A Review on Eco-Friendly Green Biolubricants from Renewable and Sustainable Plant Oil Sources

Nadia Salih ^{1,*}^(D), Jumat Salimon ¹^(D)

- ¹ Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia; nadiaalnami@hotmail.com (N.S.); jumatsal@gmail.com (J.S.);
- * Correspondence: nadiaalnami@hotmail.com;

Scopus Author ID 24072094400 Received: 17.12.2020; Revised: 28.01.2021; Accepted: 2.02.2021; Published: 8.02.2021

Abstract: The seed oils of domesticated oilseed crops are major agricultural commodities used primarily for nutritional applications, but in recent years, there has been increasing use of these oils to produce biofuels and chemical feedstocks. This is being driven in part by the rapidly rising costs of petroleum, increased concern about the environmental impact of using fossil oil, and the need to develop renewable domestic sources of fuel and industrial raw materials. Biolubricants are gaining popularity and acceptance globally due to their sustainable, non-toxic, and environmentally friendly properties. Besides that, they are also derived from renewable plant-based oils. The chemical structure of the base oil of the biolubricant is the key determinant of its biodegradability. Many factors like humidity, pressure, metal type, air, and temperature change the chemical composition of base oils used in biolubricants. In other words, biodegradability hinges on how the chemical structure of the base oil changes during service. National and international labeling programs have been developed to minimize confusion in the marketplace, increase public awareness, and create thoughtfulness for environmentally preferable products. The labeling programs can aid in removing uncertainty in buying environmentally preferable products. This review highlights the recently published data and works of literature related to the development of green biolubricants, biolubricant advantages/disadvantages, chemical modification reactions, biolubricants worldwide eco-labeling, biodegradability, and toxicity testing methods.

Keywords: plant oil-based biolubricants; renewable resources; biodegradability; ecofriendly green biolubricants.

© 2021 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Renewable raw materials are playing an essential role in developing environmentally sustainable products. The consumption of oils and fats from plant and animal origin increases as the trend moves towards more eco-friendly products. It offers a large number of possibilities for applications that petrochemical resources can rarely meet. Lubricants are essential for almost all aspects of modern machinery. As the name implies, lubricants are substances used to lubricate surfaces in mutual contact to facilitate the movement of components and reduce friction and wear. When sustainability has become a driving force in the industry, saving energy and resources and cutting emissions, have become central environmental matters. Therefore, the scarcity of resources and the responsibility towards future generations are also a particular focus of corporate action [1, 2]. Lubricants are increasingly attracting public awareness because they support sustainability targets in economic, ecological, and social areas.

Lubricants contribute to the sparing use of resources and thereby to sustainability. Choosing the suitable lubricant for the application helps extend the lifespan of machinery and its components and increase efficiency and reliability.

A significant portion of the lubricants consumed worldwide ends up polluting the environment. Many efforts are made to minimize spillages and evaporation. These high lubricant losses into the environment were behind the development of environmentally friendly biolubricants [3-5]. Also, the idea that oil soon may no longer be available, industries have been searching for a cheap, renewable source of lubricant as we know that non-edible uses of plant oils have grown little during the last few decades. Although some markets have been explored based on plant oil oriented products, still there are many bright scopes of expansion in the field of plant oils [6-9].

Many countries like the USA, Canada, Brazil, India, Malaysia, Indonesia, etc., have great potential of producing edible and non-edible tree-borne oils, which remain untapped and can be used as a potential source for plant oil-based biolubricants. Increased markets for such uncommon seeds oils such as rapeseeds, castor, Jatropha, Karanja, etc., and plant oils such as canola, soy, sunflower, palm oils, etc., could increase farmer incomes and maximize the application of agricultural products. Plant oils have superb environmental credentials, such as being inherently biodegradable and having low toxicity towards humans, being derived from renewable resources, and contributing no volatile organic chemicals, due to which they are used in various industrial applications such as emulsifiers, biolubricants, plasticizers, surfactants, plastics, solvents, and resins. Although plant oils possess many desirable characteristics, currently, they are not widely used as biolubricant base oils. Mainly this is due to undesirable physical properties of most plant oils viz. poor oxidation stability, poor lowtemperature properties, poor viscosity index, etc. [10-13]. However, through the cutting edge technology, knowledge, and modification processes, plant oils based biolubricants has reached superb lubrication properties at par with the common lubricants. In this review, our motivation is to provide a perspective on the current situation of plant oil production in the world, lubricant demand, biolubricants biodegradability/toxicity, and worldwide eco-labeling system.

2. Lubricants Demand

According to a new report published by Grand View Research, the global lubricants demand size is expected to reach \$68.54 billion by 2022 (Figure 1). Growing demand for oilfield chemicals due to increased drilling and exploration activities is likely to positively impact the market.



Figure 1. Global lubricants market volume by product, 2012 – 2022 (Million Tons).

Growing sales of motorcycles, high demand for heavy-duty trucks and other commercial vehicles, and lightweight passenger cars have increased production in the automotive sector globally, which is considered favorable for developing lubricants demand [14].

However, the underlying regional lube market dynamics of the past 15 years were enormous in terms of quantity and quality. The Asia-Pacific region, Africa, and the Middle East accounted for a little more than one-third of global volume in 2000 and now makes more than half of it due to growing industrialization and motorization and, consequently, higher consumption. Western Europe and North America's mature markets experienced a continuous move to more quality lubricants, which resulted in extended oil change intervals and, consequently, lower demand per year. Asia-Pacific today consumes twice the lubricants amount per year than North America [15].

Since 1975, quantitative lubricant demand has significantly detached itself from gross national product and the number of registered vehicles. This quantitative view, which at first glance shows a continuous decline in lubricant volumes, gives an inadequate impression of the significance of the lubricants business today. In almost all areas, products now have a longer life and offer greater performance that is specific lubricant consumption has declined, but specific revenues have increased noticeably. This is also confirmed by the volumetrically significant group of engine oils: The doubling of requirements with extended oil change intervals in recent years has quadrupled the cost of such oils. The efforts to increase the life of lubricants are not based on the wish to reduce lubricant costs. Much more important is reducing service and maintenance costs resulting from periodic oil changing or regressing [16].

As about 50% of the lubricants sold worldwide end in the environment polluting it, every effort is made to minimize spillages and evaporation. An example is diesel engine particulate emissions, about a third of which are caused by engine oil evaporation. These high lubricant losses into the environment were behind the development of environment-friendly lubricants. A further incentive to reduce specific consumption is the ever-increasing cost of disposal or recycling of used lubricants. But this again creates new demands on lubricants because reduced leakage losses mean less topping-up and less refreshing of the used oil. The new oils must, therefore, display good aging stability [17].



Figure 2. Comparing regional per capita lubricant demand between 2007 and 2017.

Another consequence of the aforementioned developments was global consumption per capita. The Asia-Pacific region and the Rest of the World (ROW) accounted for little more than 35% of global volume in 2007. At 2017 makes more than 43% of the total volume due to growing industrialization, motorization, and consequently higher consumption (Figure 2). The mature markets, Western Europe and North America experienced a continuous move to higher quality lubricants with longer oil drain intervals, which produced lower consumption due to these efficiencies. Europe and the Americas lost in equal relative terms what Asia-Pacific and the ROW gained with regard to lube volume consumption. The Asia-Pacific region, sharing 43% of global demand, consumes twice the lubes per annum than North America does, with a share of about 18%. Even more impressive was the fact that North America's lube consumption per capita of 20kg was still twice as much as Western Europe's 10kg, which of course was the result of a quantity vs. quality issue [18].

Considering the growth potential in Asia, where per capita consumption in some areas is still extremely low and a continuing reduction in volumes or stagnation in Western industrialized countries, overall, a modest global growth is forecast. The value growth will be more pronounced because the rapid globalization of technologies will promote high-value products even in the developing and emerging lubricant markets such as India. The machines and plants used in these countries will be similar or identical to those used in the developed industrialized countries [19, 20].

3. Plant Oils

Plant oil is the fat extracted from plant sources. We may extract oil from other parts of a plant, but seeds are the primary plant oil source. The plant oils are classified on different bases, which are given below [21]:

- i) Classification based on source:
 - tree crop oil: palm oil, coconut oil, and olive oil;
 - annual crop oil: groundnut oil, sunflower oil, etc.;
 - by-product oil: rice bran oil and soy bean oil.
- ii) Classification based on availability:
 - major oil: coconut oil, groundnut oil, sunflower oil, soybean oil;
 - minor oils: almond oil, apricot oil, avocado oil, and candlenut oil.
- iii) Classification based on end use:
 - edible oils: coconut oil, sunflower oil, soybean oil, and palm oil;
 - non-edible oils: castor oil, Jatropa curcas oil and Jojoba oil, etc.

3.1. Plant oils chemical structure.

Chemically, plant oils are completely different from mineral oils. The major component of plant oils is triacylglycerols (TAGs) (98%) with varying fatty acids composition depending on the plant, the crop, the season, and the growing conditions. The minor components of plant oils are diacylglycerols (DAGs) (0.5%), monoacylglycerols (MAGs) (0.2), fatty acids (FAs) (0.1%), sterols (0.3%), and tocopherols (0.1%) [56] (Figure 3). Most of these minor components are removed in processing, and some are valuable by-products.

Plant oil composition is expressed in terms of their building units, "fatty acids", which are long-chain molecules with 8-24 carbon atoms. Plant oils' efficacy is determined by their chemical composition, which varies from place to place due to various geographical factors.

Since fatty acids make larger portions of triacylglycerols, most of the plant oils' physical and chemical properties result from the constituent fatty acids [22-24].



Figure 3. Systematic representation of the major component (TAG) and the minor components (DAG, MAG, FAs, sterols, tocopherols) of plant oils.

The TAGs that are found in oilseeds usually display the saturated fatty acids in the *sn*-1,3 positions, whereas the *sn*-2 position of glycerol is esterified to an unsaturated or polyunsaturated acyl moiety. This is caused by the specificity of the different enzymes participating in their biosynthesis. Tri-saturated fatty acids are not common in plants growing in temperate climates, but they can be found in oils from tropical species, mainly in palm oil and lauric fats (coconut and palm kernel fats). They are not suitable for lubrication due to their high melting points (Table 1), so they should be removed from native oils by fractionation techniques [25-27].

TAG type	Name	Melting point (°C)	Viscosity at 80 °C (cST)
Trisaturated	Glyceryl tripalmitine	66.4	13.17
	Glyceryl tristearate	73.5	16.31
Disaturated	Glyceryl distearate oleate	42.0	-
	Glyceryl distearate linoleate	37.0	-
	Glyceryl palmitate oleate stearate	37.0	-
Monosaturated	Glyceryl palmitate dioleate	18.5	-
	Glyceryl palmitate dioleate	23.0	-
	Glyceryl palmitate dilinoleate	-3.0	-
	Glyceryl stearate oleate linoleate	-4.0	-
Triunsaturated	Glyceryl trioleate	-5.0	12.22
	Glyceryl trilinoleate	-11.0	-
	Glyceryl trilinolenate	-24.2	-

Table 1. Properties of some common triacylglycerol species.

3.2. Plant oils' general properties.

Plant oils are esters of glycerol with fatty acids except for the jojoba oil, consisting of esters of fatty acids with long-chained alcohols. The chain length of these fatty acids usually ranges from C_{12} to C_{22} . So, fatty acids account for about 85% of the plant oils' weight, determining their properties. Plant oils' properties are directly proportional to the fatty

composition of triacylglycerols, closely related to their source [28]. Table 2 presents the fatty acid compositions of some commonly used plant oils.

	Fatty acid								
Plant oil	C12:0	C14:0	C16:0	C18:0	C16:1	C18:1	C18:2	C18:3	Others
Castor	-	-	0.5-1	0.5-1	-	4-5	2-4	0.5-1	83-85#
Coconut	44-52	13-19	8-11	1-3	-	5-8	0-1	-	-
Corn	-	-	11-13	2-3	0.3	25-31	64-60	1	-
Jatropha curcas	-	1.4	13-16	6-8	-	38-45	32-38	-	-
Karanja	-	-	11-12	7-9	-	0.08	13-21	73-79	-
Linseed	-	-	4-5	2-4	0-0.5	19.1	12-18	56.6	-
Mahua	-	-	28	23	-	41-51	10-14	-	-
Neem	-	-	18	18	-	45	18–20	0.5	-
Olive	-	-	13.7	2.5	1.8	71	10	0-1.5	-
Palm	-	1	37-41	3-6	0.4	40-45	8-10	-	-
Peanut	-	-	10-11	2-3	-	48-50	39-40	-	-
Rapeseed	-	-	4-5	1-2	0.21	56-64	20-26	8-10	-
Saffower	-	-	5-7	1-4	0.08	13-21	73-79	-	-
Soybean	-	-	11-12	3	0.2	24	53-55	6-7	-
Sunflower	-	-	7	5	0.3	20-25	63-68	0.2	-

Table 2. Fatty acid compositions (%) of commonly used plant oils [29-34].

#Ricinoleic acid

Fatty acids are carbon chains containing 4 to 24 carbon atoms and are classified according to the different degrees of unsaturation: saturated, monounsaturated, and polyunsaturated [35]. Saturated fatty acids are those fatty acids that do not contain any double bonds between their carbon atoms. They exhibit relatively high melting points and are the most chemically stable due to the molecule's conformation. Therefore, as the number of carbons in the chain increases, the fatty acid's melting point also increases [36]. Examples of saturated fatty acids include stearic acid (C_{18:0}), palmitic acid (C_{16:0}), myristic acid (C_{14:0}), lauric (C_{12:0}), and butyric acid (C_{4:0}).

Monounsaturated fatty acids are fatty acids with only one double bond between the carbon atoms. This double-bound can be trans or cis configuration. If stored properly, they can be relatively resistant to rancidity and are liquid at room temperature. However, they are less stable to oxidation than saturated fatty acids [37]. Erucic acid (C_{22:1}), oleic acid (C_{18:1}), and palmitoleic acid (C_{16:1}) are some of the examples of monounsaturated fatty acids. Meanwhile, polyunsaturated fatty acids (PUFAs) are fatty acids that are characterized by the presence of two or more double bonds in their carbon chain and are typically liquid at room temperature. The higher the number of unsaturations implies a higher biological and oxidative instability of polyunsaturated fatty acids [38]. Examples of polyunsaturated fatty acids are tetracosapentaenoic acid (C24:5), docosatetraenoic acid (C22:4), docosapentaenoic acid (DPA) (C_{22:5}), arachidonic acid (C_{20:4}), linolenic acid (C_{18:3}), and linoleic acid (C_{18:2}). The compositions of fatty acids of the oils can be determined by different analytical methods such as nuclear magnetic resonance (NMR) spectroscopy [39-41], gas chromatography (GC) [42, 43], high-performance liquid chromatography (HPLC) [44, 45], near-infrared transfectants spectroscopy (NITR) [46], and Fourier transform infrared spectra [47, 48].

Plant oils are obtained from oil containing fruits, nuts, or seeds by distinctive solvent extraction, processing methods, or a combination of both [49]. Unrefined oils obtained are exposed to several refining processes, both chemically and physically. The plant oils' physicochemical properties are dependent on fatty acid distribution. The number of double

bonds as well as their positions within the aliphatic chain strongly affects the properties of the oil. Table 3 summarises some relevant properties of common plant oils and fatty acids. The actual number of carbon atoms making up the aliphatic chains performs an extremely less significant part, simply because most of these triacylglycerols have 18 and a few 16 carbon atoms [50]. Iodine number estimates the degree of unsaturation of the fats and oils. It is the number of iodine in grams consumed by 100 g of a chemical substance under investigation. Based on their iodine value, plant oils are sub-divided into three categories. Therefore, oils are classified as "non-drying" if their iodine value is below 90, "semi-drying" if the factor comprised is between 90 and 130, and "drying" if the iodine value is greater than 130 [51].

Name	Viscosity (mpa ^{-s})	Specific gravity	Refractive index	Melting point (°C)			
Oleic acid	3.41 at 110 °C	0.850 at 80 °C	1.445 at 60 °C	16.3			
Stearic acid	2.79 at 110 °C	0.839 at 80 °C	1.4337 at 70 °C	69.6			
Palmitic acid	3.47 at 110 °C	0.841 at 80 °C	1.421 at 70 °C	62.9			
Myristic acid	2.78 at 110 °C	0.844 at 80 °C	1.427 at 70 °C	54.4			
Sunflower oil	33.31 at 37.8 °C	0.916 at 20 °C	1.473-1.477 at 20 °C	-17			
Soybean oil	31.80 at 37.8 °C	0.917 at 20 °C	1.473-1.477 at 20 °C	-16			
Palm oil	30.92 at 37.8 °C	0.890 at 20 °C	1.453 - 1.456 at 20 °C	35			
Linseed oil	29.60 at 37.8 °C	0.925 at 20 °C	1.480- 1.483 at 20 °C	-24			
Castor oil	293.40 at 37.8 °C	0.951 at 20 °C	1.473 - 1.480 at 20 °C	-18			
Rapeseed oil	44.90 at 37.8 °C	0.920 at 20 °C	1.472 - 1.476 at 20 °C	-10			
Erucic acid	32.30 at 37.8 °C	0.912 at 20 °C	1.453 - 1.447 at 20 °C	33.8			
Ricinoleic acid	15.44 at 37.8 °C	0.940 at 20 °C	1.469 - 1.472 at 20 °C	5.5			

Table 3. Some specific physical properties of triacylglycerols oils and fatty acids [47-50].

There are numerous plant oils derived from various sources. These include the popular plant oils: the foremost oilseed oils - soybean, cottonseed, peanuts and sunflower oils; and others such as palm oil, palm kernel oil, coconut oil, castor oil, rapeseed oil and others. They also include the less commonly known oils such as rice bran oil, tiger nut oil, patua oil, koėme oil, niger seed oil, piririma oil and numerous others. Their yields, different compositions and, by extension, their physicochemical properties determine their usefulness in various applications aside from edible uses.

Cottonseed oil was developed over a century ago as a by-product of the cotton industry [49]. Its processing includes the use of hydraulic pressing, screw pressing, and solvent extraction [52]. It is classified as a polyunsaturated oil, with palmitic acid consisting of 20-25%, stearic acid 2-7 %, oleic acid 18-30%, and linoleic acid 40-55% [53]. Its primary uses are food-related - as a salad oil, frying, margarine manufacture, and manufacturing shortenings used in cakes and biscuits.

Palm oil, olive oil, cottonseed oil, peanut oil, and sunflower oil are classed as oleic – linoleic acid oils, seeing that they contain a relatively high proportion of unsaturated fatty acids, such as monounsaturated oleic acid and polyunsaturated linoleic acid [54, 55]. They are characterized by a high ratio of polyunsaturated fatty acids to saturated fatty acids. They, thus, have relatively low melting points and are liquid at room temperature. Iodine values, saponification values, specific compositions, melting points, and other physical properties have been determined and widely available in the literature [56, 57].

Other plant oils fall under various classes, such as erucic acid oils, oleic acid oils, linoleic acid oils and lauric acid oils. These are due to their specific dominant fatty acids content in oils. Rapeseed and mustard seed oil are important oils in this class. Canola oil is a type of rapeseed oil with reduced erucic acid content [58], used in salad dressings, margarine, and

shortenings. Soybean oil is an important oil with numerous increasing applications in the modern-day world. It is classed as a linolenic acid oil since it contains the more highly unsaturated linolenic acid. Other oils include castor oil, which contains triacylglycerols of ricinoleic acid [59]. Also worthy of note is that coconut oil, unlike most plant oils, is solid at room temperature due to its high proportion of saturated fatty acids (92%), particularly lauric acid. Due to its almost homogenous composition, coconut oil has a reasonably sharp melting point, unlike other fats and oils, which melt over a range [49]. Oils from several sources are the subject of recent researches. Examples include corn oil [60], *Camelina sativa* oil [61], Palmarosa oil [62], and Cineole oil [63].

3.3. Plant oils lubrication properties.

Plant oil as a replacement for conventional mineral-based lubricant has gained much interest in recent years. This is due to the problematic issues with using a conventional mineral-based lubricant that can cause negative effects on the manufacturing cost, operators' health, and the environment. Several studies have proven that mineral-based lubricants may contain carcinogenic additives and impurities in their formulation, which causes dermatitis and skin cancer. Furthermore, mineral oil is inferior in biodegradability, with a range of 15-35% biodegradation. The said biodegradation values are below the accepted guideline for environmentally acceptable lubricant, 80% [64-67].

The rise in environmental issues and health concerns from mineral oil use causes the plant's increased use as the base oil of a biolubricant. The triacylglycerols inside the chemical structure of plant oils with three long chains of fatty acids contributed to the biolubricants having desirable lubricating properties. Furthermore, plant oils have a high viscosity index, miscibility with other fluids, very low volatility due to the high molecular weight of the triacylglycerol molecules, etc., making them the best alternative to mineral oil. Besides, plant oils have high solubilizing power for polar contaminants and additive molecules. Also, most plant oils have separate regions of polar and nonpolar groups in the same molecule. The presence of polar groups in plant oil makes it amphiphilic, allowing it to adhere to metal surfaces and possess good lubricity [68]. So, using plant oils as a biolubricants base stock have many advantages, however, their usage has been restricted due to low oxidation properties and poor low-temperature properties.

3.3.1. Low oxidative stability.

Plant oils are low in oxidative stability due to the double bond (C=C) in their fatty acid composition. The higher the composition of unsaturated fatty acids (double bond), the more susceptible plant oils to the oxidation process. Plant oils that undergo the process of oxidation will increase in their viscosity and produce varnish and sludge deposits, which degrades the quality of plant oils. Table 4 shows the composition (%) of unsaturated and saturated fatty acid inside several types of plant oils. Table 6 shows that most of the plant oils have a high composition of unsaturated fatty, which means that most of the plant oils are susceptible to oxidation [69].

 Table 4. The saturated/unsaturated fatty acid compositions (%) of commonly used plant oils.

Plant oil	Fatty acid compositions (%)			
	Saturated	Unsaturated		
Jatropha curcas	12.6	87.4		
Safflower	9.6	90.3		

	Fatty acid compositions (%)			
Plant oli	Saturated	Unsaturated		
Sunflower	12.3	87.3		
Soybean	15.1	84.4		
Corn	19.5	80.5		
Canola	11.5	88.5		
Hazelnut	13.8	86.2		
Coconut	92.1	7.8		
Palm kernel	82.1	17.8		
Palm	49.9	49.7		
Jojoba	3.6	96.4		
Rapeseed	7.5	92.5		
Olive	19.4	80.6		
Linseed	9.4	90.6		
Mahua	49.3	49.7		
Flax seed	8.83	91.18		

3.3.2. Poor low-temperature properties.

The other issue that restricted using plant oils as biolubricant base stock is that they have poor low-temperature properties. This can cause the biolubricant to exhibit cloudiness, precipitation, poor flow ability, and solidification at room condition temperature (24°C). There is a contradicting opinion on the source of poor properties of plant oils at low temperatures. One opinion stated that the composition of saturated fatty acid in plant oils' chemical structure contributes to the poor low-temperature properties [70, 71]. On the other hand, it stated that polyunsaturated fatty acids (multiple double bonds in one chain of fatty acid) cause the said poor performance [72, 73]. However, most researchers favor the theory that saturated fatty acid's composition is the main influence on poor low-temperature performance. This is because, at low-temperature, the carbon atoms of saturated fatty acid chains tend to bundle rapidly than the unsaturated fatty acid, turning into a crystalline form. The low-temperature properties of plant oils are identified by examining the pour point (PP) temperature.

Researchers have used various fatty acids and plant oils and subjected them to many chemical modification methods to obtain biolubricant properties suited for industrial applications. The following is a summary of some of these studies: Agrawal *et al.* (2017) [36] synthesized biolubricant base stocks from chemically-modified non-edible oils (crude Mahua oil and Karanja oil)-based-triesters via transesterification of the oil methyl ester with polyol alcohol, such as trimethylolpropane (TMP). The properties of the resulting products (a Mahua biolubricant and a Karanja biolubricant) were determined and compared with 2T engine oil. The result showed that the synthesized biolubricant derived from Karanja oil and Mahua oil had a higher viscosity index than the mineral oil lubricant and had reduced flash point and fire point to match the mineral oil-based lubricants properties.

Another study done by Fadzel *et al.* (2019) [17] on the synthesis of biolubricants from palm stearin showed the possibility of synthesizing a biolubricant from palm stearin saturated fatty acids with pentaerythritol via esterification to produce a palm stearin fatty acid-based-tetraester. The results showed that the yield of tetraester was 69%. The palm stearin saturated fatty acids-based biolubricant-tetraester recorded a pour point of 44°C, a flashpoint of 243°C, a viscosity index of about 140, and oxidative stability at 269°C. The tetraester has good lubrication properties similar to ISO VG 46 commercial grade lubricant.

Heikal *et al.* (2017) [38] conducted a two-stage transesterification of palm oil and jatropha oil to develop biodegradable lubricants. First, methanol was used in KOH to form

biodiesel. In the second state, sodium methoxide was used as a catalyst, and the biodiesel was reacted with trimethylolpropane. The study recorded a 97.8% maximum yield of trimethylolpropane triesters from palm oil and a 98.2% maximum yield of trimethylolpropane triesters from Jatropha oil. The latter had a high viscosity index (140), a low pour point temperature of -3°C, moderate thermal stability, and met the ISO VG46 commercial grade industrial oil requirement. Figure 4 summarizes the reaction pathways of the plant oils' major chemical modification methods.

4. Environmental Friendly Biolubricants

Most lubricants end up in the environment, either by leakage during transportation and equipment utilization or by intentional disposal at the end of their lifetimes. To minimize environmental damage, biodegradable biolubricants have attracted attention. Biolubricants (also commonly called bio-lubes, bio-based, green, environmentally friendly biolubricants or plant-oil-based lubricants) are made from a variety of plant oils such as rapeseed, palm, sunflower, soybean, coconut, and canola. The main components of plant oils are triacylglycerols (natural esters), the precise chemical nature of which is dependent on both the plant species and strain from which the oil is obtained. Outside the U.S., rapeseed is the most commonly used crop for creating plant oil biolubricants. In the U.S., the most commonly used crops for producing plant oil biolubricants are canola, soybeans, and sunflowers [74].

Plant oils can be used as biolubricants in their natural forms. They have several advantages when considered for industrial and machinery lubrication. Plant oils can have excellent lubricity, far superior to that of mineral oil. Their lubricity is so potent that in some applications, such as tractor transmissions, friction materials must be added to reduce clutch slippage. Plant oils also have a very high viscosity index (VI). Another critical property of plant oils is their high flashpoints. More importantly, Plant oils are biodegradable, generally less toxic, and renewable compared to petroleum oils.

Employing tests developed by the American Society for Testing and Materials (ASTM) and the Organization for Economic Cooperation and Development (OECD), oil is inoculated with bacteria and kept under controlled conditions for 28 days. The percentage of oxygen consumption or carbon-dioxide evolution is monitored to determine the degree of biodegradability. Most plant oils have shown to biodegrade more than 70% within that period, as compared to petroleum oils biodegrading at nearly 15 to 35%. For a test to be considered readily biodegradable, there must be more than 60% degradation in 28 days. Table 5 shows the biodegradation percentage for typical types of lubricants [75].

Lubricant types	Biodegradation percentage (%)
Plant oils	90 - 100 %
Plant oils based esters	$80 - 100 \ \%$
Polyols and diesters	55 - 100 %
Polyalkylene glycol (PAG)	10 - 20 %
Polyalphaolfien (PAO)	5-30 %
Polyether	0-25 %

Table 5. Biodegradation percentage (%) for typical types of lubricants.

Due to these facts, attention has been focused on developing technologies that use plant and animal oils and fats to produce biolubricants, as they are non-toxic and renewable. Plant and animal oils and fats in industrial applications, especially as biolubricants, have been in practice for many years.



Figure 4. Reaction pathways of the three chemical modification methods. Red, green, and solid blue arrows represent the pathway of transesterification/esterification, epoxidation/ring-opening, respectively, and estolide formation.

Economic concerns and environmental issues first paved the way for this technology to come into existence. Climatic and geographic factors are known to affect the ability of plant oils to produce biolubricants. For example, the US normally uses soybean oil to make biolubricants, while Europe turns to rapeseed and sunflower oils. Meanwhile, Asia depends on palm and coconut oils to make biolubricants [76].

4.1. Biolubricant advantages, effects and the global industry (2020 to 2025).

Biolubricants are preferable for all applications that may present risks to the environment. This is the case for:

- Lost oils (chainsaw chain oils, 2-stroke engine oils, formwork release agents, and greases);
- Oils may leak accidentally (hydraulic oils, oils for engines, gearboxes, axles, etc.).

The use of biolubricants is particularly recommended when environmental protection is a constant concern, for example, in aquatic, mountain, agricultural, and forest environments or deep quarries [77]. Biolubricants hold great potential for environmental conservation and economic development as an alternative lubricant. Table 6 summarizes some of the key advantages of biolubricants.

-	High biodegradability results in fewer ill-effects to the environment
-	Lower toxicity
-	Good lubricating properties
-	High viscosity index
-	High flashpoint
-	Safer use due to inflammable nature, constant viscosity, less vapor, and oil mist production
-	Longer equipment life
-	Reduction in oil losses through evaporation
-	Higher boiling points leads to fewer emissions

Table 6. Key advantages of biolubricants.

- Cost-effective due to reduced costs of maintenance, disposal, and storage

The global market size for biolubricants was USD 2.20 billion in 2019 and is projected to reach USD 2.46 billion by 2025, at a compound annual growth rate (CAGR) of 4.1% between 2020 and 2025. Stringent regulations and the growing acceptance among end-users are projected to drive the bio-lubricants market. The global biolubricants industry has witnessed growth primarily because of countries' strict regulations across the world. There has been growing acceptance among end-use industries due to the continuous technological advancement to justify the premium cost of biolubricants. Hydraulic oil application is projected to witness the highest CAGR during the forecast period. The hydraulic oil application of the biolubricants market is projected to witness the highest growth during the forecast period, both in terms of value and volume. This segment's growth is attributed to its usage in hydraulic elevators, sweepers, garage trucks, forklifts, motor graders, and end loaders, which are used in many industries.

The industrial segment is projected to lead the bio-lubricants market from 2020 to 2025. The industrial segment includes the marine and agriculture & construction industries. These two industries are the most extensive and fastest-growing end-use industries, respectively. Various regulations such as the general vessel permit (VGP) in the US and eco-label in Europe have made it mandatory to use biolubricants or environmentally accepted lubricants (EAL) to be used in shipping vessels. Europe is projected to account for the maximum share of the

biolubricants market during the forecast period. Europe is projected to lead the global biolubricants market from 2020 to 2025. Stringent regulations and the ongoing transition towards bioeconomy in countries such as Germany, Italy, Nordic countries, Benelux, and France are promoting the use of bio-based chemicals such as biolubricants, which is driving the market in the region [78-80].

4.2. Biolubricants worldwide eco-labeling: sustainability certifications.

Over the past few decades, there has been a rising concern about industrialization's adverse impacts on the environment. There has been mounting pressure on industries to adopt eco-friendly manufacturing processes and disposals. Labeling and certification are two tools that provide consumers with information that was previously unknown to them. Effective labeling and certification mechanisms may shift consumption and production towards socially responsible and sustainable patterns. Eco-labels are affixed to products that pass eco-friendly criteria laid down by government, association, or standards certification bodies. The criteria utilize extensive research based on the product's life cycle impact on the environment. Eco-labels may focus on certain environmental aspects of the product, e.g., energy consumption, water use, timber source, etc. They may encompass multiple environmental aspects. Eco-labels differ from green symbols and environmental claims. The latter are unverified and created by the manufacturer or service provider. Products awarded an eco-label have been assessed and verified by an independent third body and are guaranteed to meet certain environmental performance requirements. Eco-labels are usually funded and backed by the national government but administered by an independent body [81].

Industry, government, and consumers are vital stakeholders in any eco-labeling scheme. Government backing for eco-labeling schemes is essential. Almost all international eco-labeling schemes require government funding and support. Since eco-labels are voluntary, the support of the industry is fundamental. Other key stakeholders are the scientific community, standard bodies, and industry associations.

Environmental labeling is a significant issue for every international body that deals with the environment or trade. While organizations such as the UN Conference on Trade and Development (UNCTAD), the UN Environment Programme (UNEP), and World Trade Organisation have concentrated on the policy side of the issue, the International Organisation for Standardisation (ISO) has been carrying out work on standardizing environmental labeling schemes [82].

In January 1993, the ISO work was being carried out under the rubric of the ISO Technical Committee number 207 (TC207). TC207 is the umbrella body for environmental standards-setting. It works on standards ranging from corporate activity (environmental management systems, environmental auditing) to product evaluation (environmental labeling, environmental performance evaluation).

As part of its ISO 14000 series of environmental standards, the ISO has drawn up a group of standards governing environmental labeling. It contains guiding principles for the development and use of certain types of environmental labels [83]. These labels apply to biolubricants, which are directly marketed to consumers. Many types of biolubricants are evaluated by eco-labeling organizations worldwide. When comparing similar biolubricants, eco-labels, and other voluntary environmental performance criteria can be used to inform purchasing decisions and procure greener biolubricants [84-88].

5. Biolubricant Biodegradability

Despite significant advances in connector, hose, and seal technology in recent years, there is no guarantee that lubricating systems won't leak. Leaks can still result from improper assembly, misapplication, and simple wear and tear of the equipment. There now exists greater awareness of the need to reduce leakage in lubricating systems. The US Environmental Protection Agency (EPA) and other worldwide regulatory bodies have sought to reduce spills through stricter regulation, including the possibility for fines, penalties, and costly remediation. Increasingly, there is the awareness that lubricants coming into contact with soil, water, wetlands, and other sensitive areas can negatively impact the environmentally acceptable alternatives, such as biodegradable and non-toxic. These biodegradable and non-toxic biolubricants can offer performance comparable to mineral oil-based fluids in some applications.

Customers have found the use of biodegradable and non-toxic biolubricants to be suitable for environmentally sensitive applications in construction, mining, forestry, agriculture, hydroelectric dams, and various marine uses, including dockside cargo handling, harbor dredging, off-shore drilling, stern tubes, azipods, and hydraulic deck equipment.

5.1. Definition of biodegradation.

The biodegradation of a biolubricant is its biochemical oxidation. It is initiated and performed by the enzymes of microorganisms such as algae and microfungi. Although similar to combustion, this biochemical process is much longer, comprising several small bio-oxidation steps *via* long-chain alcohols and carboxylic acids, as well as shorter chain acids down to acetic acid and carbon dioxide (Figure 5). This process delivers energy to the microorganisms. Another side reaction inside these "microbugs" uses long-chain carboxylic acids to form amino acids and proteins. This reaction makes the microorganisms grow in size and number.



Figure 5. Biodegradation process of biolubricant.

Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane and water. Biolubricant can be degraded aerobically, with oxygen, or anaerobically, without oxygen. Certain chemical structures are more susceptible to microbial breakdown than others; plant oils and synthetic esters, for example, will, in general, biodegrade more rapidly than mineral oils under the same conditions. Biodegradation is one of the most important factors when considering the environmental friendliness of different biolubricants. Biodegradation measurements in different environments

are essential, considering biodegradation in nature. Because of the different behavior of the organic materials in nature, measuring conditions outside of the laboratory are of considerable importance. The biodegradation reaction in nature is usually slower than it is under standard conditions. Therefore the rates of biodegradation in different circumstances need to be measured or evaluated [89].

When biolubricant is spilled into natural water containing the usual microorganisms, biodegradation's initial speed is very slow, as not all "bugs" present accept this material as "food". Those who eat and grow in number and size produce a faster biodegradation speed until this food (the added substrate) is fully consumed. The resulting degradation/time curve of any biolubricant usually has three stages: the lag (or adaptation) phase, the degradation (or exponential) phase, and the stationary phase, where the new biomass dies away if no additional food is added [90]. This type of degradation curve is found whenever the concentration of added biolubricant is observed (Figure 6).



Figure 6. Kinetics of biodegradation process.

However, when the resulting carbon dioxide is measured, the shape is somewhat different due to the side reaction into proteins and the time-consuming dying-off process of the biomass produced. This should be noted when comparing the results of biolubricant removal tests with other methods measuring carbon-dioxide production [91]. The U.S. Federal Trade Commission (FTC) has defined criteria for marketing statements or claims for biodegradable biolubricants in their 1992 Guidelines on Environmental Marketing Claims, 16 CFR Part 260. The FTC guidelines provide that a biodegradable claim should be substantiated by evidence that the entire biolubricant will completely break down and return to nature, that is, decompose into elements found in nature within a reasonably short period of time after customary disposal [92, 93]. The FTC does not define a reasonably short period of time. The qualification for claims regarding the time factor as required by the FTC is: "Claims of degradability, biodegradability or photo-degradability should be qualified to the extent necessary to avoid consumer deception about: (1) the product or package's ability to degrade in the environment where it is customarily disposed of; and (2) the rate and extent of degradation" [94, 95].

Outside the U.S., various other countries, including Germany (i.e. Blue Angel standard), Japan (Eco-mark), and regions (Nordic Swan, Europa Ecolabel, Nordic Eco-label for biolubricants) have definitions for the use of the biodegradable term when applying for eco-labels [96].

5.2. Biodegradation testing methods.

Biodegradability is a property or characteristic of a substance and a system's concept, i.e., a system with its conditions determines whether a substance within it is biodegraded. When

the material is released into the environment, its fate depends upon a whole range of physicochemical processes and its interaction with living organisms.

Common test methods, such as those developed by the OECD, the Coordinating European Council (CEC), and the ASTM, for determining lubricant biodegradability are OECD 301B (the Modified Strum test), ASTM D-5864, and CEC L-33-A-934. Both OECD 301B and ASTM D-5864 measure ready biodegradability, defined as converting 60% of the material to CO₂ within a ten-day window following the onset of biodegradation, which must occur within 28 days of test initiation [97]. In contrast, the CEC method tests the overall biodegradability of hydrocarbon compounds. It requires 80% or greater biodegradability as measured by the infrared absorbance of extractable lipophilic compounds [98, 99]. Unlike the OECD and ASTM methods, the CEC method does not distinguish between primary and ultimate biodegradability and is considered a less stringent test [100].

The OECD in their guidelines distinguish four major forms of biodegradation [93, 94]:

- ultimate biodegradation (mineralization): The level of degradation achieved when the test biolubricant is totally utilized by microorganisms resulting in carbon dioxide, water, mineral salts, and new microbial cellular constituents (biomass).
- Primary biodegradation (biotransformation): The alteration in the chemical structure of a biolubricant, brought about by biological action, resulting in the loss of a specific property of that substance.
- Readily biodegradable: An arbitrary classification of biolubricants that have passed certain specified screening tests for ultimate biodegradability; these tests are so stringent that it is assumed that such biolubricants will rapidly and completely biodegrade in aquatic environments under aerobic conditions.
- Inherent biodegradable: A classification of biolubricants for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability.

Various methods exist for the testing of the biodegradability of biolubricants. Biodegradability is assessed by following specific parameters that are considered to indicate the consumption of the test biolubricant by microorganisms or the production of simple basic compounds that indicate the mineralization of the test biolubricant. Hence various biodegradability testing methods measure the amount of carbon dioxide (or methane, for anaerobic cases) produced during a specified period. There are those that measure the loss of dissolved organic carbon for water-soluble substances; those that measure the loss of infrared hydrocarbon bands; and others measure the uptake of oxygen by the activities of microorganisms biochemical oxygen demand (BOD) [101, 102].

The biodegradability test procedure selection is difficult since most biolubricating base oils do not dissolve in water. These oils form a layer on the water's surface, reducing oxygen exchange, resulting in depleting dissolved oxygen [103-105]. The studies have shown that the biodegradation of oils in soil was very slow, taking over a year to generate extractable residues. Besides, the effects of contamination by different oils on growth rate and yield of spring wheat varied from small reductions to complete seed germination inhibition. Since the biodegradability of material is environment-dependent, it readily undergoes degradation following one of these conditions: Plant or animal-derived constituents are generally readily biodegradable; Aromatic compounds are resistant to biodegradation; Straight chain hydrocarbon compounds degrade more readily than branched hydrocarbon compounds. The presence of sterically hindered groups decreases the biodegradability; The biodegradability of plant oil products decreases with the chain length. However, OECD described six test methods that permit the screening of biolubricants for ready biodegradability in aerobic conditions (Table 7) [106-113].

Name of the test	Measured parameters and comments
DOC Dia Away	DOC* (OECD 301 A) -Analyzes the dissolved organic carbon (DOC) and is
DOC DIE-Away	suitable for the compounds which are adsorbing in nature
CO ₂ evolution (Modified Sturm	CO ₂ (OECD 301 B)-Evaluates the CO ₂ concentration and is suitable for poorly
Test)	soluble and adsorbing compounds
	BOD [†] (OECD 301 C)-Evaluates the oxygen consumption and is useful for most of
	the compounds
Closed Pottle	BOD/COD (OECD 301 D)-Evaluates the dissolved oxygen and is useful for most
Closed Bottle	of the compounds
Modified OECD Screening	DOC [‡] (OECD 301 E) - Analyzes the Dissolved Organic Carbon (DOC) and is
Modified OECD Screening	suitable for the compounds which are adsorbing in nature
Manamatria Pasniromatry	BOD/COD (OECD 301 F) - Evaluates the oxygen consumption and is useful for
Manometric Respirometry	most of the compounds.

Table 7. OECD standard tests for biodegradability

*DOC: Dissolved organic carbon is the organic carbon present in solution or that passes through a 0.45-micrometer filter or remains in the supernatant after centrifuging at approx. 4000 g (about 40.000 m sec⁻²) for 15 min; [†]BOD: Biochemical oxygen demand (mg) is the amount of oxygen consumed by microorganisms when metabolizing a test compound; also expressed as mg oxygen uptake per mg test compound; [‡]DOC: Dissolved organic carbon is the organic carbon present in solution or that which passes through a 0.45-micrometer filter or remains in the supernatant after centrifuging at approx. 4000 g (about 40.000 m sec⁻²) for 15 min; [‡] MITI (I): Ministry of international trade and industry, Japan

6. Biolubricant Toxicity

Toxicology is the study of chemical substances that harm biological organisms. Toxic exposure can occur transdermally through contact with the skin, orally, and *via* inhalation. Toxicity testing is necessary to provide some basis for regulating substances that humans and other living things may come into contact with, intentionally or not [114]. Toxicity is an important parameter that must be controlled since some components of biolubricant formulations are environmentally toxic and can irreversibly affect living things. Toxicity tests can provide preliminary information on the toxic nature of a biolubricant for which no other toxicology information is available. In most toxicity tests, each test animal is administered a single (relatively high) dose of the test substance, observed for 1 or 2 weeks for signs of treatment-related effects, then necropsied. Some acute toxicity tests (such as the "classical" LD₅₀ test) are designed to determine the mean lethal dose of the test biolubricant. The lethal dose (or LD_{50}) is defined as the dose of a test biolubricant that is lethal for 50% of the animals in a dose group. The LD₅₀ is one way to measure the short-term poisoning potential (acute toxicity) of a biolubricant. Toxicologists can use many kinds of animals, but testing is often done with rats and mice. It is usually expressed as the amount of biolubricant administered (e.g., milligrams) per 100 grams (for smaller animals) or per kilogram (for bigger test subjects) of the bodyweight of the test animal. In general, the smaller the LD₅₀ value, the more toxic the chemical is. The opposite is also true: the larger the LD50 value, the lower the toxicity. A biolubricant is not considered toxic when the LD₅₀ is above 1000 ppm [97].

Another toxicity test is the lethal concentration (or LC_{50}). LC values usually refer to the concentration of a biolubricant in air. However, it can also mean the concentration of a biolubricant in water in environmental studies. According to the OECD guidelines for testing biolubricants, a traditional experiment involves groups of animals exposed to a concentration (or series of concentrations) for a set time (usually 4 hours). The animals are clinically observed for up to 14 days. LC₅₀ value is the concentration of biolubricant in the air at which 50% of the

test animals die during the observation period. Other durations of exposure (versus the traditional 4 hours) may apply depending on specific laws [93].

In general, biolubricants are defined as products with low toxicity and excellent biodegradability. Biolubricants are not necessarily derived from plant-based oils and some of them are derived from petroleum fatty acids based. However, biolubricants that eco-friendly environmental compliance is usually derived from these oils. Thus, it can be classed as renewable because plants can be regrown. Biolubricants may also be synthetic esters, partially derived from various natural sources such as solid fats, waste materials, and tallow. The United States Secretary of Agriculture defined the term 'biobased product' as 'commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant and animal) or forestry materials'. Biolubricants can be categorized as sustainable because it is derived from renewable raw materials. As mentioned by Willing [97], the sustainability of raw materials' application can be classified into two aspects; the origin of the resources and the pollution caused by it. In the case of biolubricants (oleochemicals), it is discharged *via* several pathways at the end of their lifespan. The organic chemicals are disintegrated into carbon dioxide and water. The carbon cycle of biolubricants is closed because the amount of carbon dioxide released equals the carbon dioxide produced by the plants from the atmosphere. Therefore, it has zero effect with regard to the carbon dioxide balance of the atmosphere. The life cycle of biolubricants derived from renewable sources is shown in Figure 7.



Figure 7. The biolubricants life cycle.

Besides possessing a certain percentage of readily biodegradable biolubricant, environmentally acceptable biolubricants (EABLs) must also demonstrate low toxicity to aquatic organisms. Test methods to demonstrate toxicity include the OECD tests series 201-4, 209-212; and corresponding the United States Environmental Protection Agency (USEPA) environmental effect test guidelines from USEPA 560/6-82-002. The most common aquatic toxicity tests for assessing EALs are the 72-hour growth test for algae (OECD 201), the 48-hour acute toxicity test for daphnia (OECD 202), and the 96-hour toxicity test for fish (OECD 203) [99]. A listing of all of the OECD aquatic toxicity tests is shown in Table 8. In general, the plant oil and synthetic ester base oils have low toxicity towards marine organisms, with the

LC₅₀ for fish toxicity reported as being ~10,000 ppm for fatty acid esters and glycerol esters (see Table 9) [115]. Water-soluble PAGs may demonstrate increased toxicity to aquatic organisms by directly entering the water column and sediments rather than remaining on the water column surface as a sheen [116].

Test title, with species	Test number
Growth Inhibition Test, Alga	OECD 201
Acute Immobilization Test, Daphnia sp.	OECD 202
Acute Toxicity Test, Fish	OECD 203
Prolonged Toxicity Test: 14-Day Study, Fish	OECD 204
Respiration Inhibition Test, Bacteria	OECD 209
Early-Life Stage Toxicity Test, Fish	OECD 210
Reproduction Test, Daphnia magna	OECD 211
Short-term Toxicity Test on Embryo and Sac-fry Stages, Fish	OECD 212

Fable 8. OE	CD aquatic	toxicity	tests.
-------------	------------	----------	--------

ry

Lubricant base oil	Base oil source	Toxicity
Mineral oil	Petroleum	High
Polyalkylene glycol (PAG)	Petroleum - synthesized hydrocarbon	Low ^a
Synthetic ester	Synthesized from biological sources	Low
Plant Oils	Naturally occurring plant oils	Low

Table 9 Summary of comparative toxicity of base oils

^a Solubility may increase the toxicity of some PAG

7. Conclusions

In general, more than 50% of all lubricants used worldwide to enter the environment due to spills, accidents, volatility, and improper disposal, contaminating the air, soil, water, and affecting human and plant life to a great extent. The issues related to environmental conservation have brought about renewed interest in using bio-based biolubricants, which are renewable, biodegradable, and environmentally friendly lubricants, which has resulted in the widespread use of natural plant oils and fats. Plant oils are promising candidates as the base fluid for eco-friendly biolubricants due to their excellent lubricity, biodegradability, viscositytemperature characteristics, and low volatility. The biodegradability of plant oils is the strongest point in the case for their industrial use. With established biodegradability in the range of 70-100%, their eco-friendliness is not in doubt. Biodegradable biolubricants show less emission because of the higher boiling temperature range of esters. They are free of aromatics, over 90 % biodegradable, and non-water is polluting. While numerous terms are presently used for advertising biolubricants as having desirable environmental properties, there is growing consensus to use the term "environmentally acceptable" or eco-friendly to denote a biodegradable biolubricant and exhibits low toxicity to aquatic organisms. In the light of more concerns about the environmental impact of industrial lubricants' use, plant oils offer, in theory, the most plausible solution to the issue of obtaining renewable and eco-friendly biolubricants.

Funding

This research was funded by Universiti Kebangsaan Malaysia grant no. UKM-OUP-BTT-28/2007, UKM-GUP-NBT-08-27-113, UKM-OUP-NBT-29-150/2010 and Ministry of Science, Technology and Innovation (MOSTI,) research grant no. 05-01-02-SF0186, 05-01-02-SF0199, respectively.

Acknowledgments

The authors acknowledge the direct contributions of the support staff from the Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia and Ministry of Science and Technology.

Conflicts of Interest

The authors declare no conflict of interest.

References

- Owuna, F.J.; Dabai, M.U.; Sokoto, M.A.; Dangoggo, S.M.; Bagudo, B.U.; Birnin-Yauri, U.A.; Hassan, L.G.; Sada, I.; Abubakar, A.L.; Jibrin, M.S. Chemical modification of vegetable oils for the production of biolubricants using trimethylolpropane: A review. *Egyptian Journal of Petroleum* 2020, 29, 75-82, https://doi.org/10.1016/j.ejpe.2019.11.004
- Owuna, F.J. Stability of vegetable based oils used in the formulation of ecofriendly lubricants A review. Egyptian Journal of Petroleum 2020, 29, 251-256, https://doi.org/10.1016/j.ejpe.2020.09.003
- 3. Lourenço, S.C.; Moldão-Martins, M.; Alves, V.D. Antioxidants of natural plant origins: From sources to food industry applications. *Molecules* **2019**, *24*, 4132, https://doi.org/10.3390/molecules24224132.
- 4. Afida, S.; Ghazali, R.; Yeong, S.; Hassan, H. Biodegradability of palm-based lubricants. 2015, 27, 425-432.
- Cecilia, J.A.; Ballesteros Plata, D.; Alves Saboya, R.M.; Tavares de Luna, F.M.; Cavalcante, C.L.; Rodríguez-Castellón, E. An Overview of the Biolubricant Production Process: Challenges and Future Perspectives. *Processes* 2020, 8, 257, https://doi.org/10.3390/pr8030257.
- Sajeeb, A.; Rajendrakumar, P.K. Comparative evaluation of lubricant properties of biodegradable blend of coconut and mustard oil. *Journal of Cleaner Production* 2019, 240, 118255, https://doi.org/10.1016/j.jclepro.2019.118255.
- Sun, S.; Wang, G.; Wang, P. A cleaner approach for biodegradable lubricants production by enzymatic glycerolysis of castor oil and kinetic analysis. *Journal of Cleaner Production* 2018, *188*, 530-535, https://doi.org/10.1016/j.jclepro.2018.04.015.
- 8. Luna, F.M.T.; Cavalcante, J.B.; Silva, F.O.N.; Cavalcante, C.L. Studies on biodegradability of bio-based lubricants. *Tribology International* **2015**, *92*, 301-306, https://doi.org/10.1016/j.triboint.2015.07.007.
- Rani, S.; Joy, M.L.; Nair, K.P. Evaluation of physiochemical and tribological properties of rice bran oil– biodegradable and potential base stoke for industrial lubricants. *Industrial Crops and Products* 2015, 65, 328-333, https://doi.org/10.1016/j.indcrop.2014.12.020.
- 10. Nagendramma, P.; Kaul, S. Development of ecofriendly/biodegradable lubricants: An overview. *Renewable and Sustainable Energy Reviews* **2012**, *16*, 764-774, https://doi.org/10.1016/j.rser.2011.09.002.
- 11. Bahadi, M.; Yusoff, M.F.; Derawi, J.S.; Darfizzi. Optimization of response surface methodology by Doptimal design for alkaline hydrolysis of crude palm kernel oil. *Sains Malaysiana* **2020**, *49*, 29-41, https://doi.org/10.17576/jsm-2020-4901-04.
- 12. Panchal, T.M.; Patel, A.; Chauhan, D.D.; Thomas, M.; Patel, J.V. A methodological review on bio-lubricants from vegetable oil based resources. *Renewable and Sustainable Energy Reviews* **2017**, *70*, 65–70, https://doi.org/10.1016/j.rser.2016.11.105.
- Moreira, D.R.; Chaves, P.O.B.; Ferreira, E.N.; Arruda, T.B.M.G.; Rodrigues, F.E.A.; Neto, J.F.C.; Petzhold, C.L.; Maier, M.E.; Ricardo, N.M.P.S. Moringa polyesters as eco-friendly lubricants and its blends with naphthalenic lubricant. *Industrial Crops and Products* 2020, *158*, 112937, https://doi.org/10.1016/j.indcrop.2020.112937.
- Kushairi, A.; Ong-Abdullah, M.; Nambiappan, B.; Hishamuddin, E.; Bidin, M.; Ghazali, R.; Subramaniam, V.; Sundram, S.; Parveez, G.K.A. Oil palm economic performance in Malaysia and R&D progress in 2018. *Journal of Oil Palm Research* 2019, *31*, 165-194, https://doi.org/10.21894/jopr.2019.0026.
- Bahadi, M.; Yusoff, M.F.; Salimon, J.; Derawi, D. Optimization of response surface methodology by Doptimal design for synthesis of food-grade palm kernel based biolubricant. *Industrial Crops and Products* 2019, 139, 111452, https://doi.org/10.1016/j.indcrop.2019.06.015.
- 16. Ferreira, M.M.; de Oliveira, G.F.; Basso, R.C.; Mendes, A.A.; Hirata, D.B. Optimization of free fatty acid production by enzymatic hydrolysis of vegetable oils using a non-commercial lipase from Geotrichum

candidum. *Bioprocess and Biosystems Engineering* **2019**, *42*, 1647-1659, https://doi.org/10.1007/s00449-019-02161-2.

- 17. Fadzel, F.M.; Salimon, J.; Derawi, D. Biolubricant production from palm stearin fatty acids and pentaerythritol. *Malaysian Journal of Chemistry* **2019**, *21*, 50–63.
- 18. Efendy Goon, D.; Sheikh Abdul Kadir, S.H.; Latip, N.A.; Rahim, S.A.; Mazlan, M. Palm oil in lipid-based formulations and drug delivery systems. *Biomolecules* **2019**, *9*, 64, https://doi.org/10.3390/biom9020064.
- 19. Karmakar, G.; Ghosh, P.; Sharma, B.K. Chemically modifying vegetable oils to prepare green lubricants. *Lubricants* **2017**, *5*, 44, https://doi.org/10.3390/lubricants5040044.
- Gul, M.; Masjuki, H.H.; Kalam, M.A.; Zulkifli, N.W.M.; Mujtaba, M.A. A Review: Role of fatty acids composition in characterizing potential feedstock for sustainable green lubricants by advance transesterification process and its global as well as Pakistani prospective. *BioEnergy Research* 2020, *13*, 1-22, https://doi.org/10.1007/s12155-019-10040-7.
- Han, L.; Zhang, S.; Qi, B.-K.; Li, H.; Xie, F.-Y.; Li, Y. Molecular distillation-induced deacidification of soybean oil isolated by enzyme-assisted aqueous extraction: Effect of distillation parameters. *Applied Sciences* 2019, *9*, 2123, https://doi.org/10.3390/app9102123.
- Liu, C.; Meng, Z.; Chai, X.; Liang, X.; Piatko, M.; Campbell, S.; Liu, Y. Comparative analysis of graded blends of palm kernel oil, palm kernel stearin and palm stearin. *Food Chemistry* 2019, 286, 636-643, https://doi.org/10.1016/j.foodchem.2019.02.067.
- 23. Nor, N.M.; Derawi, D.; Salimon, J. Esterification and evaluation of palm oil as biolubricant base stock. *Malaysian Journal of Chemistry* **2019**, *21*, 28–35.
- Afifah, A.N.; Syahrullail, S.; Wan Azlee, N.I.; Che Sidik, N.A.; Yahya, W.J.; Abd Rahim, E. Biolubricant production from palm stearin through enzymatic transesterification method. *Biochemical Engineering Journal* 2019, *148*, 178-184, https://doi.org/10.1016/j.bej.2019.05.009.
- Bahadi, M.A.; Yusoff, M.F.; Salimon, J.; Japir, A.A.W.; Derawi, D. Optimization of low-temperature methanol crystallization for unsaturated fatty acids separation from crude palm fatty acids mixture using response surface methodology. *Asian Journal of Chemistry* 2019, 31, 1617–1625, https://doi.org/10.14233/ajchem.2019.21974.
- Folayan, A.J.; Anawe, P.A.L.; Aladejare, A.E.; Ayeni, A.O. Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass. *Energy Reports* 2019, *5*, 793-806, https://doi.org/10.1016/j.egyr.2019.06.013.
- dos Santos, L.K.; Hatanaka, R.R.; de Oliveira, J.E.; Flumignan, D.L. Production of biodiesel from crude palm oil by a sequential hydrolysis/esterification process using subcritical water. *Renewable Energy* 2019, *130*, 633-640, https://doi.org/10.1016/j.renene.2018.06.102.
- Nie, J.; Shen, J.; Shim, Y.Y.; Tse, T.J.; Reaney, M.J.T. Synthesis of trimethylolpropane esters by basecatalyzed transesterification. *European Journal of Lipid Science Technology* 2020, 122, 1900207, https://doi.org/10.1002/ejlt.201900207.
- 29. Rao, T.; Rani, A.M.A.; Awang, M.; Baharom, M.; Uemura, Y.; Iskandar, P.D.R. An overview of research on biolubricants in Malaysia and Japan for tribological applications. *Jurnal Tribologi* **2018**, *18*, 40-57.
- Sande, D.; Colen, G.; dos Santos, G.F.; Ferraz, V.P.; Takahashi, J.A. Production of omega 3, 6, and 9 fatty acids from hydrolysis of vegetable oils and animal fat with Colletotrichum gloeosporioides lipase. *Food Science and Biotechnology* 2018, 27, 537-545, https://doi.org/10.1007/s10068-017-0249-1.
- Zainal, N.A.; Zulkifli, N.W.M.; Gulzar, M.; Masjuki, H.H. A review on the chemistry, production, and technological potential of bio-based lubricants. *Renewable and Sustainable Energy Reviews* 2018, 82, 80-102, https://doi.org/10.1016/j.rser.2017.09.004.
- Bahadi, M.A., Japir, A.A.W.; Salih, N.; Salimon, J. Free fatty acids separation from Malaysian high free fatty acid crude palm oil using molecular distillation. *Malaysian Journal of Analytical Sciences* 2016, 20, 1042-1051, https://doi.org/10.17576/mjas-2016-2005-08.
- Bahadi, M.A.; Salimon, J.; Japir, A.-W.M. The physicochemical and thermal properties of Malaysian high free fatty acid crude palm oil. *AIP Conference Proceedings* 2016, 1784, 030002, https://doi.org/10.1063/1.4966740.
- Japir, A.A.-W.; Salimon, J.; Derawi, D.; Bahadi, M.; Al-Shuja'a, S.; Yusop, M.R. Physicochemical characteristics of high free fatty acid crude palm oil. *Oilseeds & fats Crops and Lipids* 2017, 24, https://doi.org/10.1051/ocl/2017033.

- 35. Japir, A.A.-W.; Salimon, J.; Derawi, D.; Yahaya, B.H.; Bahadi, M.; Al-Shuja'a, S.; Yusop, M.R. A highly efficient separation and physicochemical characteristics of saturated fatty acids from crude palm oil fatty acids mixture using methanol crystallisation method. *Oilseeds & fats Crops and Lipids* **2018**, *25*, https://doi.org/10.1051/ocl/2018003.
- 36. Agrawal, A.J.; Karadbhajne, V.Y.; Agrawal, P.S.; Arekar, P.S.; Chakole, N.P. Synthesis of biolubricants from non edible oils. *International Research Journal of Engineering and Technology* **2017**, *4*, 1753–1757.
- Ashrafi, J.; Semnani, A.; Langeroodi, H.S.; Shirani, M. Direct acetylation of sunflower oil in the presence of boron trioxide catalyst and the adduct usage as the base stock and lubricant additive. *Bulletin of the Chemical Society of Ethiopia* 2017, *31*, 39-49, https://doi.org/10.4314/bcse.v31i1.4.
- Heikal, E.K.; Elmelawy, M.S.; Khalil, S.A.; Elbasuny, N.M. Manufacturing of environment friendly biolubricants from vegetable oils. *Egyptian Journal of Petroleum* 2017, 26, 53-59, https://doi.org/10.1016/j.ejpe.2016.03.003.
- 39. Minami, I. Molecular science of lubricant additives. *Applied Sciences* **2017**, *7*, 445, https://doi.org/10.3390/app7050445.
- Nor, N.M.; Derawi, D.; Salimon, J. Chemical modification of epoxidized palm oil for biolubricant application. *Malaysian Journal of Analatical Sciences* 2017, 21, 1423-1431, https://doi.org/10.17576/mjas-2017-2106-25.
- Pei, H.J.; Shen, Y.J.; Shen, C.G.; Wang, G.C. Application of castor oil-based cutting fluids in precision turning. *Applied Mechanics and Materials* 2012, 130-134, 3830-3834, https://doi.org/10.4028/www.scientific.net/amm.130-134.3830.
- 42. Craske, J.D.; Bannon, C.D. Gas liquid chromatography analysis of the fatty acid composition of fats and oils: A total system for high accuracy. *Journal of American Oil Chemist's Society* **1987**, *64*, 1413-1417, https://doi.org/10.1007/bf02636990.
- Delmonte, P.; Fardin Kia, A.-R.; Kramer, J.K.G.; Mossoba, M.M.; Sidisky, L.; Rader, J.I. Separation characteristics of fatty acid methyl esters using SLB-IL111, a new ionic liquid coated capillary gas chromatographic column. *Journal of Chromatography A* 2011, *1218*, 545-554, https://doi.org/10.1016/j.chroma.2010.11.072.
- 44. Brondz, I. Development of fatty acid analysis by high-performance liquid chromatography, gas chromatography, and related techniques. *Analytica Chimica Acta* **2002**, *465*, 1-37, https://doi.org/10.1016/S0003-2670(01)01467-2.
- Holčapek, M.; Jandera, P.; Zderadička, P.; Hrubá, L. Characterization of triacylglycerol and diacylglycerol composition of plant oils using high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry. *Journal of Chromatography A* 2003, *1010*, 195-215, https://doi.org/10.1016/s0021-9673(03)01030-6.
- Azizian, H.; Kramer, J.K.G. A rapid method for the quantification of fatty acids in fats and oils with emphasis on trans fatty acids using fourier transform near infrared spectroscopy (FT-NIR). *Lipids* 2005, 40, 855-867, https://doi.org/10.1007/s11745-005-1448-3.
- Maggio, R.M.; Kaufman, T.S.; Carlo, M.D.; Cerretani, L.; Bendini, A.; Cichelli, A.; Compagnone, D. Monitoring of fatty acid composition in virgin olive oil by Fourier transformed infrared spectroscopy coupled with partial least squares. *Food Chemistry* 2009, *114*, 1549-1554, https://doi.org/10.1016/j.foodchem.2008.11.029.
- Vlachos, N.; Skopelitis, Y.; Psaroudaki, M.; Konstantinidou, V.; Chatzilazarou, A.; Tegou, E. Applications of Fourier transform-infrared spectroscopy to edible oils. *Analytica Chimica Acta* 2006, 573-574, 459-465, https://doi.org/10.1016/j.aca.2006.05.034.
- 49. Bennion, M.; Scheule, B. *Introductory foods*; 10th ed, Prentice-Hall Inc., Upper Saddle River: New Jersey, USA: 1995.
- 50. Bailey, A.E. Bailey's industrial oil and fat products; Wiley, New York: 1996.
- 51. Mang, T.; Dresel, W. Lubricants and lubrication; John Wiley & Sons: 2007.
- 52. Wolf, W.J. Soybeans and other oilseeds. *Kirk-Othmer encyclopedia of chemical technology*; 3rd ed.; John Wiley and Sons Inc., New York, 1978.
- 53. Battersby, N.S. The biodegradability and microbial toxicity testing of lubricants some recommendations. *Chemosphere* **2000**, *41*, 1011-1027, https://doi.org/10.1016/s0045-6535(99)00517-2.
- 54. Dunn, R.O. Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). *Fuel Processing Technology* **2005**, *86*, 1071-1085, https://doi.org/10.1016/j.fuproc.2004.11.003.

- 55. Gertz, C.; Parkash Kochhar, S. A new method to determine oxidative stability of vegetable fats and oils at simulated frying temperature. *Oilseeds & fats Crops and Lipids* **2001**, *8*, 82-88, https://doi.org/10.1051/ocl.2001.0082.
- 56. Willams, K.A. Oils, Fats and fatty foods their practical examination. New York Elsevier: 1966.
- 57. Oyedeji, F.O.; Oderinde, R.A. Characterization of isopropanol extracted vegetable oils. *Journal of Applied Sciences* **2006**, *6*, 2510-2513, https://doi.org/10.3923/jas.2006.2510.2513.
- Quinchia, L.A.; Delgadoa, M.A.; Franco, J.M.; Spikes, H.A.; Gallegos, C. Low-temperature flow behaviour of vegetable oil-based lubricants. *Industrial Crops and Products* 2012, 37, 383–388, https://doi.org/10.1016/j.indcrop.2011.12.021.
- 59. Peter Mgeni, C.; Müller, K.; Sieber, S. Reducing edible oil import dependency in Tanzania: A computable general equilibrium CGE approach. *Sustainability* **2019**, *11*, 4480, https://doi.org/10.3390/su11164480.
- Vergara, J.; Silva Martínez, S.; Hernández, M. Degradation of corn oil wastes by fenton reaction and under mildly basic media in the presence of oxidants assisted with sun light. *American Journal of Environmental Sciences* 2008, *4*, 602-607, https://doi.org/10.3844/ajessp.2008.602.607.
- 61. Abramovič, H.; Abram, V. Physico-chemical properties, composition and oxidative stability of *Camelina* sativa oil. Food Technology and Biotechnology **2005**, 43, 63-70.
- 62. Mohanan, S.; Maruthamuthu, S.; Muthukumar, N.; Rajasekar, A.; Palaniswamy, N. Biodegradation of palmarosa oil (green oil) by *Serratia marcescens*. *International Journal of Environmental Science and Technology* **2007**, *4*, 277-281, https://doi.org/10.1007/bf03326285.
- 63. Rodríguez, P.; Sierra, W.; Rodríguez, S.; Menéndez, P. Biotransformation of 1, 8-cineole, the main product of *Eucalyptus* oils. *Electronic Journal of Biotechnology* **2006**, *9*, 232-236, https://doi.org/10.2225/vol9-issue3-fulltext-28.
- Mobarak, H.M.; Mohamad, E. N.; Masjuki, H.H.; Kalam, M.A.; Al Mahmud, K.A.H.; Habibullah, M.; Ashraful, A.M. The prospects of biolubricants as alternatives in automotive applications. *Renewable and Sustainable Energy Reviews* 2014, 33, 34–43, https://doi.org/10.1016/j.rser.2014.01.062.
- Alfieri, A.; Imperlini, E., Nigro, E.; Vitucci, D.; Orrù, S.; Daniele, A.; Buono, P.; Mancini, A. Effects of plant oil interesterified triacylglycerols on lipemia and human health. *International Journal of Molecular Sci*ences 2018, 19, 104, https://doi.org/10.3390/ijms19010104.
- 66. Gulluoglu, L.; Bakal, H.; Arioglu, H. Oil content and composition of soybean genotypes grown in different growing seasons under Mediterranean conditions. *Journal of Environmental Biology* **2018**, *39*, 211-215, https://doi.org/10.22438/jeb/39/2/MRN-318.
- Ho, C.K.; McAuley, K.B.; Peppley, B.A. Biolubricants through renewable hydrocarbons: A perspective for new opportunities. *Renewable and Sustainable Energy Reviews* 2019, 113, 109261, https://doi.org/10.1016/j.rser.2019.109261.
- 68. Jimenez-Lopez, C.; Carpena, M.; Lourenço-Lopes, C.; Gallardo-Gomez, M.; Lorenzo, J.M.; Barba, F.J.; Prieto, M.A.; Simal-Gandara, J. Bioactive compounds and quality of extra virgin olive oil. *Foods* **2020**, *9*, 1014, https://doi.org/10.3390/foods9081014.
- Leku, M.T.; Djoulde, D.; Delattre, C.; Michaud, P. Purification and valorization of waste cotton seed oil as an alternative feedstock for biodiesel production. *Bioengineering* 2020, 7, 41, https://doi.org/10.3390/bioengineering7020041.
- Liu, Z.; Sharma, B.K.; Erhan, S.Z.; Biswas, A.; Wang, R.; Schuman, T.P. Oxidation and low temperature stability of polymerized soybean oil-based lubricants. *Thermochim. Acta* 2015, 601, 9-16, https://doi.org/10.1016/j.tca.2014.12.010.
- Dian, N.; Hamid, R.A.; Kanagaratnam, S.; Isa, W.R.A.; Hassim, N.A.M.; Ismail, N.H.; Sahri, M.M. Palm oil and palm kernel oil: Versatile ingredients for food applications. *Journal of Oil Palm Research* 2017, 29, 487-511, https://doi.org/10.21894/jopr.2017.00014.
- 72. Erhan, S.Z.; Sharma, B.K.; Perez, J.M. Oxidation and low temperature stability of vegetable oil-based lubricants. *Industrial Crops and Products* **2006**, *24*, 292–299, https://doi.org/10.1016/j.indcrop.2006.06.008.
- 73. Nor, N.M.; Salih, N.; Salimon, J. Optimization of the ring opening of epoxidized palm oil using D-optimal design. *Asian Journal of Chemistry* **2021**, *33*, 67-75, https://doi.org/10.14233/ajchem.2021.22938.
- 74. Sagan, A.; Blicharz-Kania, A.; Szmigielski, M.; Andrejko, D.; Sobczak, P.; Zawiślak, K.; Starek, A. Assessment of the properties of rapeseed oil enriched with oils characterized by high content of α-linolenic acid. *Sustainability* **2019**, *11*, 5638, https://doi.org/10.3390/su11205638.
- 75. Reeves, C.J.; Siddaiah, A.; Menezes, P.L. A Review on the science and technology of natural and synthetic biolubricants. *Journal of Bio- and Tribo-Corrosion* **2017**, *3*, 11, https://doi.org/10.1007/s40735-016-0069-5.

- Mannekote, J.K.; Kailas, S.V.; Venkatesh, K.; Kathyayini, N. Environmentally friendly functional fluids from renewable and sustainable sources-A review. *Renewable and Sustainable Energy Reviews* 2018, *81*, 1787-1801, https://doi.org/10.1016/j.rser.2017.05.274.
- 77. Saboya, R.M.A.; Cecilia, J.A.; García-Sancho, C.; Sales, A.V.; de Luna, F.M.T.; Rodríguez-Castellón, E.; Cavalcante, C.L. Assessment of commercial resins in the biolubricants production from free fatty acids of castor oil. *Catalysis Today* **2017**, *279*, 274-285, https://doi.org/10.1016/j.cattod.2016.02.020.
- Salih, N.; Salimon, J.; Abdullah, B.M.; Yousif, E. Thermo-oxidation, friction-reducing and physicochemical properties of ricinoleic acid based-diester biolubricants. *Arabian Journal of Chemistry* 2017, 10, S2273-S2280, https://doi.org/10.1016/j.arabjc.2013.08.002.
- Abdullah, B.M.; Zubairi, S.I.; Huri, H.Z.; Hairunisa, N.; Yousif, E.; Basu, R.C. Polyesters based on linoleic acid for biolubricant basestocks: Low-temperature, tribological and rheological properties. *PLOS One* 2016, 11, e0151603, https://doi.org/10.1371/journal.pone.0151603.
- Sarno, M.; Iuliano, M.; Cirillo, C. Optimized procedure for the preparation of an enzymatic nanocatalyst to produce a bio-lubricant from waste cooking oil. *Chemical Engineering Journal* 2019, 377, 120273, https://doi.org/10.1016/j.cej.2018.10.210.
- Shahabuddin, M.; Mofijur, M.; Kalamc, M.A.; Masjuki, H.H. Study on the friction and wear characteristics of bio-lubricant synthesized from second generation Jatropha methyl ester. *Tribology in Industry* 2020, 42, https://doi.org/10.24874/ti.2020.42.01.04.
- Singh, Y.; Farooq, A.; Raza, A.; Mahmood, M.A.; Jain, S. Sustainability of a non-edible vegetable oil based bio-lubricant for automotive applications: A review. *Process Safety and Environmental Protection* 2017, *111*, 701-713, https://doi.org/10.1016/j.psep.2017.08.041.
- Syahir, A.Z.; Zulkifli, N.W.M.; Masjuki, H.H.; Kalam, M.A.; Alabdulkarem, A.; Gulzar, M.; Khuong, L.S.; Harith, M.H. A review on bio-based lubricants and their applications. *Journal of Cleaner Production* 2017, *168*, 997-1016, https://doi.org/10.1016/j.jclepro.2017.09.106.
- 84. Xiong, Z.; Fu, F.; Li, X.; Li, Y. Preparation of an environmentally friendly emulsion-type lubricant based on crude rice bran wax. *Petroleum* **2019**, *5*, 77-84, https://doi.org/10.1016/j.petlm.2018.09.002.
- 85. Sniderman, D. Food grade lubricants and their regulation. *Tribology & Lubrication Technology* **2016**, *72*, 26, https://doi.org/10.1002/fsat.3002_18.x.
- 86. Samidin, S.; Salih, N.; Salimon, J. Production of hyperbranched nonaoleate trimethylpropane for biolubricants basestock. *Malaysian Journal of Analytical Sciences* **2015**, *19*, 129-137.
- 87. Salimon, J.; Abdullah, B.M.; Yusop, R.M.; Salih, N. Synthesis, reactivity and application studies for different biolubricants. *Chemistry Central Journal* **2014**, *8*, 16, https://doi.org/10.1186/1752-153x-8-16.
- Salimon, J.; Ahmed, W.A.; Salih, N.; Yarmo, M.A.; Derawi, D. Lubricity and tribological properties of dicarboxylic acid and oleyl alcohol based esters. *Sains Malaysiana* 2015, 44, 405-412, https://doi.org/10.17576/jsm-2015-4403-12.
- Salih, N.; Salimon, J.; Yousif, E. The physicochemical and tribological properties of oleic acid based triester biolubricants. *Industrial Crops and Products* 2011, 34, 1089-1096, https://doi.org/10.1016/j.indcrop.2011.03.025.
- Salimon, J.; Salih, N.; Yousif, E. Synthesis, characterization and physicochemical properties of oleic acid ether derivatives as biolubricant basestocks. *Journal of Oleo Science* 2011, 60, 613-618, https://doi.org/10.5650/jos.60.613.
- Battersby, N.S.; Ciccognani, D.; Evans, M.R.; King, D.; Painter, H.A.; Peterson, D.R.; Starkey, M.; Force, C.B.T. An 'inherent' biodegradability test for oil products: Description and results of an international ring test. *Chemosphere* 1999, *38*, 3219-3235, https://doi.org/10.1016/s0045-6535(98)00552-9.
- Salimon, J.; Salih, N.; Yousif, E. Biolubricants: Raw materials, chemical modifications and environmental benefits. *European Journal of Lipid Science and Technology* 2010, 112, 519-530, https://doi.org/10.1002/ejlt.200900205.
- 93. Biodegradability, R. OECD Guideline for testing of chemicals. OECD 1992, 71, 1-9.
- 94. Salimon, J.; Salih, N.; Yousif, E. Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant applications. *Arabian Journal of Chemistry* **2012**, *5*, 193-200, https://doi.org/10.1016/j.arabjc.2010.09.001.
- 95. Davis, J.W.; Madsen, S. Factors affecting the biodegradation of toluene in soil. *Chemosphere* **1996**, *33*, 107-130, https://doi.org/10.1016/0045-6535(96)00152-x.

- 96. Yvon-Durocher, G.; Allen, A.P.; Bastviken, D.; Conrad, R.; Gudasz, C.; St-Pierre, A.; Thanh-Duc, N.; del Giorgio, P.A. Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. *Nature* 2014, 507, 488-491, https://doi.org/10.1038/nature13164.
- 97. Willing, A. Lubricants based on renewable resources an environmentally compatible alternative to mineral oil products. *Chemosphere* **2001**, *43*, 89-98, https://doi.org/10.1016/s0045-6535(00)00328-3.
- Ravasio, N.; Zaccheria, F.; Gargano, M.; Recchia, S.; Fusi, A.; Poli, N.; Psaro, R. Environmental friendly lubricants through selective hydrogenation of rapeseed oil over supported copper catalysts. *Applied Catalysis A: General* 2002, 233, 1-6, https://doi.org/10.1016/s0926-860x(02)00128-x.
- Orsavova, J.; Misurcova, L.; Ambrozova, J.V.; Vicha, R.; Mlcek, J. Fatty acids composition of vegetable oils and its contribution to dietary energy intake and dependence of cardiovascular mortality on dietary intake of fatty acids. *International Journal of Molecular Sciences* 2015, *16*, 12871-12890, https://doi.org/10.3390/ijms160612871.
- 100.Momchilova, S.; Antonova, D.; Marekov, I.; Kuleva, L.; Nikolova-Damyanova, B.; Jham, G. Fatty acids, triacylglycerols, and sterols in neem oil (*Azadirachta Indica A. Juss*) as determined by a combination of chromatographic and spectral techniques. *Journal of Liquid Chromatography & Related Technologies* 2007, 30, 11-25, https://doi.org/10.1080/10826070601034188.
- 101.Production and use of food-grade lubricants. *Trends in Food Science & Technology* **2007**, *18*, S79-S83, https://doi.org/10.1016/j.tifs.2006.11.019.
- 102.Nagendramma, P.; Kaul, S.; Bisht, R.P.S. Study of synthesised ecofriendly and biodegradable esters: fire resistance and lubricating properties. *Lubrication Science* **2010**, *22*, 103-110, https://doi.org/10.1002/ls.108.
- 103.Meier, M.A.R.; Metzger, J.O.; Schubert, U.S. Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews* 2007, *36*, 1788-1802, https://doi.org/10.1039/b703294c.
- 104. Völtz, M.; Yates, N.C.; Gegner, E. Biodegradability of lubricant base stocks and fully formulated products. *Journal of Synthetic Lubrication* **1995**, *12*, 215-230, https://doi.org/10.1002/jsl.3000120305.
- 105.Bhaumik, S.; Paleu, V.; Pathak, R.; Maggirwar, R.; Katiyar, J.K.; Sharma, A.K. Tribological investigation of r-GO additived biodegradable cashew nut shells liquid as an alternative industry lubricant. *Tribology International* 2019, 135, 500-509, https://doi.org/10.1016/j.triboint.2019.03.007.
- 106. Aluyor, E.O.; Obahiagbo, K.O.; Ori-jesu, M. Biodegradation of vegetable oils: A review. *Scientific Research and Essay* **2009**, *4*, 543-548.
- 107.Luna, F.M.T.; Rocha, B.S.; Rola Jr, E.M.; Albuquerque, M.C.G.; Azevedo, D.C.S.; Cavalcante Jr, C.L. Assessment of biodegradability and oxidation stability of mineral, vegetable and synthetic oil samples. *Industrial Crops and Products* **2011**, *33*, 579–583, https://doi.org/10.1016/j.indcrop.2010.12.012.
- 108.Cecutti, C.; Agius, D. Ecotoxicity and biodegradability in soil and aqueous media of lubricants used in forestry applications. *Bioresour. Technol.* 2008, 99, 8492-8496, https://doi.org/10.1016/j.biortech.2008.03.050.
- 109.Darminesh, S.P.; Sidik, N.A.C.; Najafi, G.; Mamat, R.; Ken, T.L.; Asako, Y. Recent development on biodegradable nanolubricant: A review. *International Communications in Heat and Mass Transfer* 2017, 86, 159-165, https://doi.org/10.1016/j.icheatmasstransfer.2017.05.022.
- 110.Nallathambi Gunaseelan, V. Anaerobic digestion of biomass for methane production: A review. *Biomass Bioenergy* **1997**, *13*, 83-114, https://doi.org/10.1016/s0961-9534(97)00020-2.
- 111. Aravind, A.; Joy, M.L.; Nair, K.P. Lubricant properties of biodegradable rubber tree seed (*Hevea brasiliensis Muell. Arg*) oil. *Industrial Crops and Products* 2015, 74, 14-19, https://doi.org/10.1016/j.indcrop.2015.04.014.
- 112. Oulego, P.; Faes, J.; González, R.; Viesca, J.L.; Blanco, D.; Battez, A.H. Relationships between the physical properties and biodegradability and bacteria toxicity of fatty acid-based ionic liquids. *Journal of Molecular Liquids* 2019, 292, 111451, https://doi.org/10.1016/j.molliq.2019.111451.
- 113.Garcés, R.; Martínez-Force, E.; Salas, J.J. Vegetable oil basestocks for lubricants. *Grasas y Aceites* **2011**, *62*, 21-28, https://doi.org/10.3989/gya.045210.
- 114.Zurlo, J.; Rudacille, D.; Goldberg, A.M. Animals and alternatives in testing: History, science, and ethics: 2002.
- 115.Lin, L.; Allemekinders, H.; Dansby, A.; Campbell, L.; Durance-Tod, S.; Berger, A.; Jones, P.J.H. Evidence of health benefits of canola oil. *Nutrition Reviews* **2013**, *71*, 370-385, https://doi.org/10.1111/nure.12033.
- 116. Habereder, T.; Moore, D.; Lang, M. Eco requirements for lubricant additives. *Lubricant Additives* **2009**, 647-666, https://doi.org/10.1201/9781420059656.