Review

Chemically Modifying Vegetable Oils to Prepare Green Lubricants

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Abstract: Chemically modifying vegetable oils to produce an alternative to petroleum-based materials is one of the most important emerging industrial research areas today because of the adverse effects of petroleum products on the environment and the shortage of petroleum resources. Biolubricants, bioplasticizers, non-isocyanate polyurethanes, biofuel, coating materials, biocomposites, and other value-added chemicals can easily be produced by chemically modifying vegetable oils. This short review discusses using vegetable oils or their derivatives to prepare lubricants that are environmentally safe. Chemically modified vegetable oils are generally used as base fluids to formulate environmentally friendly lubricants. Reports of their application as sustainable additives have attracted special attention recently because of their enhanced multifunctional performances (single additives perform several functions, i.e., viscosity index improver, pour point depressant, antiwear products) and biodegradability compared with commercial additives. Here, we have reviewed the use of chemically modified vegetable oils as base fluids and additives to prepare a cost-effective and environmentally friendly lubricant composition.

Keywords: vegetable oil; triglyceride; chemical modification; biolubricant; base stock; additive

1. Introduction

Producing materials from renewable feed stocks that are useful to various industrial fields as alternatives to depleting petro-originated resources has attracted considerable attention in recent years. Vegetable oils (VOs) have low ecotoxicity and are readily available and biodegradable. They can be used to produce a variety of environmentally safe chemicals that can compete or even surpass the performance of the existing petroleum-based materials. Materials obtained from vegetable oils (edible or nonedible), such as soybean oil, sunflower oil, palm oil, rapeseed oil, castor oil, and vernonia oil, have an application in various fields, including foods, fuels (biofuels), biolubricants, coatings and paints, adhesives, cosmetics, pharmaceuticals, plasticizers, and construction materials. This review highlights the application of vegetable oils to formulate biolubricants.

Lubricants are the materials (generally liquids, but may be solids or semi-solids) used to lubricate machinery parts to reduce friction and increase their lifetimes. Lubricants have a significant role in tribology, and are formulated from a range of base fluids and chemical additives. Depending on the nature of the base oil, which is the main component of lubricants, they might be categorized as mineral (petroleum origin), synthetic (e.g., polyalphaolefins, polyalkylene glycols, synthetic esters, silicones, etc.), or as a biolubricant/green lubricant. Mineral lubricants, currently the most commonly used commercial lubricants around the world, are a complex mixture of paraffinic (linear/branch), olefinic, naphthenic, and aromatic hydrocarbons of 20 to 50 carbon atoms. They are quite stable (higher oxidation stability) and less expensive than other types of lubricants. However, mineral lubricants

have poor biodegradability and release toxic materials into the environment. As compared with vegetable-based lubricants, mineral lubricants have lower viscosity indices, higher boundary friction coefficients, and a higher volatility. Moreover, the non-renewable petroleum resources used to produce mineral lubricants are depleting. In order to address the problems associated with petro-based mineral lubricants, the demand to produce environmentally acceptable lubricants from renewable resources is increasing. Lubricant additives that are produced from petroleum resources such as acrylates and zinc dialkyldithiophosphates (ZDDP) create many materials that are harmful to the environment, including heavy metals and sulfur compounds [1,2]. The friction modifier, such as molybdenum dithiocarbamate complexes used in solid lubricants, releases heavy metals and sulfur compounds, and their activity decreases with fluid aging [3]. Therefore, interest in research on bio-based lubricant additives is also increasing. Synthetic lubricants have advantages over mineral lubricants, such as they are environmentally benign, have a higher viscosity index, lower pour points, and higher oxidative stability. However, synthetic lubricants also have some disadvantages, as mentioned below:

- They are more expensive than mineral lubricants [4];
- They are relatively more toxic than vegetable oil-based lubricants;
- They are less readily biodegradable than vegetable oil-based lubricants;
- They have a lower friction tolerance and their exhausts pose problems in the environment;
- They do not work well with mineral oils.

Although biolubricants produced from vegetable oils are more costly than mineral lubricants, they are a promising alternative to synthetic and mineral oil-based lubricants because of their specific functional attributes such as high viscosity index, good lubricity, superior anticorrosion properties, high flash point, high biodegradability, and low aquatic toxicity [5,6]. With its long fatty acid chain and polar end groups, the structure of vegetable oil is amphiphilic in nature. Oils are suitable as a base stock for easily blending different kinds of environmentally acceptable additives, and are used as both boundary and hydrodynamic lubricants. Additives prepared from vegetable oils showed excellent tribological properties and performed well at extreme pressures. Li et al. [7] illustrated the application of an extract of natural garlic oil as a high-performing and environmentally friendly extreme pressure additive in lubricating oils. Ossia et al. [8] showed that eicosanoic and octadecanoic acids present in castor and jojoba oil enhanced the tribological and oxidation stability of castor and jojoba oil as well as mineral oil base-stocks. Erhan et al. [9] disclosed the use of poly (hydroxy thioether) vegetable oil derivatives as antiwear/antifriction additives for environmentally friendly industrial oils in automotive applications. Different methods of making fatty acid ester derivatives from unsaturated fatty acids through formation of their epoxides have also been described by Erhan et al. [10,11]. Doll et al. [12] disclosed a novel process of preparing chemically modified triglycerides by the reaction of epoxidized triglyceride oils or alkyl esters thereof with phosphorus-based acid hydroxide or esters. The phosphorus-containing triglyceride derivatives so produced have a found utility as antiwear/antifriction additives for industrial oils and automotive applications. Biswas et al. [13] described a method of preparing nitrogen-containing fatty acid derivatives by reacting epoxidized fatty acids, their esters, or triglyceride oils with amines of cyclic or aromatic hydrocarbons. These fatty acid derivatives are used as antiwear/antifriction additives for industrial oils and automotive applications. Heise et al. [14] described the preparation of boron-containing fatty acid derivatives by reacting epoxidized fatty acids, their esters, or triglyceride oils with borate compounds which have a found application as antifriction additives in the automotive industry.

Erickson et al. [15] disclosed the methods for preparing lubricant additives (antiwear) by combining triglyceride vegetable oils (meadowfoam oil, rapeseed oil, or crambe oil) with at least one sulfurized vegetable oil and a phosphite adduct of vegetable oil. The same group also reported the preparation of bio-based lubricant additives that comprise a combination of meadowfoam oil as a triglyceride or a wax ester, sulfurized triglyceride meadowfoam oil or sulfurized wax ester of meadowfoam oil, and phosphate adducts of triglyceride meadowfoam oil or wax ester of meadowfoarn

oil [16]. Few bio-based additives showed multifunctional performances [17–20]. Therefore, we do not need to blend different kinds of additives with the base stock. However, there are some limitations in using vegetable oils. The major component of VOs is a triglyceride of long-chain fatty acids of mostly unsaturated carbon atoms. The double bonds of the fatty acid chains are mostly unconjugated. They have low thermo-oxidative stability, poor bio-resistance, poor hydrolytic stability, and poor fluidity at lower temperatures [21–23]. Therefore, they cannot be used directly as lubricant-based stocks/additives. The presence of bis-allylic protons in the chain makes VOs very prone to oxidative degradation [24]. This ultimately results in an insoluble deposit formation in vegetable oils which increases oil acidity, viscosity, corrosion, and volatility. Another drawback of VOs is their higher cost of production compared with mineral lubricants. This cost currently prohibits the complete replacement of mineral lubricants by biolubricants for commercial purposes. These limitations can, however, be mitigated by chemically modifying VOs to reach a desirable performance level without increasing the cost. Extensive research is being conducted worldwide to produce lubricant base stocks or additives from vegetable oils more economically [25–28].

2. Chemical and Physical Properties/Characteristics of Vegetable Oils

Chemical and physical properties of VOs mainly depend on the composition of unsaturated fatty acids, which in turn depend on the climate of cultivation, genetic modification of the oil-producing crops, and so forth. Fatty acids present in vegetable oils are mostly long and straight-chained with unconjugated double bonds, and most of these unsaturated fatty acids possess a *cis* configuration (Figure 1). However, some fatty acid chains, such as ricinoleic and vernolic acids, contain hydroxyl and epoxy functional groups, respectively [29,30]. In the triglycerides of vegetable oils, such as soybean, sunflower, palm, linseed, etc., oleic acid, linoleic acid, and linolenic acid predominate. In castor oil and vernonia oil, however, ricinoleic acid (Figure 2) and vernolic acid (Figure 3) are the major constituents, respectively. Fatty acid compositions of commonly used vegetable oils are listed in Table 1. The higher the percentage of unsaturation, the better the VOs will be in preparing environmentally acceptable lubricants (base stock/additives). Vegetable oils can be classified as edible or nonedible. Coconut, olive, soybean, sunflower, palm, peanut, canola, corn, and so forth belong to the class of edible oils. Since they are used to formulate biolubricants, their demand is always very high. The non-edible vegetable oils such as neem, castor, mahua, rice bran, karanja, jatropha, linseed etc. are comparatively less expensive and therefore have an advantage over edible oils for the production of biofuel/biolubricants [31–33].
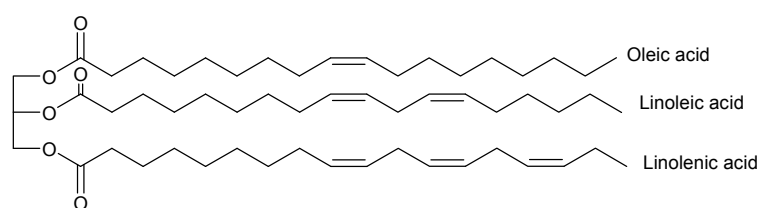

Figure 1. General structure of triglyceride esters of edible vegetable oils.

The percentage of unsaturated fatty acids, which largely varies among different types of VOs, can be determined by measuring the iodine value (IV) [34]. Larger IV values indicate a greater degree of unsaturation per vegetable oil triglyceride. Depending upon the IV values, vegetable oils can further be classified as drying oils (IV > 130), semi-drying oils (100 < IV < 130), or non-drying oils (IV < 100). The more unsaturated the fatty acid, the more susceptible it is to functionalization. Linseed oil, soybean oil, sunflower oil, castor oil, and so forth contain more than 80% unsaturated acids, and therefore can easily be chemically modified. So the derivatives of these oils are largely applied to formulate biolubricants (base stocks/additives) [17,18,20,21,29].

The quality/performance of a biolubricant depends largely on their physical properties, which include the viscosity index [35], pour point [36], flash point, cloud point [37], thermal stability [38], oxidation stability, shear stability [39], iodine value, and density. A better lubricant should have a higher viscosity index, flash point, thermo-oxidation stability, shear stability, and lower pour point and cloud point. The fatty acid compositions of different VOs are listed in Table 2.
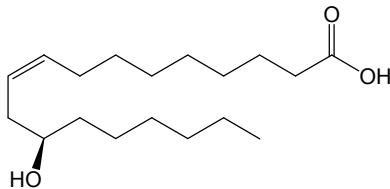

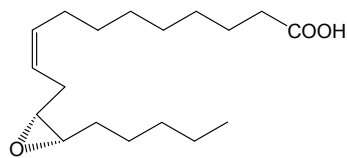**Figure 2.** Ricinoleic acid, the major content of castor oil.

Figure 3. Vernolic acid, the major content of vernonia oil.

Table 1. Fatty acid compositions of commonly used vegetable oils [40–52].

Vegetable Oils	C12:0	C14:0	C16:0	C18:0	C16:1	C18:1	C18:2	C18:3	Others
Soybean oil	-	-	11–12	3	0.2	24	53–55	6–7	-
Sunflower oil	-	-	7	5	0.3	20–25	63–68	0.2	-
Rapeseed oil	-	-	4–5	1–2	0.21	56–64	20–26	8–10	9.1 (20:1)
Palm oil	-	1	37–41	3–6	0.4	40–45	8–10	-	-
Rice bran oil	-	-	20–22	2–3	0.19	42	31	1.1	-
Cotton seed oil	-	1	22–26	2–5	1.4	15–20	49–58	-	-
Coconut oil	44–52	13–19	8–11	1–3	-	5–8	0–1	-	-
Corn (Maize) oil	-	-	11–13	2–3	0.3	25–31	54–60	1	-
Peanut/Ground nut	-	-	10–11	2–3	0	48–50	39–40	-	-
Sesame oil	-	-	7–11	4–6	0.11	40–50	35–45	-	-
Safflower oil	-	-	5–7	1–4	0.08	13–21	73–79	-	-
Karanja oil	-	-	11–12	7–9	-	52	16–18	-	-
Jatropha oil	-	1.4	13–16	6–8	-	38–45	32–38	-	-
Rubber seed oil	-	2–3	10	9	-	25	40	16	-
Mahua oil	-	-	28	23	-	41–51	10–14	-	-
Tung oil	-	-	2.67	2.4	-	7.88	6.6	80.46 *	-
Neem oil	-	-	18	18	-	45	18–20	0.5	-
Castor oil	-	-	0.5–1	0.5–1	-	4–5	2–4	0.5–1	83–85 [#]
Linseed oil	-	-	4–5	2–4	0–0.5	19.1	12–18	56.6	-
Olive oil	-	-	13.7	2.5	1.8	71	10	0–1.5	-

* Alpha-eleostearic acid. # Ricinoleic acid.

Table 2. Physical properties of vegetable oils.

Vegetable Oils	Iodine Value	Pour Point (°C)	Cloud Point (°C)	Kinematic Viscosity at 40 °C (mm^2/s)	Flash Point (°C)	Density at 15 °C (g/cm^3)	Ref.
Soybean oil	138–143	−12	−4	29	254	0.914	[53–55]
Sunflower oil	125–140	−15	−9.5	36	274	0.916	[53–56]
Rapeseed oil	98–105	−15	−2	35	246	0.912	[53–55]
Palm oil	48–58	23.6	25.2	39.4	252	0.919	[57]
Rice bran oil	103	13	16	38.2	184	0.906	[41]
Cotton seed oil	90–119	−4.5	−0.5	34	234	0.918	[41,56]
Coconut oil	8–11	12.7	13.1	27	266	0.918	[53–56]
Peanut/Ground nut/Arachis oil	84–100	−7	4.5	40	271	0.903	[53–55, 58]
Sesame oil	104–116	−11	−8	36	260	0.918	[41,56, 58]
Karanja oil	81–90	−4	2	38.8	212	0.9358	[48,49]
Jatropha oil	82–98	−6	11	34	225	0.94	[53–55]
Rubber seed oil	104	18	25	33.89	228	0.928	[59,60]
Mahua oil	58–70	11	20	37.18	238	0.945	[61]
Neem oil	81	7	13	35.8	200	0.918	[52]
Castor oil	83–86	−21	−18	251	229	0.960	[53–56]
Linseed oil	168–204	−15	5	26–29	241	0.938	[41,58]
Safflower oil	145	−7	−2	28.3	260	0.914	[53–55]
Olive oil	75–94	−14	−11	39	177	0.918	[41,56]

3. Chemical Modification/Derivatization of Vegetable Oils

Vegetable oils used directly as base stocks or lubricant additives cannot perform satisfactorily. They have lower thermo-oxidative stability, higher viscosity, and lower volatility. They burn incompletely and form deposits in fuel injectors of engines due to a high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility. Therefore, before using vegetable oils as biofuel/biolubricants, they must be chemically modified. This can be performed in two different ways: reactions at the carboxyl groups of fatty acids/esters/triglycerides of vegetable oils or reactions at the olefinic functionalities of the fatty acid chain. Transesterification of VOs is the most important initial step in producing biofuel/lubricants. Fatty acid alkyl esters along with glycerol are produced by transesterification of VOs. There are several examples in which transesterified VOs were used as a biofuel/biolubricant [62–65]. These fatty acids can be further converted into their derivatives by one or multistep strategies involving numerous reactions to produce various types of lubricants/additives based on industrial needs. Glycerol obtained from triglyceride esters can also be converted into water-based lubricant additives [66] along with other different essential chemicals.

Functionalization of the olefin functional groups of unsaturated fatty esters or free fatty acids of vegetable oils can be performed by various reactions such as epoxidization, carbonation, maleation, acrylation, hydroxylation, hydroformylation, reduction, thiol-ene addition, and polymerization to produce plasticizers, polyurethanes, adhesives, paints, coatings, and envirsonmentally friendly additives for lubricants [40,67–71]. The different modes of chemical vegetable oil transformation to produce base stocks/additives for biolubricants are discussed below.

Transesterification: Transesterification of vegetable oils with different alcohols produces fatty acid alkyl esters (and glycerol) that can be used as biofuel or biolubricants (Figure 4). Transesterification reactions can be catalyzed by both homogeneous [72,73] and heterogeneous catalysts [74] (alkalies and acids). In a transesterification reaction, homogeneous alkali catalysts are commonly used. In most cases, short-chain alcohols such as methanol/ethanol are used (for biodiesel production) as a base, and either potassium or sodium hydroxide is used as a catalyst. Potassium hydroxide is found to be more suitable for ethyl ester biodiesel production, but either base can be used for methyl ester production. As the base catalyst is mostly used for biodiesel production, fats and oil used for this purpose must be free of fatty acids (i.e., a good quality feedstock). Low quality feed stocks, including non-edible vegetable oils, animal fats, waste cooking oils, and grease, contain a significant amount of free fatty acids (FFAs) [75]. When FFAs are present, the base catalyst cannot be used because of

soap formation. Acid catalysts work much more slowly than a base catalyst in a transesterification reaction [76]. Moreover, because of the corrosive nature of acid catalysts; expensive acid-resistant reactors must be used. Therefore, in order to convert a low quality feedstock into biodiesel, first the FFAs present in the feedstock should be converted into esters with an acid catalyst to obtain a mixture of fatty acid alkyl esters and triglycerides. The esters in the second step are transesterified with methanol/ethanol catalyzed by a base to obtain biodiesel. An acid-catalyzed process, although slow and requiring a higher temperature, can be used with any type of feedstock. It is mostly used for transesterification of high free fatty acid-containing feedstock such as yellow grease, crude palm oil, and karanja, as in these cases a base catalyst cannot be used. Regardless of whether an acid or a base catalyst is used, homogeneous catalysts present certain disadvantages. Homogeneous catalysts require a high energy consumption and are corrosive (acid catalysts are more corrosive than base catalysts). They are also difficult to recover from the solution. Because of these disadvantages, the application of heterogeneous solid catalysts in the transesterification process has become more popular recently. Heterogeneous acid catalysts, such as ion-exchange resins (Amberlyst-15, Nafion) [77,78], sulfated inorganic oxides [79], inorganic superacids (WO_3/ZrO_2, WO_3/ZrO_2-Al_2O_3) [80] and basic catalysts such as alkaline earth oxides (CaO, MgO), alkali-supported catalysts (KF/K_2CO_3 or KNO_3 supported Al_2O_3) [81], zeolites [82] and guanidine-supported catalysts [83] have attracted considerable interest recently. Extensive research on preparing the biodiesel or lubricant-based stocks/additives through transesterification of vegetable oils is ongoing [61–65]. Sulek et al. showed that the friction coefficient of diesel fuel was decreased by 20% and wear by two-fold due to blending fatty acid methyl esters derived from rapeseed oil with the fuel [84]. A significant reduction of wear scar diameter from the addition of 5% rapeseed oil methyl esters in diesel fuel was disclosed by Sukjit et al. [85]. It was reported that the lubrication performance of diesel base oils was improved when palm oil methyl esters are blended [86,87]. Masjuki and Maleque (1997) reported that adding 5% (*v/v*) of palm oil methyl ester in the base oil lubricant resulted in a low wear rate of an EN31 steel ball bearing [88]. Malavolti et al. [89] has synthesized biodiesels through the transesterification of castor oil with various alcohols in the presence of trimethylchlorosilane (TMSCl) as an acidic mediator. The potential use of castor oil methyl esters as biolubricants, with its high viscosity, low pour point, and good lubricity, was explained by Madankar et al. [90].

Glycerol obtained as a co-product in the transesterification process can be converted into biofuels, green additives for water-based lubricants, foods, pharmaceuticals, cosmetics, liquid detergents, antifreeze, and toothpaste by numerous reactions including esterification [87], acetalization [40], oxidation [40], hydrogenolysis [40], internal dehydration, and oxidative carbonylation [40]. Low-cost glycerol aqueous solutions with a good biocompatibility and low temperature properties have reportedly been applied in multiple fields as a better green lubricant [91]. High molecular weight polyglycerol derivatives, useful as thickening agents for water-based lubricants, are prepared by oxyalkylation of a polyglycerol with ethylene oxide or a mixture of ethylene oxide and propylene oxide [92].
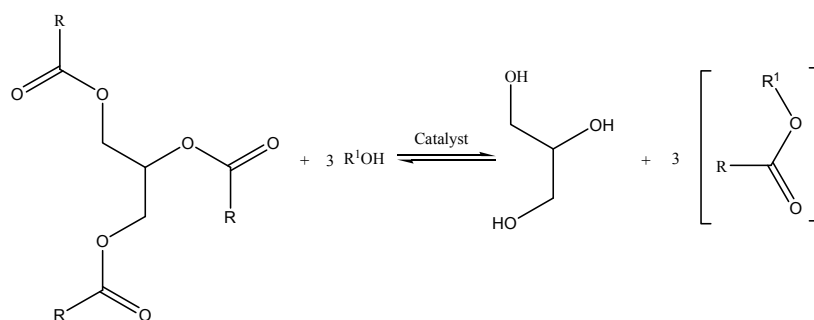

Figure 4. Transesterification of triglyceride ester of fatty acids.

Hydrolysis: The hydrolysis of triglyceride esters or the fatty esters produced from them by the transesterification process produces free fatty acids. These fatty acids are converted into their corresponding esters, used as biolubricants, when treated with higher alcohols (C8 to C14) in the presence of a suitable catalyst [93]. The process can be successfully used as an alternative method for producing biodiesel/biolubricants from waste cooking oils/fats, which otherwise have no immediate potential use [94]. The hydrolysis of oils, prior to saponification, provides the possibility of overcoming many problems associated with the recovery of the by-product glycerol. Besides biodiesel production, fatty acids are major components used to prepare a wide variety of products such as soaps, surfactants, lubricants, plasticizers, paints and coatings, pharmaceuticals, and foods and agricultural, industrial, and personal care products. Different catalysts have been used to hydrolyze VOs/fatty esters. Avisha et al. discovered a novel synthetic method to produce biolubricants by using the two-step process of *Candida rugosa* lipase-mediated hydrolysis of waste cooking oil (WCO) to FFAs followed by Amberlyst 15H esterification of them with octanol [95]. The octyl esters thus produced have been used as the desired biolubricant. Vescovi et al. also produced biodiesel from WCO via enzymatic hydrolysis followed by esterification [96]. Waghmare et al. [97] synthesized biodiesel by ultrasound-assisted enzyme catalyzed hydrolysis of waste cooking oil under solvent-free conditions. Soares et al. [98] manufactured biodiesel from soybean soap stock acid oil by hydrolysis in subcritical water, followed by lipase-catalysed esterification. Luo et al. reported the hydrolysis of vegetable oils catalyzed by SO_3H-functional Brønsted acidic ionic liquids at a moderate temperature and reaction time [99]. Syaima et al. has reported the synthesis of the biolubricant from palm oil mill effluent (POME) using enzymatic hydrolysis and non-catalytic esterification [100]. They studied the effect of different parameters such as temperature, agitation speed, enzyme loading, POME concentration, and the ratio of alcohol to fatty acids on the rate of hydrolysis and esterification reaction. The optimum hydrolysis rate was achieved at 40 °C with enzyme loading at 20 U/mL, pH 7.0, and the concentration of POME 50% (*v/v*). They also evaluated the viscosity and density of the biolubricants.

Fatty acids can easily be converted into their derivatives such as amides and amines or reduced into alcohols. These compounds are very significant for industrial application, especially as an antiwear lubricant additive.

Fatty amines: Fatty amines, obtained from fatty acids or fatty acid alkyl esters by reaction with ammonia at a high temperature followed by dehydration and hydrogenation, are used in the lubricant industry as a friction modifier in engine oils [101,102]. The preparation of fatty amines occurs in two steps (Figure 5). In the first step, fatty acids or fatty acid alkyl esters are treated with ammonia in the presence of a dehydration catalyst to form fatty nitriles. The nitriles are hydrogenated into fatty amines by a metal catalyst in the second step. Oleic acid, when treated with excess ammonia at 408 K and 35 bar, yields oleonitrile, which under catalytic hydrogenation at 413 K, gives stearyl amine with a yield close to 96% [40,103]. These additives are far better than the commercial ZDDP type antiwear additives.
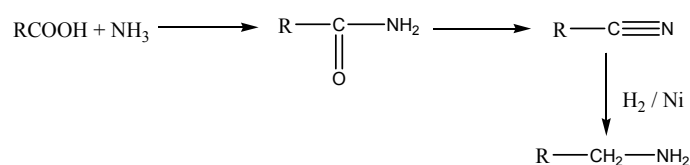

Figure 5. Preparation of fatty amine.

The use of a partly neutralized fatty amine salt as a friction modifier for lubricating oil, especially for an internal combustion engine, was claimed by Lundgren [104,105]. The inventor found that a partially neutralized fatty amine salt works as an excellent friction modifier for a lubricating oil to be used in an internal combustion engine or a gearbox. Laufenberg et al. [106] disclosed the production of lubricant concentrates and aqueous lubricant solutions containing at least one polyamine derivative

of a fatty amine and/or a salt of such an amine for lubricating, cleaning, and disinfecting automatic chain and belt conveyor systems.

Fatty amides: Fatty amides can be prepared by base catalyzed aminolysis of fatty acids or esters using ammonia or a primary or secondary amine (e.g., dimethylamine, ethanolamine, isopropanolamine, or diethanolamine). These amines are valuable in preparing a wide variety of value-added materials, such as cleaners, fabric treatments, hair conditioners, personal care products (liquid cleansing, conditioning bars, oral care), antimicrobial compositions, agricultural uses, and most importantly, as an antiwear additive in oil field applications. Pramanik et al. [107] reported the effect of soybean oil-based fatty amides as a rheology modifier additive in coatings. It has been reported that the fatty amide formed by reacting fatty acids with diethanolamine was used as an active ingredient to manufacture dry cleaning soaps, fuel oil additives, rust inhibitors, textile scouring, dye leveling agents, and woolen cloths [108,109]. Amides prepared from hydrogenated soybean oil or coconut oil glycerides and a hydroxyalkyl polyamine have been reported as an ingredient useful in lubricating and softening textile materials such as rayon fabrics [110]. The lubricity of fuels can be increased by blending and adding fatty amides. Gentry et al. disclosed the application of alkanolamide of a fatty acid, an alkanolamide of a modified fatty acid, or a mixture as lubricity aids in low sulfur diesel fuels and spark ignition fuels [111]. It was reported that a modified mixed amide derived from the reaction of a substantially saturated fatty acid triglyceride with a deficiency of dialkanolamine, either alone or in combination with a sulfurized substantially unsaturated fatty acid triglyceride, were used as an improved friction modifier or antiwear additive to crankcase oils [112].

Fatty alcohols: Fatty alcohols or their derivatives can be used for the production of different industrially useful materials such as biolubricants, plasticizers, surfactants, etc. Fatty alcohols are easily obtained from fatty esters of vegetable oils/natural fats by catalytic reduction reaction. The selective reduction of unsaturated esters to unsaturated alcohols is generally performed by a metal-based solid hydrogenation catalyst under high pressure and temperature. Methyl oleate was converted into the corresponding unsaturated alcohol selectively when treated with Ru-Sn-B/Al$_2$O$_3$ catalysts at a high temperature (523–573 K) and pressure (25–35 MPa) in a liquid-phase slurry-bed process [113]. Giraldo et al. developed an environmentally friendly Ni-Cu-Zeolite as a bimetallic catalyst for selective hydrogenation of the preparation of palm oil-based fatty alcohols [114]. The larger chain alcohols are suitable for producing biofuels and as non-ionic surfactants or emulsifiers, as well as emollients and thickeners in the cosmetics and food industries. Mueller et al. disclosed information on the application of linear and/or branched fatty alcohols (containing at least 12 carbon atoms) or mixtures of such fatty alcohols with carboxylic acid esters as a lubricating additive in water-based drilling fluids used in geological exploration [115]. The fatty alcohol-based lubricants or lubricant systems are particularly suitable for use in water-based alkali metal silicate drilling muds, which are known to be distinguished by comparatively high pH values. These fatty alcohols are also used as an antifoam additive for lubricants.

Epoxidation of fatty acids/esters and their application as a biolubricant: One of the most important steps in preparing a biolubricant (base stock and/or additive) from vegetable oils is the epoxidation of its olefinic functionalities. The epoxidation of free fatty acids/esters/vegetable oils can be carried out in the presence of peracids through an in-situ or ex-situ process by varying the reaction parameters: reactant molar ratio, temperature, nature of the solvent, presence or absence of a catalyst (mineral acids/ion exchange resins), stirring speed, type of peroxyacid (peracetic, performic, m-chloroperbenzoic acid), mode and rate of the addition of H$_2$O$_2$/acetic or formic acid, the reaction period, and contacting patterns (batch/semi-batch mode/azeotropic distillation) [116–118]. To avoid the corrosive nature and undesirable side reactions (ring opening of oxirane) of mineral acids, heterogeneous catalyst systems such as acidic ion exchange resins [119], transition metal-based catalysts such as Ti-silica [120], Nb(V)-silica [121], sulfated-SnO$_2$ [122] and polyoxometalate [123] have become known recently for their ability to perform the epoxidation reaction. To characterize the epoxidation products, different analytical methods, such as measurement of the iodine value,

oxirane content, FTIR, ^{1}H NMR, and ESIMS are performed. Iodine values of the FAMEs (fatty acid methyl esters) and vegetable oils expressed as gram per 100-gram sample (g per 100 g) are generally determined according to Wij's method [124]. Alves et al. (2013) found that modified vegetable oils such as epoxidized sunflower and soybean oils resulted in a lower friction coefficient than the mineral and synthetic oils [125].

Because of their higher reactivity, the oxirane rings of the epoxides can easily be opened by different reagents such as acids, alcohols, thiols, and amines to provide different value-added compounds such as biolubricants (base stocks/additives), bio-plasticizers, and other industrially useful chemicals. The epoxidized vegetable oils/fatty esters are used to prepare antiwear/antifrictional additives for lubricants. Because of their higher solubility in biodegradable vegetable oils and synthetic esters, these additives showed a considerably better performance than conventional petroleum-based additives. Schafer et al. described the development of corrosion-protection additives from an epoxidized methyl ester of an unsaturated fatty acid and a sulphonic acid [126]. Rowland et al. disclosed different antifrictional additives from an epoxidized ester of fatty acids to reduce lead corrosion in lubricants and fuels [127]. Lathi et al. discussed the preparation of lubricant base stock/additives by opening the rings of epoxidized soybean oil with different alcohols (n-butanol, iso-amyl alcohol, and 2-ethylhexanol) followed by esterification of the resulting hydroxy group through alcoholysis using the same catalyst [128]. The furnished lubricants showed significant improvement in pour point values. It was further observed that as the chain length of branched alcohol increased, it gives lower pour point values and 2-ethylhexanol showed lowest pour point value as compared to other alcohols. Hydroxy thio-ether derivatives of vegetable oils prepared by opening the epoxy rings of epoxidized soybean oil with common organic thiols are used as sustainable antiwear/antifrictional additives for lubricants [129,130]. The incorporation of sulfur in the triglyceride backbone in this process introduces polar functionalities in the molecule which improved the adsorption power of the derivatives on metal surface resulting in reduced wear and friction coefficient. They showed better antiwear performance compared to commercial additive packages. Ester hydroxy derivatives of methyl oleate, obtained by opening the epoxy rings of epoxidized methyl oleate by different organic acids (propionic, levulinic, octanoic, hexanoic, or 2-ethylhexanoic acid) showed better pour point and cloud point values [28]. They also showed improved thermo-oxidation stability and tribological and lubricity properties when used as lubricant additives. The opening of epoxy rings with different amines produces substituted derivatives of β-amino alcohols that are used in the medical field as antioxidant derivatives for lubricants [131]. Carbonated derivatives of fatty esters, which are also used to prepare biolubricants and other essential value-added materials, can easily be prepared from epoxy derivatives of fatty esters/vegetable oils [132].

The opening of the epoxy rings of vegetable oils/fatty derivatives to produce different value-added compounds that have an application in the formulation of biolubricants are shown in Scheme 1.
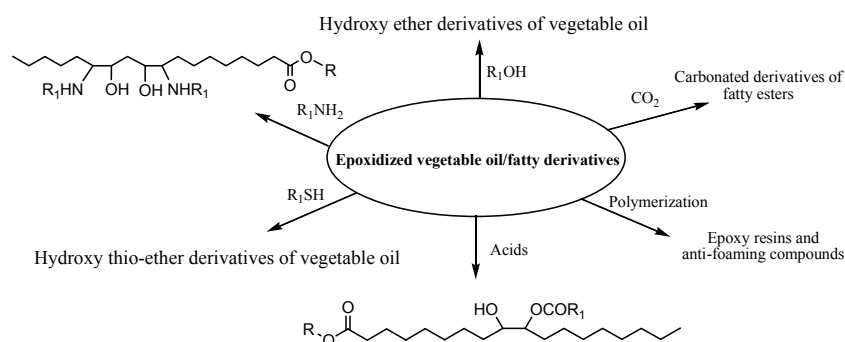
Scheme 1. Epoxidized vegetable oil/fatty derivatives as a starting material to prepare different biolubricants/additives for lubricants.

Conversion of the olefinic functional groups into cyclic carbonates and the use of different nucleophiles to open the rings: Cyclic carbonates are attractive green intermediates that are non-toxic, biodegradable, and can easily be prepared by coupling carbon dioxide with epoxy fatty esters (Figure 6). Fatty ester carbonates have the physical and chemical properties useful for preparing different valuable chemicals for many applications [132–135]. There are two main benefits of the conversion of fatty acid derivatives/epoxidized oils into cyclic carbonates. The first one is the preparation of novel materials from renewable resources, and the second is recycling and exploiting of carbon dioxide into the value chain. The coupling reaction of epoxides with CO_2 is an intensively studied field of research, and various homogeneous and heterogeneous catalysts have been reported for this reaction [133–135]. Han et al. [136] employed imidazolium-based ionic liquids with varied alkyl chain lengths bearing different anions as a heterogeneous catalyst for preparing cyclic carbonates. Tamami et al. reported on the synthesis of carbonated soybean oil from epoxidized soybean oil at an atmospheric CO_2 pressure using tetra-n-butylammonium bromide ([Bu_4N]Br) as a catalyst [137]. An improved protocol for the synthesis of carbonated oleo compounds was described by Doll et al. [133]. They have synthesized carbonated methyl oleate and carbonated methyl linoleate from epoxy derivatives of fatty esters using supercritical carbon dioxide directly with a catalytic amount of tetrabutylammonium bromide. The synthesized compounds have potential uses as industrial lubricants or fuel additives. Shorter chain linear carbonates are useful as emollients, and longer chain carbonates have been used as lubricants and fuel additives [138].

Schäffner et al. [67] tested simple alkali halides combined with a phase transfer catalyst in the reaction of epoxidized methyl linoleate with CO_2 to prepare the respective bis-carbonate. Sodium iodide and 15-crown-5 as well as the combination of potassium iodide and 18-crown-6 were proven to be very active catalyst systems in the model reaction at 100 °C, 100 bar, and 17 h with a conversion of 94% and 90%, respectively [139].

The carbonated ring of the fatty esters can easily be opened by a variety of nucleophiles to produce phthalate-free bio-plasticizers [140], non-isocyanate polyurethane [141], biolubricants [68], adhesives, and many other value-added products.
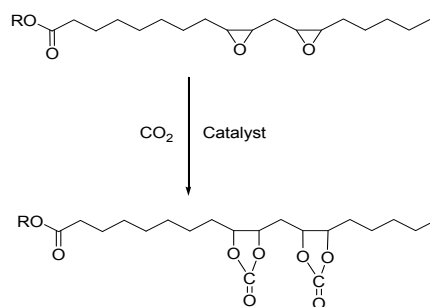

Figure 6. Carbonation of epoxy fatty esters.

Polymerization and preparation of polymer nanocomposites: Biolubricants (additives/base stocks) can also be prepared through homopolymerization of vegetable oils/fatty esters or their epoxy derivatives or copolymerization with suitable co-monomers. Polymerization of vegetable oil or their derivatives can be conducted by different techniques, e.g., cationic, free radical, ring opening, and condensation polymerization. Thermally polymerized soybean oil mixed with additives and diluents was used as a bio-based gear oil [142]. In our previous work, free radical polymerization of vegetable oils and their application as eco-friendly lubricant additives has been discussed [17–19,143,144]. Biresaw et al. [145] described the application of bio-based polyesters as an extreme pressure additive in mineral oil. The synthesis and evaluation of telomerized vegetable oil, sulfurized and phosphorus derivatives of telomerized vegetable oils, and combinations thereof for use as thermal oxidative stability enhancers and viscosity improvers have been reported by Landis [146]. Telomerization

induces vegetable oil that contains no more than 4% polyunsaturated fatty acids to help enhance its thermo-oxidative stability. The invention is further related to telomerized triglyceride vegetable oils as a lubricating composition base stock substitute. Recently, relatively new polymerization methods such as acyclic diene metathesis polymerization [147] and ring-opening metathesis polymerization [148,149] of functionalized fatty alcohols have been employed to synthesize vegetable oil-based polymers as well. Polymerization of vegetable oils/derivatives in the presence of different organic or inorganic nanofillers produces polymer nano-composites, which are extensively applied in the automotive industry, especially as an antiwear coating/additive in lubricants [150].

4. Conclusions

In this short review we highlighted the chemical transformation of vegetable oils to produce different materials that have an application in the formulation of biolubricants. The study is significant in the present context of increasing global environmental pollution and decreasing petroleum resources. The main advantages of vegetable oil-based lubricants are its high biodegradability and low aquatic toxicity. Recently bio-based lubricants are blended with commercial ones to prepare eco-friendly lubricant compositions. However, we have not yet been able to completely replace the commercial mineral lubricants with bio-based lubricants. This is due to the current lower production of vegetable oils which increases the cost of bio-based lubricants compared with petroleum-based ones Although the vegetable oil-based lubricants (base fluids or additives) are more costly than commercial petroleum-based lubricants, they are emerging as future green products because of their nontoxic and biodegradable nature. These oils have a higher viscosity index, better wear performance, higher flash point, and lower pour point and cloud point than other lubricants. Research is still being conducted to develop a new methodology for manufacturing biolubricants from vegetable oil-based materials that would be more economical and greener, and will one day replace mineral oil-based lubricants with bio-based products in environmentally sensitive applications.

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