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Lubricant oils are known to decrease the friction coefficient between two contacting surfaces. It is essential for the correct function of almost the totality of mechanical machinery working in the entire world. Lubricant oils consist of about 80% of oily base stocks which attributes to their properties of viscosity, stability, and pour point to the lubricant plus additives supplemented to improve these properties. Petroleum lubricants are usually environmentally unacceptable due to their low biodegradability and toxicity. These oils contaminate the air, soil, and drinking water and affect human and plant life to a great extent. Thus, the demand for environmentally acceptable lubricants is increasing along with the public concerns for a pollution-free environment. Plant oils are promising as base fluid for biolubricants because of their excellent lubricity, biodegradability, viscosity–temperature characteristics, and low volatility. The purpose of this paper is to present a survey of the current status of biolubricating oil. This research provides an overview on the synthesis, tribochemical behavior; the effect of structure on friction/wear, load-bearing capacity, resistance to rise in specimen temperature, and varying response of antiwear/extreme-pressure additives in the presence of vegetable oil/derivative structures has also been discussed. Though a significant number of papers have been published in this area, there is still much to explore. A proper selection of base oil and additives is therefore essential for an efficient synthesis of biolubricating oil.

Keywords: vegetable oil; additives; biolubricant; oxidative stability; low-temperature stability; renewable
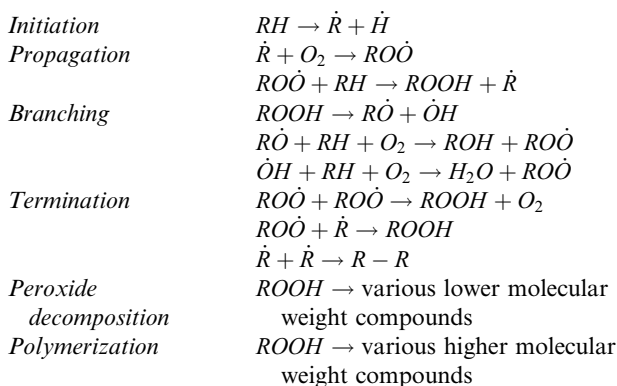
1. Introduction

It is well known that petroleum crude oil reserves are decreasing while the risk of exhaustion of the existing reserves and oil prices is increasing at a rapid pace (*1*). Conventional mineral lubricants are usually environmentally unacceptable due to their low biodegradability and toxicity (*2, 3*). These oils contaminate the air, soil, and drinking water and affect human and plant life to a great extent. Therefore, strict specifications on various environmental issues such as biodegradability, toxicity, health and safety, and emissions are required in certain specific areas (*4*). Thus, the demand for environmentally acceptable lubricants is increasing along with the public concerns for a pollution-free environment (*2, 3*). Because of an increasing concern over the environmental issues, the lubricant industries have been trying to formulate biodegradable lubricants with quality superior to those based on petroleum oil (*5*). Alternatively, environmentally friendly lubricants should be used wherever possible (*4*). Due to a combination of biodegradability, renewability, and excellent lubrication performance, vegetable oils are a potential source of environmentally favorable (ecofriendly) lubricants (*6–11*). A majority of vegetable oils consist of mainly two broad chemical categories: triesters and monoesters. Most vegetable oils are triesters (triglycerides), which are glycerol molecules with three long-chain fatty acids attached at the hydroxy groups via ester linkages. A small fraction of vegetable oils are monoesters of long-chain fatty acid and fatty alcohols of different chemistry (*10, 11*). The fatty acids in vegetable oil triglycerides are all of similar length (14–22 carbons long) with varying levels of unsaturation (*10, 12, 13*). Most vegetable oils have separate regions of polar and nonpolar groups in the same molecule. The presence of polar groups in vegetable oil makes it amphiphilic, thus allowing it to be used as both boundary and hydrodynamic lubricant (*8, 14*). In addition, vegetable oils have many advantages such as low volatility due to high molecular weight triacylglycerol molecule, good boundary lubrication characteristics due to the polar ester group and high viscosity index, high solubilizing power for polar contaminants and additive molecules, and lower cost than synthetic oils (*4, 7, 9, 15–21*).

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The triglyceride structure is also responsible for the inherent disabilities of vegetable oils as lubricant. For many reactions, unsaturated double bonds in the fatty acids act as active sites. There are two major problems associated with vegetable oils as functional fluids offer low resistance to thermal oxidative stability (*9*, *22–30*) and poor low-temperature properties (*24*, *25*, *29*, *31–34*).

The thermal and oxidative instability of plant-based oils is due to the structural "double bond" elements in the fatty acid and the "-CH group" of the alcoholic components (*7*, *34*). The poor oxidative stability of a vegetable oil is because of the rapid reactions at the double-bond functional groups (*35*). A variety of triacylglycerol-based vegetable oils contains unsaturated fatty acids and is susceptible to oxidation. The greater the level of unsaturation, the more susceptible the oil becomes to oxidation (*20*, *21*). Moser and Erhan (*36*) have studied the mechanism for the autoxidation of vegetable oils, and a classical representation of the oil autoxidation mechanism is shown as:

Initiation	$RH \rightarrow \dot{R} + \dot{H}$
Propagation	$\dot{R} + O_2 \rightarrow RO\dot{O}$
	$RO\dot{O} + RH \rightarrow ROOH + \dot{R}$
Branching	$ROOH \rightarrow R\dot{O} + \dot{O}H$
	$R\dot{O} + RH + O_2 \rightarrow ROH + RO\dot{O}$
	$\dot{O}H + RH + O_2 \rightarrow H_2O + RO\dot{O}$
Termination	$RO\dot{O} + RO\dot{O} \rightarrow ROOH + O_2$
	$RO\dot{O} + \dot{R} \rightarrow ROOH$
	$\dot{R} + \dot{R} \rightarrow R - R$
Peroxide decomposition	$ROOH \rightarrow$ various lower molecular weight compounds
Polymerization	$ROOH \rightarrow$ various higher molecular weight compounds

In plant oils, oxidation is initiated by the formation of free radicals. These free radicals can be easily formed from the removal of a hydrogen atom from the methylene group near the double bond. Free radicals sharply react with oxygen to form a peroxy radical. The peroxy radical then attacks another lipid molecule to remove a hydrogen atom to form a hydroperoxide and another free radical, propagating the oxidation process (*20–21*, *37*).

Oxidative degradation leads to an increased viscosity that limits the useful life span of vegetable oil-based fluids (*26*). Cloudiness and solidification become apparent in vegetable oil at low temperatures upon prolonged exposure to low temperature (–10 to 0°C) (*38*, *39*). Transformation of alkene groups of vegetable oil to other stable functional groups can improve the oxidative stability, whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve temperature performance (*40*).

Vegetable oils also show poor corrosion protection (*41*). The ester functionality present in the triacylglycerol structure renders these oils susceptible to hydrolytic breakdown (*42*). Therefore, at every stage, contamination with water in the form of emulsions must be prevented. Low oxidation and thermal stability along with poor low-temperature properties, however, limit their potential application as industrial lubricants (*43*). Vegetable oils exhibit particularly effective boundary lubricants as the high polarity of the entire base oil allows strong interactions with the lubricated surfaces. Boundary lubrication performance is affected by attraction of the lubricant molecules to the surface and also by possible reaction with the surface.

For tribological systems, the main function of lubricants is to reduce friction and wear. These results from the formation of a lubricant film separating the rubbing surfaces. Lubricant film's thickness depends upon the chemistry of base oil and additives, as well as upon the operating conditions such as on the applied load and the sliding velocity (*44*). Lubrication processes occur in any one out of three lubrication regimes: boundary, hydrodynamic, and mixed (*45*). The efficiency of lubricating oil is greatly influenced by its viscosity and it can be understood by the relationship of the coefficient of friction in a lubricated system to the lubricant viscosity (*46*). At high speed, high viscosity or low load, sufficient hydrodynamic pressure is generated so that the solid surfaces are fully separated by a thin film of lubricant. This condition is known as hydrodynamic lubrication while at lower speeds and viscosities, or higher loads, the hydrodynamic pressure generated is insufficient to fully separate the surfaces and asperities on the opposing surfaces come into contact, a condition known as boundary lubrication (*47*, *48*).

Vegetable oils can be used in all three regimes. There are two major factors that affect the boundary lubrication properties of vegetable oils. They are adsorption and reaction (*6*, *8*). Adsorption refers to the ability of the oil to adsorb onto friction surfaces and prevent their contact during the tribological process. Adsorption occurs by virtue of the interaction of the functional groups of vegetable oil with the friction surface and can be quantified using free energy of adsorption (ΔG_{ads}). Reaction refers to the tendency of the vegetable oils to react by themselves or with oxygen, moisture, metal, etc., in the interface or friction zone. Reaction occurs due to the high temperature, pressure, and shear of the lubrication process. These reactions, called tribochemical reactions, are poorly understood and are responsible for a number of phenomena such as degradation of oil because of oxidation and generation of friction polymers. Biresaw

et al. (*8*) investigated the level of attraction between lubricant and surface by the Gibbs free energy of adsorption using the appropriate models.

Several modern technologies have been adopted to solve the issues regarding the application of plant oils in lubricants. Some of them are genetic modification, additive treatment, and chemical modification (*16*). However, low resistance to thermal oxidative and low thermal stability still remains a major drawback of using plant oil in lubricants (*49*).

The desirable characteristics of vegetable oils make them attractive as lubricants for chain saws, railroads, etc., and also for hydraulic fluids in power equipment, two-stroke engines, boat engines, etc.

This review presents the methods involved in producing biolubricating oil, experimental investigation on different oils, merits, demerits, and challenges faced by biolubricating oil. The methods used to assess and improve the oxidation and low-temperature stability have also been discussed. This will provide a significant insight on the potential of biolubricating oil, its past, and its glorious future.

2. Modifications of plant-based oils for lubricants

In order to use vegetable oils as lubricants, several approaches have been adopted to improve the properties of vegetable oils. Genetic modification, additive treatment, transesterification, epoxidation, chemical modification, structural modification, and/or biotechnology are some of the techniques that have been employed. These methods improve the performance and stability of vegetable oils for their direct applications. Large numbers of experiments have been carried out using various techniques with vegetable oils as alternative for lubricating oil all over the world. Some of them have been summarized below.

2.1. Esterification/transesterification

Transesterification of the triglyceride or the esterification of the fatty acids is the most prevalent method for the modification of the carboxyl group of the fatty acid chain. Transesterification leads to the cleavage of esters and the reaction is generally catalyzed with acidic or basic catalysts (*50*). The features of the substrates directly influence the properties of the ester. The lubricant properties can be changed by the choice of various alcohols and acids.

Some examples of esterification and transesterification products are: trimethylolpropane (TMP) esters derivatives of TMP and rapeseed oil methyl ester (*51*) or jatropha methyl ester (JME) (*52*). They possess cold stability, friction and wear characteristics, and resistivity against oxidation at elevated temperatures. Polyolesters formed from polyols have extraordinary stability (*50*). Arbain and Salimon (*53*) conducted biolubricant production of ester TMP from esterification of fatty acid of *Jatropha curcas* oil with TMP in the presence of sulfuric acid (Figure 1).

It was observed that ester TMP has a high potential for the production of lubricants with pour point as low as –30°C, flash point >300°C, and viscosity 79 cP. More recently, Resul et al. (*54*) have synthesized jatropha biolubricant by transesterification of JME with TMP and sodium methoxide as catalysts. The viscosity index range from 178 to 183, and the other properties such as oxidative stability, wear scar, and viscosities are found comparable to other plant-based biolubricant, namely palm oil- and soybean-based biolubricant.

A new class of fatty acid polyol esters by esterification of 10-undecenoic acid with three different polyols namely TMP, neopentyl glycol, and pentaerythritol as potential lubricant base stocks was reported by Padmaja et al. (*55*). Among the three polyol esters, TMP esters of 10-undecenoic acid showed superior lubricant properties like low pour point, high flash point, and better oxidation stability while the TMP triester of 10-undecenoic acid has similar oxidation stability compared to TMP trioleate.

2.2. Partial/selective hydrogenation

Hydrogenation of vegetable oil is an important process in oil and fat and oleochemical industries
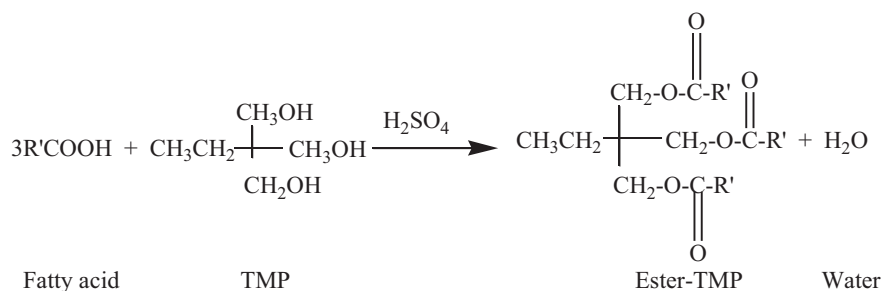

Figure 1. Esterification of fatty acid of *Jatropha curcas* oil with TMP (*53*).

both to modify the oil's physical characteristics for specific application and to increase its stability toward oxidation and decomposition (*56*). By selective hydrogenation, the unsaturated fatty acids can be transformed into single unsaturated fatty acids without increasing the saturated part of the substance. Natural fats and oils often contain multiple unsaturated fatty acids such as linoleic and linolenic acids, which seriously impair the aging stability of the oil even if they are present in very small quantities. By selective hydrogenation, the easily oxidizable compounds are transformed into more stable components. This significantly improves the aging behavior of the oils essential for their use as lubricants. It is desirable to selectively hydrogenate the polyunsaturated acids to the monoenic level (*57*). However, during the hydrogenation, the monoenic acids, originally present or formed as products, may isomerize to form the *cis* and *trans*-acids. *Cis*-isomer remains liquid at ambient temperature compared to *trans*-isomer. The selective hydrogenation of such vegetable oil must lead to a minimum of 80% toward *cis*-oleic acid to meet the industrial needs of biolubricants (*58*). The reaction pathway for the hydrogenation of sunflower oil ethyl esters has been represented in Figure 2.

Currently, the catalyst used in industrial hydrogenation process is a nickel catalyst deposited on a silica support (*59–62*). Studies on the hydrogenation of different vegetable oils have been also undertaken

on catalysts containing copper (*63*) or copper chromite (*64–66*). Generally, these different catalysts require a reaction temperature above 150°C and a high hydrogen pressure. Tallow hydrogenation and selective hydrogenation of sunflower seed oil and soybean oil in the presence of nickel catalyst supported on natural silicate diatomite have been done by Jovanovica et al. (*62*). It was observed that nickel catalyst has good catalytic properties in a process of tallow and fat hydrogenation, while demonstrating a high selectivity during the sunflower and soybean oils hydrogenation process; i.e., C18:3 (linolenic), C18:2 (linoleic), C18:2 (linoleic), C18:1 (oleic) and C18:1 (oleic), and C18:0 (stearic). Choo et al. (*67*) have prepared polyvinyl pyrolidone (PVP)-stabilized Pt colloids effective catalysts for the hydrogenation of palm olein at low temperature and pressure with sizes ranging from 1.3 to 3.0 nm. It was found that the initial hydrogen consumption rate was high, corresponding to the hydrogenation of the linoleate and slowed down thereafter, corresponding to the oleate hydrogenation. The particle size of the Pt clusters influences the rate of the diene much more significantly than the monoene. The smaller the average particle size, the higher is the rate for the diene and hence the higher the selectivity. The *trans*-isomer formation was comparatively low and was found to be a consequence of the partial saturation of the diene rather than the isomerization of the monoene. In
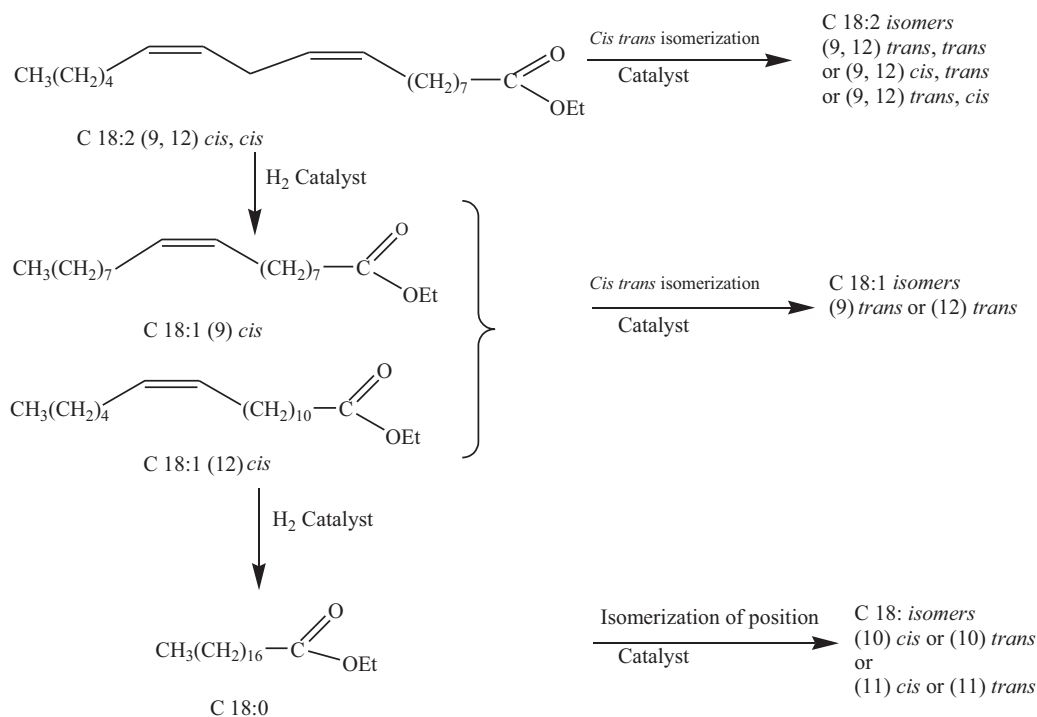

Figure 2. Reaction pathway of sunflower oil ethyl esters (SOEE) hydrogenation (*58*).

another studies, Choo et al. ([68](#)) have studied hydrogenation of polyunsaturated soybean oil by using PVP-stabilized Pt and Pd colloids with mean particle sizes ranging from 1.5 to 3.1 nm as catalysts at 35°C and atmospheric pressure. It was observed that Pt and Pd catalysts showed different rates of hydrogenation toward the double bonds. Pt catalyst had lower oleate selectivity leading to higher yields of saturated product but lower percentage of *trans*-isomer than the Pd catalyst at comparable mean particle size of 1.5 nm. The oleate selectivity increases while the linoleate selectivity as well as the activity decreases with an increase of the mean particle size. An intermediate *trans*, *trans*-linoleate was detected for the Pt catalyst with larger particle mean size. Continuous hydrogenation of sunflower seed oil has been carried out in a novel three-phase catalytic membrane hydrogenation reactor by Veldsink ([69](#)). The membrane reactor consisted of a membrane impregnated with Pd as the active catalyst, which provided a catalytic interface between the gas phase (H_2) and the oil. It was concluded that for the three-phase catalytic membrane reactor, interfacial transport resistances and intraparticle diffusion limitations did not influence the hydrogenation reaction. Over Pd catalyst and under selective conditions, the hydrogenation runs under kinetically controlled conditions showed that oleic and elaidic acid was not hydrogenated in the presence of linoleic acid. Initial formation of stearic acid was caused by direct conversion of linoleic acid into stearic acid by a shunt reaction. Ravasio et al. ([63](#)) have reported that prereduced 8% Cu/SiO₂ catalyst can be conveniently used for the stabilization of vegetable oils and of their methyl esters, showing high activity and a different selectivity with respect to unreduced ones. In case of rapeseed oil methyl esters, it was observed that the trienic component C18:3 can be eliminated and the dienic one lowered from 22 to 3–5% without raising the stearic C18:0 content and limiting the *cis*/*trans*-isomerization process. These oils, with a C18:1 content up to 88%, show remarkable oxidation stability and keep fluid down to −12 and −15°C. The oils obtained by this method were found to be suitable for their use as environmental friendly lubricants. Nohair et al. ([58](#)) have reported selective hydrogenation of ethyl esters of traditional sunflower oil (SOEE) in ethanol as solvent in presence of supported palladium catalysts. At low-temperature (40°C) reaction, it was observed that the SOEE hydrogenation reaction is insensitive to the size of the palladium particles deposited on silica, but the largest metallic particles enhance the C18:1 *cis–trans*-isomerization. Introduction of amines in the reaction medium modifies the hydrogenating properties of the

Pd/SiO₂ catalyst. According to the quantity and the nature of the added amine (aliphatic with linear or ramified chain and cyclic compounds), the catalytic activity can either be unchanged or inhibited. These evolutions result from a promoter electronic effect generated by the presence of amine and from a poison geometric effect related to the adsorption of this nitrogen-containing compound on the palladium surface. Whatever is the nature of amine, it induces an increase of the selectivity toward the *cis* C18:1. Wadumesthrige et al. ([70](#)) have modified the chemical structure of fatty acid chains of fatty acid methyl ester (FAME) by catalytic hydrogenation. The properties of hydrogenated FAME strongly depend on the hydrogenation time. The total saturated fatty acid percentage increased from 29.3% to 76.2% after 2 h of hydrogenation. This hydrogenated FAME showed higher oxidation stability and higher cetane number but poor cold flow properties.

Various researchers have studied the hydrogenation of oil, a summary which has been presented in [Table 1](#).

The catalyst activity, selectivity, and *trans*-fatty acids content increase with temperature and amount of catalyst but decrease with H_2 pressure and agitation. Among the factors influencing mass and heat transfers, the efficient solubilization of hydrogen in the oil, the transport of H_2 and triglycerides to the catalyst surface, the homogeneous distribution of the active catalyst throughout the reactor, and the available surface of the catalyst are very critical in hydrogenation reaction ([71](#)). Besides the process conditions, the catalyst formulation is an important factor contributing to the *trans*-fatty acids and saturated fatty acids production during hydrogenation. As an unavoidable side reaction occurring during the catalytic hydrogenation, the geometric isomerization producing *trans*-fatty acids can be influenced by the choice of the dispersed metal on the solid support and its surface characteristics. Therefore, it is desirable to design catalysts with tailored characteristics, offering higher selectivity toward products with *cis* configuration and lower selectivity toward saturated product formation.

2.3. Oligomerisation/estoloides

Oligomerisation is basically a modification of double bonds of unsaturated fatty acids that engage two or more fatty acid molecules attached to the residual alkyls. Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters. The secondary ester linkages formed are more stable toward hydrolysis than triglycerides (vegetable

Table 1. Detail of hydrogenation of oil by various researchers.

Oil	Catalyst	Temperature	Particle size	Pressure	Reaction time	Catalyst loading	References
Soybean oil	Ru nanoparticles	353 K	1.13–17.22 nm	1.5 MPa	12 h	–	(122)
Soybean oil	PVP-stabilized Pt and Pd colloids	35°C	1.5–3.1 nm	Atmospheric pressure	90 min	–	(68)
Palm olein	PVP-stabilized Pt colloids	35°C	1.4–2.9 nm	Atmospheric pressure	90 min	–	(56)
Edible vegetable oil	Supported nickel catalyst	150–160°C	–			–	(123)
Sunflower seed oil and soybean oil	Nickel catalyst supported on diatomite	195–200°C	–	1.5 MPa	180 min	0.33 wt.%	(62)
Ethyl esters of sunflower oil	Pd/SiO$_2$ catalyst	40°C	0.10–0.04 mm	10 bar	–	0.3–1.5 wt.%	(58)
Rapeseed oil	Cu/SiO$_2$ catalyst		–	20 or 6 bar of H$_2$	–	8–9 wt.%	(63)
Sunflower seed oil	Novel three-phase catalytic membrane, Pd as the active catalyst	74°C	5 nm pores	5 bar H$_2$ pressure	–	–	(69)
Sunflower and canola oils	Pd/SiO$_2$ catalyst	110°C	6.8 nm pores	5 atm	60 min	1 wt.%	(124)

oils/fats) with better physical properties (72) to use as biolubricants.

The extent of oligomerization of the molecule or the average number of fatty acids added to the base fatty acid is represented by estolide number (EN) (73, 74). A series of saturated estolides were developed by Cermak and Isbell (73) in which oleic acid and saturated fatty acids ranging from butyric through stearic treated with 0.4 equivalents of perchloric acid at either 45 or 55°C produce complex estolides. Yields varied between 45% and 65% after Kugelrohr distillation. The EN varied with reaction temperature as well as with the change in saturated fatty acids. The shorter chain, saturated fatty acids, i.e. butyric and hexanoic acid, provide material with higher degrees of oligomerization (EN = 3.3) than stearic acid (EN = 1.4). These new simple oleic estolides when formulated with a small amount of oxidative stability package show better oxidative stability than both petroleum and vegetable oil-based fluids. C18 fatty acids with one or more double bonds react with each other at temperatures of about 210–250°C in the presence of layered aluminosilicate catalysts (e.g. montmorillonite) forming a complex mixture of C36 dicarboxylic acids (dimeric fatty acids), C54 trimer fatty acids, and C18 monomer fatty acids (75–77). In another study by Cermak and Isbell (78), these oleic estolides were esterified with 2-ethylhexanol to obtain high yields of the corresponding ester (Figure 3).

It was observed that as the chain length of saturate capping material increased from C-4 to C-10, the pour point of the estolide 2-ethylhexyl esters decreased to −39°C. The other mid-chain, saturated estolide 2-ethylhexyl esters C-6 through C-14 had superior low-temperature properties compared with their competitors; i.e. soy-based, synthetic-based, and petroleum-based oils. The viscosity index ranged from 122 to 155 for the free acid estolides while the estolide 2-ethylhexyl esters had slightly higher indices which ranged from 172 to 196. These new estolide esters displayed far superior low-temperature properties and were more suitable as a base stock for biodegradable lubricants and functional fluids than current commercial materials. A series of esters (methyl-butyl, decyl oleyl 2-propyl 2-ethylhexyl C18-Guerbet, and C24-Guerbet) of meadow foam, Crambe and oleic fatty acids, and estolides have determined by Isbell et al. (79). The reaction scheme for the formation of oleic estolide and its Guerbet ester has been represented in Figure 4.

Pour points of the oleic estolides were measured on a series of both free acid estolides and their 2-ethylhexyl esters. The series compared the effect of oligomerization on pour point. Pour points of oleic estolides were 5–10°C higher than the corresponding derivative's melting point. The extent of oligomerization (EN) played a significant role in giving higher pour point with higher oligomerization (EN of 2.96 had a pour point of 0°C: EN of 1.1 had a pour point
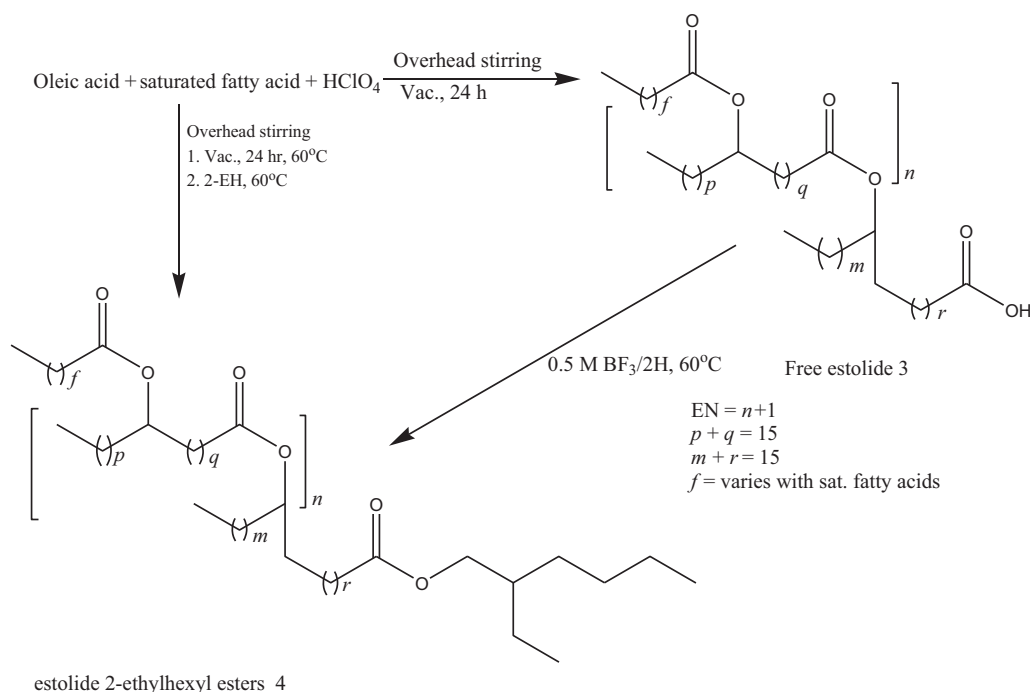
Oleic acid + saturated fatty acid + HClO₄ → (Overhead stirring, Vac., 24 h)

Overhead stirring
1. Vac., 24 hr, 60°C
2. 2-EH, 60°C

0.5 M BF₃/2H, 60°C   Free estolide 3

EN = $n+1$
$p + q = 15$
$m + r = 15$
f = varies with sat. fatty acids

estolide 2-ethylhexyl esters 4

Figure 3. Reaction scheme for the formation of the estolides and its 2-ethylhexyl ester (78).

Oleic acid

Acid = H₂SO₄ ($n = 0$–3, 65%)
Acid = HClO₄ ($n = 0$–10, 76%)
Acid = p-Toluenesulfonic ($n = 0$–3, 45%)
Acid = Montmorillonite K–10 ($n = 0$–1, 10–30%)

acid

H₂SO₄ (.005 mol%)
C18 Guerbet

Estolide

Estolide C 18 Gurebet   Estolide
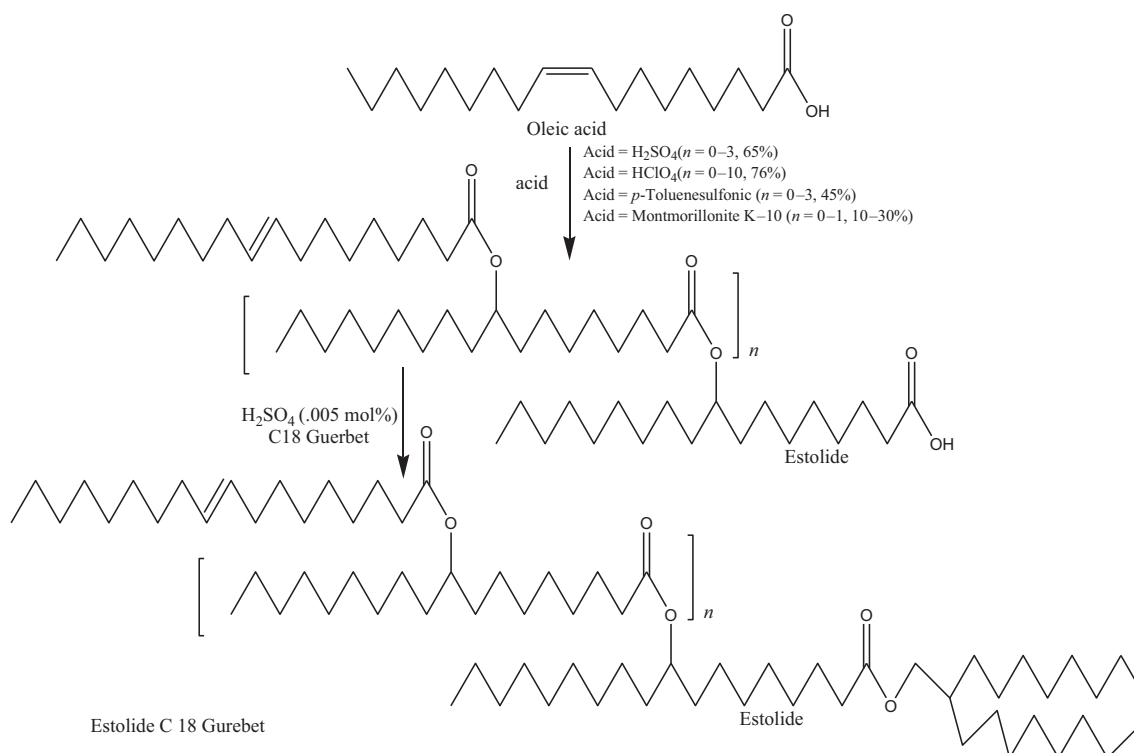
Figure 4. Reaction scheme for the formation of oleic estolide and its Guerbetester (79).

of –27°C). In a similar fashion, viscosity increased with higher oligomerization and free acid estolides were generally several hundred centistokes (cSt) more viscous than the corresponding esters. Viscosity index ranged from 151 to 238 with the fatty acid esters giving slightly higher indices than estolide esters. Cermak and Isbell (27) treated the oleic acid and lauric acid with perchloric acid at 60°C to produce

complex estolides of 45–75% after its purification by Kugelrohr distillation. The esterification of the saturated oleic estolides with 2-ethylhexanol was performed to obtain high yields of the corresponding ester. The amount of oligomerization (EN) played an important role on viscosity; viscosity increased with higher oligomerization. The free acid estolides were found to be several hundred centistokes (cSt) more viscous than their corresponding esters. The viscosity index ranged from 141 to 170 for the free acid estolides while that of complex estolide 2-ethylhexyl esters ranged from 159 to 232. These new coco-oleic estolide esters exhibited superior low-temperature properties (–36°C). Moreover, they were of reasonably low cost and more suitable as a base stock for biodegradable lubricants and functional fluids than the conventional vegetable oil-based commercial materials. In another study, Cermak and Isbell (*28*) evaluated the oxidative stability of coconut-oleic estolide 2-ethylhexyl ester (coco) and oleic estolide 2-ethylhexyl ester (oleic). In both cases, a drastic increase in the oxidative stability was observed. The coconut-oleic estolide 2-ethylhexyl ester gave the best RBOT values with 3.5% oxidative stability. The viscosity index ranged from 179 to 190 for the oleic estolide 2-ethylhexyl ester, whereas the coconut-oleic estolide 2-ethylhexyl ester had slightly lower viscosity indices ranging from 161 to 174. These two estolide esters have displayed far superior oxidative stability and are of reasonable cost. They were more suitable as a base stock for biodegradable lubricants and functional fluids than current commercial, vegetable-based materials.

In the latter studies, Cermak and Isbell (*80*) have produced estolides from the combination of castor and lesquerella fatty acid esters with different types of saturated, unsaturated, and branched fatty acids. It was investigated that castor and lesquerella estolide esters had the best cold temperature properties when capped with oleic (pour point = −54°C for castor and pour point = −48°C for lesquerella) or capped with a branched material, 2-ethylhexanoic acid (pour point = −51°C for castor and pour point = −54°C for lesquerella). As the saturation was increased in the estolide, pour and cloud points also increased. The increased saturation such as stearic capped estolides allowed for sufficient alkyl stacking of these long saturated chains producing higher pour points. Cermak et al. (*81*) synthesized tallow-oleic estolide 2-ethylhexyl (2-EH) esters using perchloric acid catalyzed one-pot process. The synthesized esters have viscosities ranged 57–80 cSt at 40°C and 10.8–14.0 cSt at 100°C with a viscosity index (VI) 169–185. Among all the esters developed the 2-EH ester had modest low-temperature properties. The oxidative stability of the esters was found to be increased with increase in saturation. In addition, the tallow-oleic estolide 2-EH esters have showed remarkably low evaporative losses of only 1% compared to a 15–17% loss for commercial materials of similar viscosity grade. Recently, Cermak and Isbell (*82*) have synthesized saturated mono-estolide methyl esters and enriched saturated mono-estolide 2-EH esters from oleic and different saturated fatty acids under three different synthetic routes. The attempts at obtaining saturated mono-estolide 2-EH esters, EN = 1, via distillation proved to be challenging and lead to estolide samples with EN > 1 and the pour point values followed the same trend as the high EN estolides. The other synthetic routes provided saturated mono-estolide methyl esters with EN = 1. The resulting pour point values showed a linear relationship between the saturated capping chain length and pour point. As the saturated capping chain length increased, the pour points also increased (higher temperatures): C-2 capped −30°C, C-10 capped −12°C, and C-18 capped 3°C. The saturated mono-estolide methyl ester viscosities also showed an increase in viscosity at 40 and 100°C as the saturated chain lengths increased. The viscosities for the C-4 saturated mono-estolide methyl ester were 9.5 cSt at 40°C and 2.6 cSt at 100°C, while medium chain length derivations (C-10 saturated mono-estolide methyl ester) were 19.7 cSt at 40°C and 4.2 cSt at 100°C and at the longer chain length derivations (C-18mono-estolidemethyl esters) were 27.6 cSt at 40°C and 10.7 cSt at 100°C. Details of the synthesis of estolides by various researchers have been discussed in Table 2.

Although ideal estolide is envisioned as a completely saturated material that retains good pour point properties but the saturated capping material adds cost to the synthesis of estolides (*72*). The EN varied with reaction temperature as well as with the change in saturated fatty acids. The short-chain saturated fatty acids provide material with higher degrees of oligomerization (EN = 3.3) than long-chain saturated fatty acids (EN = 1.4). These saturated estolides and estolide esters showed very different physical properties in terms of cold temperature properties (*82*).

Synthesis of estolides from unsaturated fatty acids opens the possibility of making estolides with wide ranging physical properties based on their point of linkage and extent of oligomerization. Estolides from unsaturated fatty acid sources are only limited by the availability of novel olefin positions.

Table 2. Details of the synthesis of estolides by various researchers.

Oil/acid species	Reaction conditions	Estolides	Pour point (°C)	Viscosity at 100°C (cSt)	Viscosity index	References
Oleic, meadow foam and Crambe fatty acids	24 h with overhead stirring in a 2:1 mole ratio, oleic:saturated fatty acids with 0.4 mole equivalents of perchloric acid. Estolide esters were synthesized by combining 1.0 mol equivalent of estolide with 1.5 mol equivalents of alcohol at 70°C in the presence of 0.005 mol equivalents of concentrated sulfuric acid.	Crambe estolide	–	58.6	151	(79)
		Crambe estolide methyl ester	–	24.8	172	
		Crambe estolide butyl ester	–	27.1	178	
		Crambe estolide decyl ester	–	26.7	179	
		Crambe estolide oleyl ester	–	30.4	181	
		Crambe estolide isopropyl ester	–	30.5	168	
		Crambe estolide 2-ethylhexyl ester	–	26.1	177	
		Crambe estolide Cl8-Guerbet ester	–	32.1	158	
		Crambe estolide C24-Guerbet ester	–	31.5	170	
		Meadow foam estolide	–	27.4	154	
		Meadow foam methyl esters	–	17.7	164	
		Meadow foam butyl esters	–	15.5	177	
		Meadow foam decyl esters	–	15	181	
		Meadow foam oleyl esters	–	16.1	185	
		Meadow foam isopropyl esters	–	17.8	167	
		Meadow foam 2-ethylhexyl esters	–	16.5	172	
		Meadow foam Cl8-Guerbet esters	–	15.8	166	
		Oleic acid	–	40	148	
		Oleic acid methyl ester	–	23.7	170	
		Oleic acid butyl ester	–	30.3	168	
		Oleic acid decyl ester	–	21.4	169	
		Oleic acid oleyl ester	–	26.8	180	
		Oleic acid isopropyl ester	–	26.7	169	
		Oleic acid 2-ethylhexylester	–	22.5	167	
		Oleic acid C18-Guerbet ester	–	27.4	169	

Table 2. (*Continued*)

| | | | | Physical properties of estolides | | |
| | | | Pour point (°C) | Viscosity at 100°C (cSt) | Viscosity index | |
Oil/acid species	Reaction conditions	Estolides				References
		Oleic estolide C24-Guerbet ester	–	24.3	175	
Oleic acid and various saturated fatty acids	24 h with overhead stirring in a 2:1 mole ratio, oleic:saturated fatty acids with 0.4 mole equivalents of perchloric acid.	Series of 2-ethylhexyl estolides esters				
		OB-EH-45	–30	19.3	175	
		OB-EH-55	–19	20	175	
		OC-EH-45	–30	17.9	174	
		OC-EH-55	–27	16.9	173	
		OO-EH-45	–36	16.8	175	
		OO-EH-55	–24	16.8	172	
		OD-EH-45	–39	15.5	176	
		OD-EH-55	–24	14.3	177	
		OL-EH-45	–36	13	179	
		OL-EH-55	–27	12.4	176	
		OM-EH-45	–25	13.9	179	
		OM-EH-55	–18	13.4	174	
		OP-EH-45	–12	13.5	174	
		OP-EH-55	–12	8.7	196	
		OS-EH-45	–15	14	177	
		OS-EH-55	–5	13.4	178	
Oleic acid and lauric acid, coco fatty acids	24 h with overhead stirring in a 2:1 molar ratio, oleic:lauric fatty acids at 45°C followed by distillation at 180/200°C, esterification reactions were run with magnetic stirring and 0.5 M BF3 at 60°C 24 h with overhead stirring under vacuum, oleic:coconut fatty acids with 0.05 equivalents of perchloric acid, then 1.2 equivalents of 2-ethylhexanol at 60°C for 2 h followed by distillation at 90/110°C.	Series of lauric-oleic estolide 2-ethylhexyl esters				(*122*)
		A-2EH	–30	14.5	169	
		B-2EH	–27	12.6	183	
		C-2EH	–36	9.8	176	
		D-2EH	–41	10	182	
		Coco-oleic estolide 2-ethylhexyl esters		Viscosity at 40°C (cSt)		
		OC-EH-AD	–21	149.5	138	
		OC-EH-BD	–24	58.4	175	
		OC-EH-CD	–27	61.1	164	
		OC-EH-DD	–33	92.8	170	
		OC-EH-ED	–33	86.3	232	
Oleic and different saturated fatty acids	24 h with overhead stirring under vacuum, with 0.1 equiv. of perchloric acid at 60°C, then excess amounts of 2-ethylhexanol at 60°C for 3–4 h followed by distillations at 90–110°C and 180–200°C followed by molecular distillation	Series of saturated mono-estolide 2-ethylhexyl esters				(*82*)
		A	–30	9.4	169	
		B	–30	9.9	163	
		C	–42	7.8	169	
		D	–42	6.8	179	
		E	–30	7.5	170	
		F	–21	7.1	173	
		G	–15	8.3	161	
		H	–0	9.5	195	
	Reactions I and J were synthesized via anhydrides and the other estolides via tin and the corresponding fatty acid	Series of saturated mono-estolide methyl esters				
		I	–30	2.6	117	
		J	–27	2.7	134	
		K	–21	2.9	151	
		L	–24	4	258	
		M	–12	4.2	121	
		N	–12	4.1	101	

Table 2. (*Continued*)

Oil/acid species	Reaction conditions	Estolides	Pour point (°C)	Viscosity at 100°C (cSt)	Viscosity index	References
				Physical properties of estolides		
		O	–15	5.3	218	
		P	–3	5.2	178	
		Q	3	10.7	407	
Lesquerella oil and castor oils	Vacuum (20 Pa) and at 80°C for 24 h	Series of unsaturated castor and lesquerella-based estolides				(*80*)
		A	–54	7.6	196	
		B	3	8.6	191	
		C	–36	6.5	186	
		D	–51	11.8	164	
		E	–48	7.8	200	
		F	3	8.2	195	
		G	–24	8.4	192	
		H	–54	10.1	189	
	Hydrogenation of lesquerella 2-ethylhexyl ester with 0.25 wt.% Pd	Series of saturated castor and lesquerella-based estolides				
		HA	–36	12.2	178	
		HB	6	8.7	186	
		HC	–12	7.9	196	
		HD	6	9.1	187	

2.4. Epoxidation

Epoxidation is widely used to improve the lubricity in lubricants by virtue of good lubricity and high oxidation stability of the epoxidized oil. Standard industrial process for epoxidation of vegetable oil is based on *in situ* epoxidation, in which peracid is generated by reacting acetic or formic acid with hydrogen peroxide in the presence of strong mineral acids such as H_2SO_4 and H_3PO_4 (*83*). Epoxidation is carried out either homogeneous (*84–86*) or by using a heterogeneous catalyst (*87*). In homogeneous catalysis, peracids such as peracetic acid generated *in situ* by mixing hydrogen peroxide with acetic acid are used to epoxidize vegetable oils. These epoxidised soybean oil are expected to show improved lubricity when used as a lubricant base fluid because of their good lubricity and high oxidation stability in comparison to pure vegetable oils. Warwel and Klaas (*88*) reported an alternative process that is milder and more selective, wherein lipase is used to catalyze the peracid formation from a fatty acid and hydrogen peroxide. This is a new and a very promising technique for epoxidation of double bonds. It has several advantages over the chemical catalysts such as: (1) mild reaction conditions, (2) formation of stable hydro-peroxides directly from fatty acid, i.e.

no need for acetic or formic acid addition, (3) high region and stereo selectivity, (4) significant suppression of side reactions, and (5) high conversion. In the recent publications, volatile organic solvents have been used as the reaction media (*89*, *90*). Vegetable oil epoxides are currently used mainly as PVC stabilizers (*75*, *91*). Furthermore, they are also used to improve the lubricity in lubricants. Because of their good lubricity and high oxidation stability in comparison to rapeseed oil, pure epoxidised rapeseed oil can also be used as a lubricant base fluid (*34*). The cleavage of the epoxy ring results in the introduction of hetero-atoms and a whole new series of oleo chemical products that can be used as base lubricants and additives (*50*). Hwang et al. (*35*) have produced soybean oil-based lubricants by reacting epoxidized soybean oil (ESBO) with various alcohols (methanol, 1-butanol, 2-butanol, 1-hexanol, cyclohexanol, 2,2-dimethyl-1-propanol, and 1-decanol) in presence of sulfuric acid. The modification of ESBO improved the oxidative stability and low pour point. Furthermore, the deposit-forming tendency of ESBO was significantly reduced by removal of multiple unsaturations in fatty acid chains (*7*). The study was further extended to evaluate the properties of ESBO (*16*). A synthetic lubricant was prepared by chemical
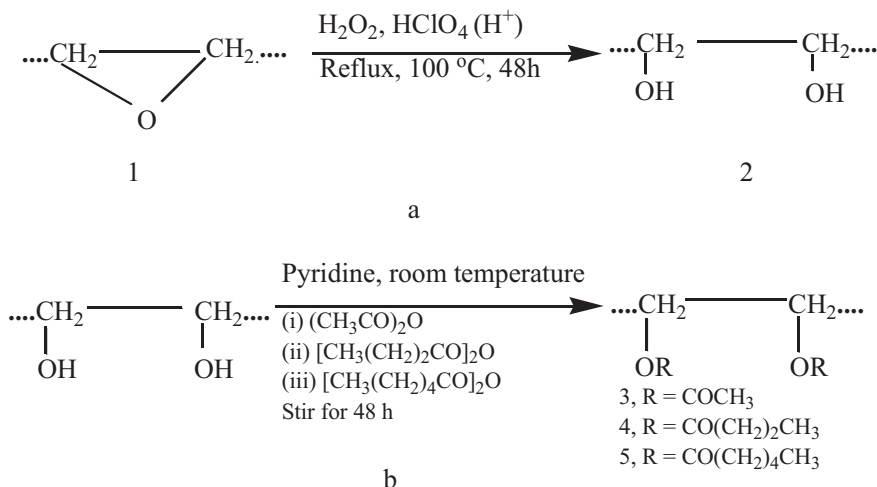
Figure 5. (a) Preparation of di-OHx-soybean oil (di-OHx-SBO) from ESBO via di-OH-SBO; (b) dihydroxy compound 2 was then reacted with different anhydride in equi-molar ratio to obtain the corresponding products 3, 4, and 5 ([5]).

modification of ESBO (Figure 5). The lubricant was characterized by improved high- and low-temperature stability. The reaction mainly consists of two-steps: (1) synthesis of dihydroxylated soybean oil from ESBO with $HClO_4$, and (2) reaction of acetic, butyric, and hexanoic anhydride with the dihydroxylated product.

This fluid shows excellent low-temperature storage stability when blended with dibutyl adipate (in 70:30 ratio) and 1% additive and is acceptable for most industrial applications.

It was revealed that low-temperature stability was excellent for hexanoic anhydride derivative. When compared with soybean oil, thermal and oxidative stabilities were found to be improved. The epoxidation of soybean oil was also investigated by Erhan et al. ([4]). It was suggested that these fluids may be formulated with other functional components such as extreme-pressure additives, antiwear additives, pour point depressants, other base stocks, and diluents.[1]

2.5. Chemical, thermal and structural modification

In another study, the authors have also studied the thermal and chemical modification of vegetable oils for use as environmentally friendly lubricants ([14]). The thermal and chemical modification of oil structure can significantly influence the wear- and load-carrying properties under boundary lubrication regimes. Moreover, chemical modification of triacylglycerol structures has great potential in achieving broad temperature range stability as well as excellent wear/ friction characteristics. The structural modification using diethyl azodicarboxylate in the absence of catalyst and solvent was conducted by Biswas et al. ([15]). It was demonstrated that the reaction is versatile and can

be conducted under different reaction conditions. Salimon et al. ([20], [21]) have presented a novel synthetic approach for the chemical modification of oleic acid derivatives to improve their oxidative stability, low temperature, and other physicochemical properties (Figure 6). The reaction carried out in four stages: (1) oleic acid epoxidation, (2) ring-opening reaction, (3) esterification of the carboxylic acid hydroxyl group, and (4) acetylation of the resulting hydroxyl group in the ring-opened products. It was revealed that ethyl-hexyl 9-(octanoyloxy)-10-(behenoxy) octadecanoate with behenyl mid-chain ester exhibited the most favorable low-temperature performance (pour point –48°C) and ethylhexyl 9-(octanoyloxy)-10-(octyloxy)octadecanoate octyl mid-chain ester showed higher oxidation stability (142°C) than the other synthetic ester oils.

Chemical modification of vegetable oils (corn, canola, and castor-lauric estolide oils) by reaction with butanethiol was reported by Biresaw et al. ([92]). Moreover, the effect of chemical modifications on viscosity, viscosity index, pour point, cloud point, oxidation stability, four-ball antiwear, and extreme pressure was also analyzed. The results showed that viscosity increase with increased oxidation stability time, reduced pour point (9–18°C), and reduced viscosity index. The sulfide estolide exhibits similar trends in viscosity index and oxidation stability but showed no change in viscosity or cold flow.

Various synthetic approaches were also adopted for the chemical modification of vegetable oils to improve their thermo-oxidative and low-temperature stabilities ([15]). Hwang et al. ([40]) have prepared synthetic lubricant base stocks with oxidative stabilities and pour points comparable with commercial synthetic lubricant base stocks (Figure 7).
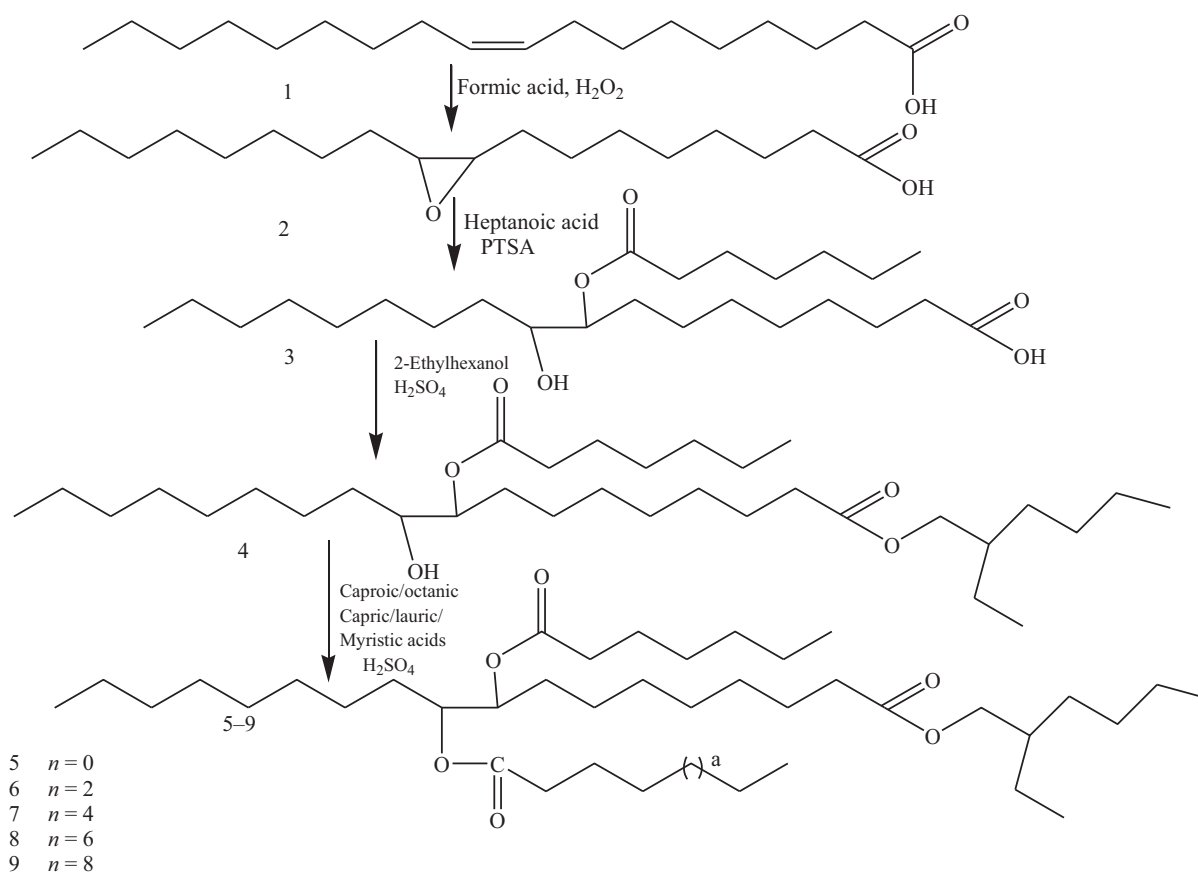
Figure 6. The reaction scheme for triester formation (*20*, *21*).

Two types of ring-opened products, 0% and 100% transesterified products, under controlled reaction conditions were obtained. Pour points of the ring-opened products ranged from −18 to −36°C without pour point depressant and from −21 to −42°C with 1% of pour point depressant. In addition, acetylation of hydroxy groups in the ring-opened products further lowered pour points that ranged from −27 to −42°C without pour point depressant and from −30 to −48°C with 1% of pour point depressant was also investigated.

2.6. Other methods

Beside these methods, some novel processes have also been proposed for the synthesis of biolubricants with improved properties by researchers.

Lathi et al. (*93*) have developed novel process for the production of biodegradable lubricant-based stocks from epoxidized vegetable oil with a lower pour point via cationic ion-exchange resins as catalysts (Figure 8). The reaction was carried out in two-steps: (1) the ring-opening reaction of ESBO with different alcohols such as *n*-butanol, iso-amyl alcohol, and 2-ethylhexanol in the presence of amberlyst

15 (dry) as a catalyst, and (2) esterification of resulting hydroxyl group in the ring-opened product of *n*-butanol with acetic anhydride in the presence of catalyst amberlyst 15 (dry).

They investigated that the introducing branching on ESBOs leads to dramatic improvement of low pour point value. Thioether hydroxy vegetable oil was synthesized using a chemical reaction of epoxidized vegetable oil and common thiols (*92*) (Figure 9).

The poly-unsaturation in the molecule was eliminated and polar functional groups were added that significantly improve adsorption on metal surfaces. The tribochemical behavior of these compounds was also investigated.

Yao et al. (*95*) reported biosynthesis of genetically altered oil seed plants with limited postharvest modification. Various ricinoleate and 12-hydroxystearate esters and estolides were synthesized and evaluated their antifriction and antiwear properties. It was concluded that melting points, viscosities, and lubricity are suitable for uses as biolubricants.

Different synthesis alternatives prior to the esterification step (reaction with an acid anhydride) were proposed by Campanella et al. (*96*) (Figure 10).
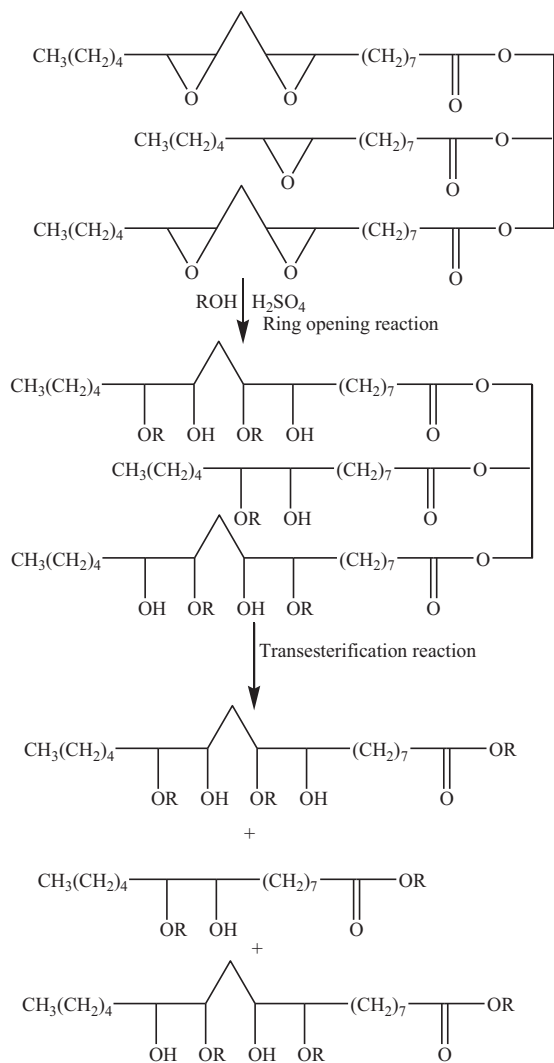
Figure 7. Reaction scheme of ring-opening reaction followed by transesterification of ESBO with a Guerbet alcohol (40).

Figure 8. Esterification of resulting hydroxyl group in the ring-opened product (93).

Two different opening reactions of the epoxide ring of epoxidized vegetable oils were studied. The former caused by the attack with glacial acetic acid and the latter using short-chain aliphatic alcohols, methanol, and ethanol in acid media. Details of the synthesis of biolubricating oil by various researchers have been discussed in Table 3.

2.7. Additives

Base oils alone sometimes fail to meet the lubrication requirements of a component. Thus, many efforts have been made to develop novel potential environmental friendly additives. Additives are thus required to overcome the limitations of lubricants and enhance the performance of base oils (97–100). They are known to provide different characteristics to base oils such as viscosity index improver, corrosion inhibitor, rusts inhibitor, antioxidant agent, antiwear agent, extreme-pressure additives, and friction modifiers (100, 101). Table 4 provides a list of several types of additives and their function.

2.7.1. Synthesis of additives for biolubricating oils

Large numbers of studies have been carried out by different researchers for the synthesis of antioxidant, antiwear, etc., agents as additives in vegetable oils to improve the properties of vegetable oils as a replacement of lubricating oil.

In the study conducted by Choi et al. (24), tribological behavior of some antiwear additives in vegetable oils was studied. An additive, dibutyl 3,5-di-t-butyl 4-hydroxy benzyl phosphonate (DBP), was synthesized. The scavenging role of free hydrogen radicals of the DBP was also investigated. It was shown that the synthesized additive has the dual function of hydrogen scavenging and protective film formation and act as an effective antiwear additive in
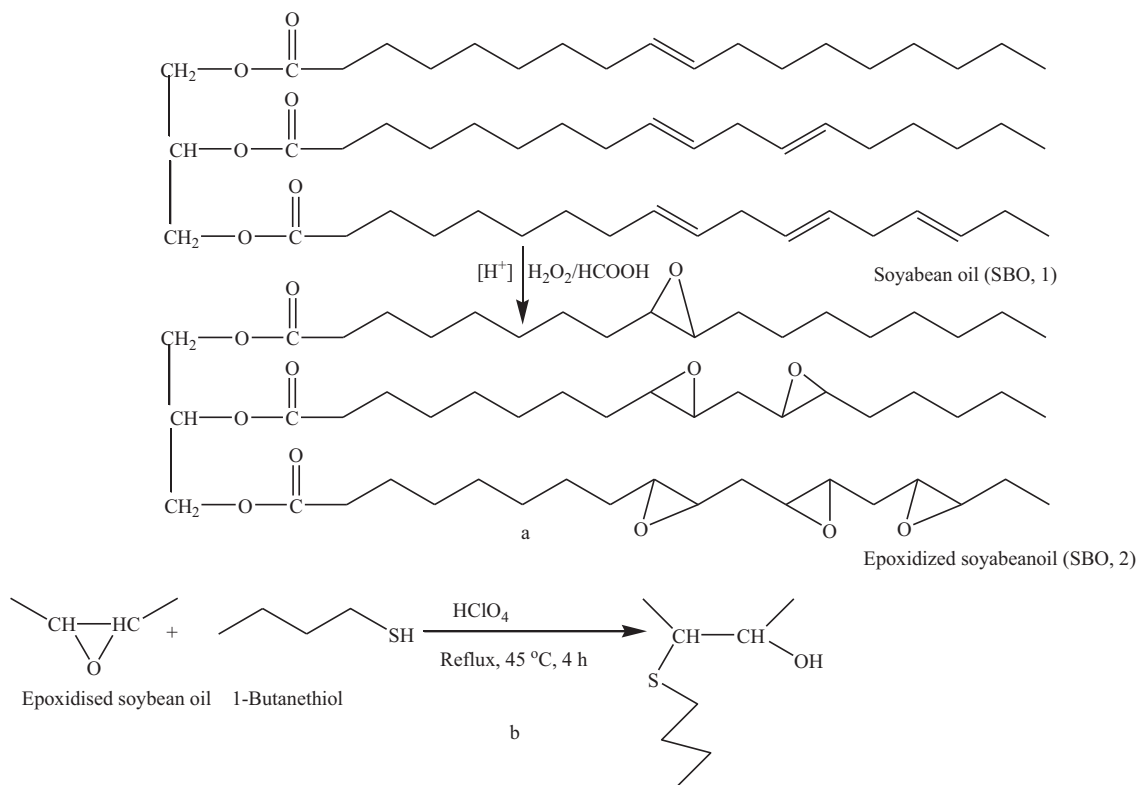
Figure 9. (a) Epoxidation of soybean oil (SBO) using performic acid to give ESBO; (b) reaction of ESBO with 1-butanethiol that produces a butyl thioether of hydroxy vegetable oil (BTHV; *19*).

various lubrication systems. Najman et al. (*102–104*) have investigated that diaryl phosphate, triaryl phosphate, amine phosphate, dialkyl dithiophosphate, and triphenyl phosphorothionate show potential as extreme-pressure and antiwear additives. Camenzind et al. (*107*) showed that an ashless acidic dialkyl dithiophosphate has superior antiwear performance with high resistibility to oxidation and hydrolysis.

Sulfurized octadecanoic acid (SOA) and sulfurized docosanoic acid (SDA) were prepared and used as additives in rapeseed oil by Cao et al. (*106*). These compounds as additives in rapeseed oil showed better antiwear and extreme-pressure properties than octadecanoic acid at relatively higher load. Unlike

Figure 10. Oxirane ring-opening reaction of epoxidized vegetable oils (*96*).

octadecanoic acid, the sulfurized fatty acids function by forming two films, adsorption film and tribochemical reaction film, during the friction process. The antiwear, friction-reducing properties, and remarkable increase in the load-carrying capacity of the base stock were also observed when [*S*-(2H-thiophen-2-yl)]-methyl alkyl xanthates were used as additives in rapeseed oil (*107*). A year later Gong et al. (*108*) synthesized two kinds of thiophosphate and explored the relationship between the additive structure and tribological properties. The synthetic thiophosphates as additives in rapeseed oil at proper concentrations were found to show enhanced tribological properties. Besides these, Sun et al. (*109*) synthesized and characterized four *N,N*-dialkyl dithiocarbamate-derived S-hydroxyethyl borates with different carbon chains and investigated their performance as additives in rapeseed oil. These compounds improved the extreme-pressure and antiwear properties of oil.

Some other additives synthesized to improve the characteristics of the base oil are a series of S, P-containing triazine derivatives (*110*), ashless triazine–dithiocarbamate derivatives (*111*), triazine derivatives (*112*), ashless and nonphosphorus oil-soluble trioctylthiotriazine derivative (*113*), novel phosphorus-free triazine derivatives (*2, 3*), ashless and nonphosphorus
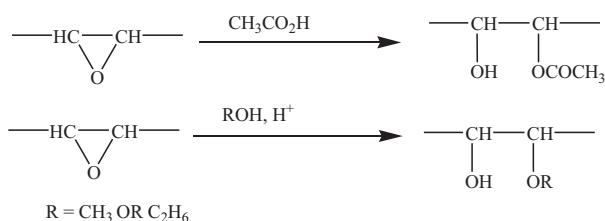
Table 3. Details of the synthesis of biolubricating oil by various researchers.

Vegetable oil species	Reactant(s)	Product(s)	Detection method(s)	Reference (s)
Rapeseed oil methyl ester	TMP	TMP esters	High-performance gel permeation chromatography, four-ball test	(51)
Rapeseed oil	Peracetic acid	Epoxidized rapeseed oil	Oven test and rotary oxygen bomb method, four-ball test	(34)
ESBO	Alcohol, sulfuric acid, pyridine, acid anhydride	CMSBO	^{1}H NMR, IR, gel permeation chromatography, micro-oxidation test	(35)
	Perchloric acid, hexanoic anhydride, pyridine	CMSBO-1	Ball-on-disk friction measurement configuration, scanning electron micrograph	(14)
	Hexanoic anhydride, ethylacetate, boron trifluoride etherate	CMSBO-2		
	Diethylamine and ZnCl$_2$	Diethylamine-functionalized soybean oil	FTIR analysis, ^{1}H NMR, PDSC	(15)
	Perchloric acid, acetic, butyric, and hexanoic anhydride	Novel-alkoxylated triacylglycerols	^{1}H and ^{13}C NMR, FTIR, PDSC, TFMO method	(16)
	1-Butanethiol	BTHV	FTIR analysis, ^{1}H NMR	(19)
	1-Decanethiol	DTHV		
	Cyclohexyl mercaptan	CTHV		
	1-Octadecanethiol	Octadecyl thioether of hydroxy vegetable oil		
	Guerbet alcohols	Synthetic lubricant base stocks	FTIR analysis, ^{1}H NMR, micro-oxidation test	(40)
	Hexanoic anhydride, boron trifluoride diethyl etherate, ethyl acetate	Acyl derivatives of vegetable oil	Differential scanning calorimetry and TFMO methods, four-ball test, ^{1}H and ^{13}C NMR, FTIR	(43)
	Appropriate anhydride, boron trifluoride diethyl etherate	CMSBO	Differential scanning calorimetry and TFMO methods, four-ball test, Ball-on-disk method	(4)
Vegetable oil	Alcohol	5% Palm oil methyl ester-blended lubricant	SEM, ball-on-plate test machine, TAN, TBN analyzers	(125)
Soybean oil, SBO		TMSBO	Ball-on-disk friction measurement configuration, scanning electron micrograph	(14)
	DEAD	Amino derivatives of soybean oil	NMR spectroscopy, SEC	(17)
Epoxidized oleic acid	9,10-Epoxystearates	α-Hydroxy esters and triesters	^{1}H and ^{13}C NMR, PDSC, FTIR	(126)
Epoxidized methyl oleate	Propionic acids	PMO	Scanning calorimetry and TFMO methods, four-ball and ball-on-disk wear test, ^{1}H and ^{13}C NMR, FTIR, GC	(43)
	Levulinic acids	The LMO		
	Hexanoic acids	The HMO		
	Octanoic acids	The OMO		
	2-Ethylhexanoic acids	The EHMO		
JME	Common polyol, TMP	TMP triesters	GC	(52)
	TMP	TMP triesters	Differential scanning calorimetry, four-ball friction and wear tester	(54)

Table 3. (*Continued*)

Vegetable oil species	Reactant(s)	Product(s)	Detection method(s)	Reference (s)
Jatropha curcas oil	TMP	ET	GC, FTIR spectroscopy, carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C)	([127])
High-oleic sunflower oil oleins	Concentrated sulfuric acid, monobasic and dibasic phosphates, THF and sodium sulfate	Estolides	Gel permeation chromatography	([128])
HYOOA	OL, SA	OLHYOOT	FTIR spectroscopy, carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C)	([129])
CO	Butanethiol	SMCO	Differential scanning calorimetry in dynamic, rotating pressurized vessel oxidation test, four-ball antiwear and extreme-pressure method, FTIR, ^{1}H NMR	([94], [130])
Canola oil	Butanethiol	SM Canola	Rotating pressurized vessel oxidation test, four-ball antiwear and extreme-pressure method, FTIR, ^{1}H NMR	([92])
Castor-lauric estolide oil		Castor-lauric 2-ethylhexyl ester estolide		
Epoxidized ricinoleic acid	*p*-Toluenesulfonic acid, butanol	Butyl 10,12-dihydroxy-9-acyl-oxystearate	^{1}H and ^{13}C NMR spectroscopy	([131])
9,12-Hydroxy-10,13-oleioxy-12-octadecanoic acid	Oleyl alcohol, sulfuric acid	Oleyl 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate	FTIR, ^{1}H, and ^{13}C NMR spectroscopy	([20], [21])

CMSBO-2, chemically modified soybean oil; ESBO, epoxidized soybean oil; TFMO, thin-film micro-oxidation; BTHV, butyl thioether of hydroxy vegetable oil; DTHV; decyl thioether of hydroxy vegetable oil; TMP, trimethylolpropane; ET, ester trimethylolpropane; TMSBO, thermally modified soybean oil; EHMO, 2-ethylhexyl ester of methyl hydroxy-oleate; SM Canola, sulfide-modified Canola; SMCO, sulf*ide*-modified corn oil; OLHYOOT, oleyl 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate; THF, tetrahydrofuran; OL, oleyl alcohol; SA, sulfuric acid; JME, Jatropha methyl ester; CO, corn oil; OMO, octanoic ester of methyl hydroxy-oleate; HMO, hexanoic ester of methyl hydroxy-oleate; LMO, levulinic ester of methyl hydroxy-oleate; SEC, size exclusion chromatography; HYOOA, 9(12)-Hydroxy-10(13)-oleioxy-12(9)-octadecanoic acid; DEAD, diethyl azo dicarboxylate; PMO, propionic ester of methyl hydroxy-oleate; PDSC, pressurized differential scanning calorimetry; SEM, scanning electron microscopy; CTHV, cyclohexyl thioether of hydroxy vegetable oil; GC, gas chromatography; FTIR, Fourier transform infrared; TAN, total acid number; TBN, total base number; 1H, Hydrogen-1; ^{13}C NMR, carbon-13 Nuclear Magnetic Resonance.

hydroxyl-containing dithiocarbamate-triazine compounds ([2], [3]), nonphosphorus and ashless novel S–N style 1,3,4-thiadiazole-2-thione derivatives ([114]), and oligo-oxypropylene diamide acids (OOPDA) derivative ([115]).

The studies found that all the synthesized compounds have good thermal stability, corrosion-inhibiting ability, good extreme pressure, antiwear, and friction-reducing properties under a wide range of test conditions. A summary of these experimental results is given in Table 5.

Although the biolubricating oil has been viewed as an effective alternative to conventional lubricants, they are associated with certain advantages ([6–9], [11], [116–119]) and disadvantages ([9], [22–26], [29], [31–33], [120]) as depicted in Table 6. These disadvantages need to be addressed before commercializing the production of biolubricants.

3. Challenges

The major challenges that face the use of vegetable oil as lubricating oils are listed below ([117], [121]):

(1) Homogeneity of the product depends on the supplier, feed stocks, and production methods; feed stock homogeneity, consistency, and reliability are questionable.

Table 5. (*Continued*)

Additive synthesized	Properties of additive	Detection methods	References
Phosphorus-free triazine derivatives	Load-carrying capacity and friction-reducing ability	SEM/EDS and XPS	(*2, 3*)
2,4,6-Tri[*N,N*-di-*n*-butyldithiocarmate-(20-hydroxyl)-propionylthio]-1,3,5-s-triazine	High thermal stabilities and good load-carrying capacities, good antiwear and friction-reducing property at relatively high concentration (41.5 wt.%)	SEM and XPS, four-ball tester, thermo-gravimetric analyzer	(*2, 3*)
5-Dodecyldithio-3-phenly-1,3,4-thiadiazole-2-thione, 5-Cetyldithio-3-phenyl-1,3,4-thiadiazole-2-thione	Good thermal stabilities, corrosion-inhibiting abilities, and excellent load-carrying capacities	Four-ball friction and wear tester. SEM and XPS	(*114*)
N,N-Dialkyl dithiocarbamate-derived S-hydroxyethyl borates	Improve the extreme-pressure and antiwear properties	Four-ball test machines, XPS	(*109*)
Oligo-oxypropylene diamide acids	Antifrictional, antiwear, and antiscoring properties	Four-ball triboapparatus	(*115*)
Dibenzyl and diethyl dithiocarbamates	Wear-reducing and frictional properties and low pollution	NMR SEM/EDS	(*134*)
S-(1H-benzotriazole-1-yl) methyl *N,N*-dialkyldithiocarbamates	Good antiwear and friction-reducing property	XPS	(*135*)

SOA, sulfurized octadecanoic acid; SDA, sulfurized docosanoic acid; XPS, X-ray photoelectron spectroscopy; SEM/EDS, scanning electron microscope coupled with an energy dispersive spectrometer; EDX, energy dispersive X-ray.

Table 6. Advantages and disadvantages of biolubricating oil.

Advantages	Disadvantages
Vegetable oil is produced domestically which helps to reduce costly petroleum imports	The price of vegetable oil is dependent on the feed stock price
Development of the biolubricating oil industry would strengthen the domestic and particularly the rural, agricultural economy of agricultural based countries	Stability in long term storage is difficult
Low volatility due to high molecular weight triacylglycerol molecule	Low resistance to thermal oxidative stability
Higher lubricity of vegetable oil due to the polar ester group resulting in lower friction losses, and hence more power and better fuel economy	Poor low-temperature properties
Vegetable oil is biodegradable and hence decreased environmental/toxicological hazards	Poor corrosion protection
Vegetable oil is a renewable that can be made from agricultural crops	Ester functionality present in the triacylglycerol structure renders these oils susceptible to hydrolytic breakdown
A higher flash point yields opportunities for increased rates of metal removal as a result of reduced smoke formation and fire hazard	
The higher boiling point and greater molecular weight of vegetable oil result in considerably less loss from vaporization and misting	
Vegetable oil has a reasonable cetane number and hence possesses less knocking tendency	
It has low sulfur content and hence environment friendly	
It is usable within the existing petroleum lubricants infrastructure	

(2) Compatibility with machine material needs to be studied further.
(3) Cold weather operation of the machine is not easy with vegetable oils.
(4) Low resistance to thermal oxidative stability.
(5) Acceptance by machine manufacturers is another major difficulty.
(6) Continuous availability of the vegetable oils needs to be assured before embarking on the major use of it in machines.

4. Technical difficulties

The major technical areas (with respect to the use of vegetable oils as lubricating oil in machines), which need further attention, are the following:

(1) Development of less expensive quality tests.
(2) Study of the effects of oxidation of oil on machine performance and its durability.
(3) Emission testing with a wide range of feed stocks.
(4) Efforts to be focused on responding to biolubricants performance, material compatibility, additive compatibility, and stability under long-term storage.
(5) Continued machine performance, emissions, durability, and oxidation testing in a variety of machines types and sizes need to be developed to increase consumer and manufacturer confidence.
(6) Environmental benefits offered by vegetable oil over petroleum lubricating oil need to be popularized.
(7) Potential markets in order to balance cost and availability; studies are needed to reduce the production cost of biolubricants and develop low-cost feed stocks and identify potential markets in order to balance cost and availability.
(8) Development of additives for improving oxidation stability, cold flow properties, and material compatibility, etc.

5. Conclusion

This review has focused on the synthesis, tribochemical behavior, and effect of structure on friction/wear and load-bearing capacity of various biolubricating oils used nowadays. It has been inferred from the literature that a tremendous demand for vegetable oils is expected in lubricant sector over the next few years. They can become an important class of base stocks for vegetable oil-based lubricants. After improvement of their disadvantageous characteristics such as higher sensitivity to hydrolysis and oxidative attacks, poor low-temperature behavior, and sometimes low-viscosity index coefficient, they can be used in almost all automotive and industrial applications. Owing to their advantages of being clean, biodegradable, non-toxic, the first applications for vegetable oils can be for chain saws, railroads, etc., and as hydraulic fluids

in power equipments, two-stroke engines, boat engines, etc. As discussed in the review, proper selection of base oil and additives is therefore essential for an efficient synthesis of biolubricating oil.

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