative stability of plant oil-based biolubricant is low, which means that if it is not handled during usage, it will undergo rapid oxidation and eventually become thicker. Pressure differential scanning calorimetry is employed to ascertain the oxidative stability of a biolubricant, as described.[147] The term "oxidative stability temperature" (OST) refers to the temperature at which the rate of oxidation starts to increase. A biolubricant with a high oxidative stability temperature is one that is highly resistant to oxidation. The oil stability index (OSI) was used in tests to assess the oxidative stability of specific plant oils. The fatty acid content and the oxidative stability of the oils were found to be strongly correlated, according to the findings. High oleic acid oils ranged in oxidative stability from 12.9 to 18.5, whereas conventional oils ranged from 5.2 to 18.5.[148]

A further investigation was conducted on a group of sunflower mutants at elevated temperatures, focussing on the alteration of the fatty acid component of their oils.[149] The oxidative stabilities of biolubricants derived from oleic acid and its derivatives vary. As an example, under oxidative circumstances, trimethylolpropane iso-stearic acid triester (TMP-ISA) showed improved oxidative stability with an activation energy of 109.8 kJ/mol.[150] According to Xie et al.,[151] the epoxidation of biomass oils, including those generated from Codonopsis pilosula, greatly increased thermal stability by raising the temperature at which thermal deterioration occurs from 234°C to 311°C. Methyl Laurate enhanced oxidative stability when added to trimethylolpropane trioleate biolubricants; optimal doses resulted in improved wettability and viscosity.[152] It has been demonstrated that adding nano-additives to biolubricants, such as graphene and maghemite, improves oxidation stability and can postpone thermal degradation by up to 37.5°C.[153]

Acid number

The acid number is the amount of acid or base present in a chemical substance.[154] The acid number is a useful parameter for quantifying the extent of lubricant deterioration. A high acid number indicates a diminished capacity of the lubricant to counteract acid and safeguard engine components against corrosion, in contrast to newly manufactured lubricants. The acid number is calculated by potentiometer titration, following the Standard Test Method outlined in ASTM D664. According to Gerbig et al.,[155] The acid values of 4.1 mg KOH/g of wheat germ, 6.1 mg KOH/g of pumpkinseed oil, hazelnut oil (2.0 mg KOH/g of oil), and sesame oil (2.0 mg KOH/g of oil) were noted. When compared to other plant oils that were looked at, the oils were said to have higher acid values. Corrosion between the lubricant and the technical component's system could result from a high acid value. As a result, it's critical to reduce the acid value.

Oleic acid-based biolubricants showed different total acid numbers (TAN). Wahyuningsih et al.[156] reported that a cyclic derivative had a TAN of 1.37 mg KOH/g, signifying low acidity and high stability. Although precise acid number values were not provided, the synthesis of biolubricants from pentaerythritol and 10-undecylenic acid similarly showed positive physico-chemical characteristics[157] The acid number is highly influenced by the feedstock selection. Transesterification of vegetable oils produces biolubricants with favourable characteristics, such as decreased acid values.[13] A product appropriate for agricultural machinery was produced by using chicken skin fat for the creation of biolubricant; however, exact acid number statistics were not given.[158]

Biodegradability

is the ability of a substance to be broken down and degraded by natural means, such as bacteria or other living organisms. Despite the numerous technological advancements, lubricating systems continue to experience leaks due to incorrect installation, inappropriate application, and regular equipment deterioration. This has heightened awareness of the necessity to minimise leaks in the lubricating system due to its potential environmental hazards.[159] There is currently a significant level of awareness regarding the pollution of air by lubricant haze, as well as the impact of lubricants on wetlands, soil, and water, which in turn affects the ecosystem. Biodegradable biolubricants are suitable for several industries such as forestry, mining, construction, and agriculture.

Biodegradability and stability of biolubricants are strongly influenced by their molecular structure, namely by the presence of double bonds and branching. Compared to first-generation varieties, second-generation biolubricants function better in high temperatures due to their superior branching.[160] Microbial activity, temperature, humidity, and other environmental variables are important in the deterioration process. The biodegradation of biolubricants is accelerated by increased microbial activity, which is fueled by increased moisture and warmth.[161] Biodegradability is also impacted by the production process. Compared to conventional chemical procedures, which frequently call for high temperatures and further purification, biolubricants synthesised through enzymatic processes are more sustainable and environmentally friendly.[160,162]

Decomposition of Biolubricant

This refers to the process of breaking down a biolubricant using the enzymes found in microorganisms like algae and microfungi. The biochemical process involves a series of bio-oxidation reactions that convert long-chain alcohols and carboxylic acids, as well as shorter-chain acids, into carbon dioxide (CO_2). The biodegradability of a lubricant involves multiple sequential stages. The biolubricant undergoes a transformation into a distinct substance, which may or may not be completely biodegradable in the initial stage. Conversely, during the second phase, the breakdown of the organic compounds into carbon dioxide and water within a period of 28 days is assessed based on the organic molecules themselves.[163] The use of infrared spectroscopy to investigate the C-H bond has been found to be effective in quantifying the initial breakdown of a biolubricant.[164]

Biodegradation processes ultimately produce carbon dioxide, methanol, and water as their final breakdown products (Figure 6), although the specific composition can vary significantly. There are two forms of degradation: aerobic degradation, which takes place in the presence of oxygen, and anaerobic degradation (absence of oxygen). Vegetable oil and synthetic ester degrade faster than mineral oils when subjected to identical conditions. When evaluating the environmental sustainability of a specific lubricant, it is important to examine its biodegradability.[85] The lag phase, also known as the adaptation phase, the degradation phase, also known as the exponential phase, and the stationary phase, where the new biomass dies in the absence of more food, are the three stages that characterise the deterioration and time curve of any biolubricant.[116] A substance is considered biodegradable if it demonstrates complete harmlessness in a 28-day biodegradability research or if it can swiftly break down in the environment and be utilised in ecologically acceptable goods. A substance is considered naturally biodegradable if its decomposition occurs by oxygen depletion or carbon dioxide production, or if its decomposition rate falls between 20% and 60% after 28 days, as determined by the Organisation for Cooperation and Development (OECD) 301 tests. Since fatty acid alkyl esters are more prone to microbial activity, their synthesis from plant oils improves biodegradability.[165] Chemical alterations, including branching and transesterification, enhance the stability and efficacy of biolubricants while preserving their environmentally beneficial characteristics.[160,166] Compared to conventional lubricants, biolubricants have a smaller environmental impact because they are non-toxic. Dykha et al.[167] state that using renewable resources, such as leftover cooking oil, helps reduce environmental damage and advance sustainability.

A biolubricant's biodegradability must be assessed based on a few factors. These measurements show how much the test biolubricant is consumed by microorganisms or how simple chemicals are produced because of the biolubricant breaking down. Therefore, several biodegradability testing methods quantify the amount of CO_2 or CH_4 produced (in anaerobic scenarios) or the amount of oxygen absorbed (in aerobic scenarios) in a certain amount of time.[168] The percentage of decomposition for the different lubricants is shown in Table 9 and figure 7.

Table 9: Percentage (%) decomposition of different lubricants [169]

Lubricants	Percentage decomposition
Diesters and polyols	55%
Plant oils	90%
Plant oils- based esters	80%
Polyalkylene glycol (PAG)	20%
Polyalphaolifen (PAO)	30%
Polyester	25%

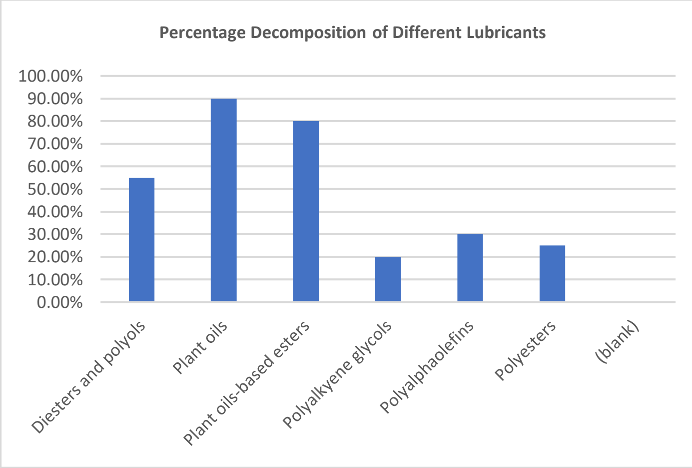


Figure 7: Percentage decomposition of different lubricants

Methods for Testing Biodegradation

Three test techniques are frequently used to measure the biodegradability of lubricants: ASTMD-5864 and CECL-33-A-934, OECD 301B and OECD 301F, and ASTMD-5864 and OECD 3013. About 60% of the material is converted into carbon dioxide within 10 days after the commencement of biodegradation, which usually happens within 28 days of the test's beginning, these techniques effectively evaluate biodegradability.[170] Yet, when determining the infrared absorbance of extractable lipophilic chemicals, the CEC technique does not differentiate between final and primary biodegradation.[171]

This method analyses the total biodegradability of a hydrocarbon compound, requiring a minimum of 80% biodegradability. The CEC technique is seen as a less rigorous examination.[172] The quantification of carbon dioxide (or methane) produced during a specific timeframe is determined by various biodegradability testing techniques. The oxygen intake through the actions of microbes' biochemical oxygen is accounted for by certain researchers.[168] The majority of biolubricant base oils exhibit low solubility in water. Therefore, the choice of biodegradability test methodologies varies. These oils create a film on the surface of the water, which hinders the exchange of oxygen, leading to a decrease in the amount of dissolved oxygen present.[173,174]

Studies indicate that the process of oil degradation in soil was characterised by a slow rate, as extractable residues did not emerge until at least one year had passed. Due to the influence of the environment, aromatic carbons exhibit resistance to biodegradation. Simultaneously, components coming from animals or plants are easily biodegradable, as straight-chain hydrocarbon molecules breakdown more readily than branched-chain hydrocarbon compounds. The presence of steric hindrance groups leads to a decrease in biodegradability. The biodegradability of plant oil is inversely proportional to its chain length. Several test techniques published by the OECD allow for the screening of biolubricants for biodegradability under aerobic circumstances (Table 10).

Table 10: OECD standard test for biodegradability

Test	Parameters	Remarks	References
Improved screening	OECD 301E (DOC 1)	Removal of inorganic carbon by acidification and purging.	175
CO2 evolution (Modified strum test)	OECD 301B (CO_2)	This estimates the concentration of carbon-dioxide.	6
Doc Die-Away	OECD 301 (Dissolved organic compound)	Estimation of Dissolved organic carbon is done. Also, It is appropriate for naturally adsorbing compounds.	176
Ministry of International Trade and Industry (MITI) (I)	OECD 301C (Biochemical oxygen demand)	It investigates the identity of intermediate compounds.	177,178
Closed Bottle	Biochemical oxygen demand /Chemical oxygen demand (OECD 301D)	It investigates the amount of oxygen is present.	179
Manometric Respirometry	Biochemical oxygen demand /Chemical oxygen demand (OECD 301F)	It is suitable for most compounds as it estimates oxygen consumption	180,181

Applications of Biolubricants

Biolubricants have been widely used in many industrial applications and maintenance.[182] Renewable resource-based biolubricants have great promise in the automotive and aerospace sectors because of their outstanding performance qualities and environmental friendliness. Biolubricants address strict environmental requirements and lessen dependency on petroleum-based products because they are non-toxic and biodegradable.[160] Using second-generation biolubricants improves their environmental profile even more because they are made using sustainable enzymatic procedures.[160]

A study has been carried out about the use of biolubricants in machinery that releases oil into the surrounding environment when it operates. Moreover, reports have indicated that biolubricants are used in equipment used in food processing and water treatment.[4] Biolubricants are widely employed in many different applications, including railway flanges, aviation jet engines, boat engines, metal working fluids, hydraulic fluids for power equipment, and greases.[4,182,183,184] Plant oil-based lubricants have been the subject of research and development due to their superior performance in medium- to heavy-duty machining and grinding of ferrous-based metals. It was found that machining operations were enhanced using plant oil-metal working fluids.

Coconut oil demonstrated superior performance compared to petroleum lubricant when turning AISI 304 austenitic stainless steel, even under high cutting speed (90m/min), feed rate (0.35 mm/rev), and depth of cut (1mm). The recorded measurements indicate that coconut oil has a surface roughness (Ra) of 4.5mm, while mineral oil has a surface roughness (Ra) of 5.5mm.[185] Biolubricants made from marine microalgae, including Coelastrella sp., have lower wear rates and friction, which makes them appropriate for high-performance uses in automotive systems. [125] According to Pawar et al.,[186] olive biolubricants boosted with additives like MoS_2 show increased tribological properties and outperformed traditional synthetic lubricants in a variety of lubrication system. Ecofriendly TMP esters are employed in various applications such as gear oils, hydraulic oils, engine oils, and additives due to their superior performance benefits.[187] Additionally, ester-based stocks have the potential to be valuable in the manufacturing of additives and lubricants.[82,184] Talib et al.[188] developed a metal cutting fluid called MJO5A, which is made from a vegetable oil base. The fluid was created by modifying Jatropha methyl oil (JME) by a process called transesterification with TMP. The utilisation of MJO5A proved to be effective in the cutting of AISI 1045, resulting in exceptional machining outcomes through the reduction of cutting force and temperature, tool chip contact length, chip thickness, and specific energy.

Conclusion

In general, there is a growing demand worldwide for a sustainable and renewable supply of lubricants. This is because about 50% of all lubricants used are either directly or indirectly released into the environment. Scenarios such as spills, improper lubricant disposal, or accidents can lead to environmental contamination and degradation. These lubricants, which come from mineral oils found in fossil fuels, may be harmful to aquatic life, plants, and people. In addition, the depletion of the world's oil reserves and the growing expense of fossil fuels force scientists to give priority to the creation of biodegradable and renewable alternatives. Due to their biodegradability, accessibility, and environmental benefits, bio-based biolubricants are becoming more and more popular. Vegetable oil has several disadvantages, including low temperature and limited oxidative stability. Yet, it is a prominent candidate for partially or completely replacing lubricants derived from fossil sources.

A biolubricant with superior physical and chemical qualities can be produced by chemically altering the plant oil using methods like hydrogenation, epoxidation, transesterification, or estolide production.[43] Enhanced thermo-oxidative stability, a lower friction coefficient, a high viscosity index, and superior lubricity are some of these characteristics. Even though biolubricants have several benefits over standard lubricants, there are still issues with cost and scalability. To overcome these obstacles and fully realise their promise in industrial applications, more research and development is necessary. Consequently, it is necessary to enhance the low-temperature and oxidative stability characteristics of plant oils. Large-scale cultivation of inedible vegetable crops could be implemented to address the issue of lubricants conflicting with the food supply. Furthermore, additional, more economical studies are required to explore the modification of plant oils for the purpose of producing lubricants. This would enable universal access to a toxin-free environment.

Conflict of Interest

The authors declare no conflict of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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