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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

M. Gul [1,2] · H. H. Masjuki [1,3] · M. A. Kalam [1] · N. W. M. Zulkifli [1] · M. A. Mujtaba [1,4]

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Abstract

High demand for crop oils is anticipated in the lubricant industry because of their renewable, non-toxic, environment-friendly nature. Crop oils typically offer high viscosities, viscosity indexes, and flashpoints. The unique structure of crop oils provides good lubrication, high flammability, and anti-corrosion ability. In contrast, petroleum-based lubricants face a difficult future because of declining petroleum reservoirs that will increase their prices. This paper reviews green-lubricant feedstock requirements, the effect of fatty acids composition to improve physicochemical properties, chemical modifications of green lubricants by applying transesterification to find suitable environmentally -friendly and cheaper feedstock to replace petroleum lubricants. Moreover, global and Pakistani indigenous crop oils are also analyzed for their potential use in green lubricants by comparing their fatty acid compositions, characteristics and reaction conditions according to applications and standards. This review discovers that cottonseed oil has great potential as a new sustainable and cheaper feedstock for the global and Pakistani green-lubricant markets. Green lubricant production rate can be enhanced significantly after upgrading the conventional production method. It is believed that this review paper will provide useful information to engineers, researchers, chemists, industrialists, and policymakers, who are interested in green-lubricants synthesis.

Keywords Crop seed oil · Physico-chemical characterization · Trimethylolpropane · Microwave-assisted transesterification · Automotive green lubricant · Cottonseed oil

Abbreviations

PCRET	Pakistan Council of Renewable Energy Technologies
AEDB	Alternate Energy Development Board
OPEC	Organization of Petroleum Exporting Countries
APLMA	Pakistan Lubricant Manufacturers Association
NPG	Neopentyl glycol
TMP	Trimethylolpropane
PE	Pentaerythritol
CSO	Crop seed Oil
FFA	Free Fatty Acids
ME	Methyl Ester
CSOME	Crop seed oil methyl ester

✉ M. Gul
mustabshirha@yahoo.com

✉ H. H. Masjuki
masjuki@um.edu.my

1 Center for Energy Science, Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

2 Department of Mechanical Engineering, University College of Engineering and Technology, Bahauddin Zakariya University, Multan 60000, Pakistan

3 Department of Mechanical Engineering, Faculty of Engineering, IIUM, 50728 Kuala Lumpur, Malaysia

4 Department of Mechanical Engineering, University of Engineering and Technology, City Campus Lahore, Lahore, Pakistan

Introduction

Most lubricants on today's global market are petroleum-based, and the remaining are formulated from chemicals or crude oil. High prices of unrefined petroleum products will be seen after 2050 because of depletion of reservoirs. Sustainable energy sources like alkyl ester and green lubricants might be complementary for the smooth running of vehicle engines [1].

A large extent of lubricants used in the industries are lost in the environment, polluting both water and soil [2]; air is also influenced by fossil-based lubricants [3]. Currently, environmental health and emission concerns are becoming increasingly critical for the public. To overcome these issues, the most practical decision is to use eco-friendly, biodegradable and prudent green lubricants instead of today's petroleum-based lubricants [4].

There are various methods for producing green lubricants by using different polyols (such as neopentylglycol, trimethylolpropane, pentaerythritol, and dipentaerythritol) [5]. These polyols do not have β-hydrogen atoms, but TMP based-transesterification is the most convenient method for adressing that lack. TMP-based green lubricants can be used as hydraulic fluids, automobile engine oil, jet engine lubricant, and refrigeration lubricants [6].

Green lubricants have recently been getting attention as alternatives to standard petroleum fuels because of their energy independence. Bio-based lubricants are esters of substantial alcohols of crop seed oils, and their lubricating properties are comparable with petroleum-based lubricants [7]. Costs of green lubricants are high compared to conventional petroleum lubricants, so industries are putting resources into R&D and genetic engineering to extract maximum oil from seeds with minimum cost [8]. A financial examination demonstrated that the high cost of green lubricants, in contrast with petroleum fuel, is because of the cost of virgin crop oil [9].

In the US, soybean oil is considered as the main feedstock for green lubricants. However, there is a competition for soy between biofuel and food, which in returns increases the price of biofuels. So in order to reduce production cost for green lubricants, efforts should be made for alternative feedstock [10]. This issue can be resolved by getting base oil from indigenous non-edible crops that could be cultivated on marginal land [11]. Malaysia and Indonesia have an abundance of the indigenous palm tree; more than 80% of global cooking oil demand is fulfilled by palm oil. Their palm oil production is increasing continuously because its utilization as a feedstock is also expanding in the biofuel market. Europe utilizes rapeseed (canola) and sunflower oils from its native crops, while the USA has high production of native soybean oil to formulate bio-based lubricants. Various research papers show that the USA, Europe, and South East Asia have been producing green lubricants from their indigenous crops and using thm in vehicles for the last few decades [12, 13]. This diversity in the utilization of crop oil from indigenous crops plays a significant role in improving the market economy of a country.

Pakistan imports an extensive amount of petroleum products from Middle East nations to fulfill energy needs. Unrefined petroleum imports were 5.9 million tons (27.1 million barrels) with an estimation of US $ 1.84 billion in July-March FY 2017, while about 24.2 million barrels of crude oil were produced domestically during July-March FY 2017 [14]. Pakistan's car industry has expanded about 25%in the past 3 years. Looking to the future, it is expected that the energy demands for transportation and power will increase up to 53% by the year 2030. This significantly increases fuel demand and purchases. Six out of 11 members of OPEC oil had depleted reservoirs, causing high costs for crude oil. The economy and prosperity of Pakistan is contingent upon the availability of affordable fuel, so it is essential to look for alternative resources which can be extracted from indigenous feedstock [15]. The PCRET and AEDB departments are already working in Pakistan to facilitate renewable energy (RE) resource projects [16, 17], while the Ministry of Petroleum & Natural Resources is working on biofuel standards for biodiesel (B-100) and its blending mandates up to B-20 [18].

At present, it is essential to discuss the valuable role of indigenous oil-yielding crops as sustainable sources of energy for green-lubricant production in Pakistan. This approach has the advantage of providing more employment to farmers [15, 19]. Alternate sources of energy will thus appear as a significant player in improving the socio-economics of Pakistan by diversifying the use of crop oils [20]. After extracting crop seed oils, the remaining oil cake can be utilized as feed for livestock. Oilseed residues can be decomposed into N (nitrogen), P (phosphorus) and K (potassium) rich biofertilizers, or it can be utilized to produce methane gas for power generation [16]. Biodiesel and green-lubricant synthesis require alcohol (methanol or ethanol), which are easily accessible from Pakistan's sugar industries.

In the past, research has been conducted on various aspects of plants and crop production for biodiesel synthesis in Pakistan [21], but no one has reviewed and studied green-lubricant prospects as an alternative energy source, or its synthesis and applications in Pakistan.

Considering the upcoming scarcity of petroleum sources, the present research work reviewed fatty acid composition of crop seed oils feedstock and its effect on physio-chemical properties of lubricants along with measuring methods and standards. This paper also gives comprehensive details on crop oil potential for green-lubricant synthesis from appropriate standardized advance methods to overcome the limitations of green lubricants in global automobile applications.

Research Methodology

This section describes the three-stage analysis framework adopted for this review.

In the first stage, a systematic literature search was conducted to collect information related to

- Current status of global and Pakistani green-lubricant markets according to region and applications

- Doctrinal methods were employed to find Pakistani crop oils' potentials as a feedstock for green-lubricant production and recent developments in green-lubricant policy in Pakistan. Data were retrieved from primary sources such as national blending mandates, alternate energy development board (AEDB), Pakistan lubricant manufacturers association (APLMA), Pakistan council of renewable energy technologies (PCRET) and Organization of Petroleum Exporting Countries (OPEC) departments
- All available feedstock for green-lubricant synthesis along with their fatty acid compositions
- Importance of transesterification as a chemical modification method and advances in this method
- Factors involved in transesterification and their effect on yield
- Effect of fatty acid composition and chemical modification on physicochemical, lubricity and tribological properties
- Advantages, demerits, and constraints of green-lubricant utilization and policy barriers in commercializing the green lubricants
- Measuring Standards and recent amendments in the laws and regulations for green lubricants made by different countries

All information is accessed from government documents, official reports, news reports, books, Google Scholar, Scopus, Web of Science, Springer, ScienceDirect, Wiley, Emerald, and Hindawi database.

The second stage involved organization, screening, and selection of relevant data by qualitative assessment and cross-referencing. Previously published reports, government documents, articles and review papers are examined and compared with the recent ones to select the most relevant literature for analysis. Findings of the articles were considered as a guideline for critical analysis.

The third stage involved the content analysis to make conclusions. Critical analysis of collected literature shows that most of the green-lubricant feedstock is obtained from edible sources (like soybean, rapeseed, corn, palm, sunflower, canola, olive, coconut, etc), which creates competition with food and increases its prices in the global market. So to find the potential of new alternative non-edible sources of green lubricant feedstock, it is necessary to investigate the effect of fatty acids composition of crop oils on their physicochemical, lubricity and tribological properties.

Moreover, Pure crop seed oils have very low thermo-oxidative stability and poor pour points. Most of the research papers focus on production processes and the use of additives to enhance these limitations. No one has critically reviewed the significance of the fatty acid structural compositions of crop oils. The aim of this paper is also to highlight the importance of laws, regulations and measuring standards. In general, the reports and research articles cited in this review paper not only cover the span of 2007 to present (2019), but also systematically communicate limitations, modifications, development, and effectiveness of green lubricants.

Current Status of Global and Pakistani Green Lubricant Markets

According to a recent report, the world's green lubricant market was valued from about USD 2.24 billion in 2017. This revenue is expected to increase up to 6.2% with a value of 3.41 billion USD in 2024 with, automotive applications dominating [22]. The global green lubricant market segment and its utilization by region and applications are shown in Figs. 1 and 2, respectively. Figure 2b also shows that maximum utilization of green lubricants is in automotive and transport.

According to APLMA, Pakistan's annual lubricant demand is about 400,000 tons. Figure 3 presents automotive growth and lubricant consumption by automobiles in Pakistan, which is increasing continuously. Mineral and synthetic-based lubricants are used in Pakistan at a large extent, while green lubricants share is less than 1%. Most of lubricant market share is fulfilled by national (local) brands of Pakistan, with only 22% of lubricant being imported, as shown in Fig. 4. Therefore, local brands of Pakistanhave a role to play in replacing petroleum lubricants with green lubricants.

Feedstock Considerations for Green Lubricants

Bio-based lubricants e(specially oleochemicals) are usually, but not essentially, based on various crop seed oils (CSOs). Crop oils can easily solubilize polar type additive molecules, so desired properties can easily be achieved for particular applications. Green lubricants can also be synthetic esters that are partly extracted from bioresources, or they can be a combination of crop seed oils and other chemicals. Green lubricants are better than mineral oil-based lubricants because of renewability, low toxicity, biodegradability, high viscosity, high lubricity, high flash points (low volatility) and less friction and wear. However, these have poor pour points and oxidative stability, which limit their use in those applications where the green lubricant is utilized "once-through", and where very less toxicity is needed; examples include mold release, chain drive or sawmill blades, transmission fluids, cutting fluids and some two-stroke engine lubricants [26–28]. Most green lubricants are extracted from edible and non-edible crop seed oils or some other sources as mentioned in Table 1.

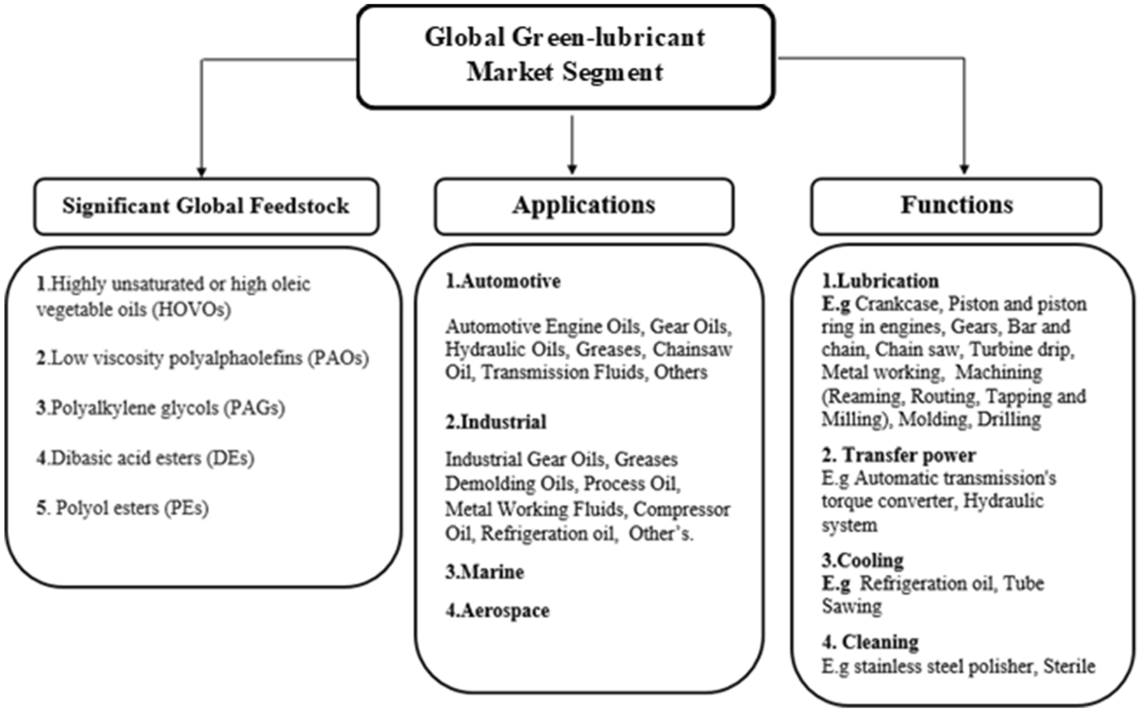


Fig. 1 Green lubricant Market Segment

Non-edible crops are attractive for cultivation because of having no competition with edible agricultural sources. Non-edible crop cultivation for green lubricant production has very little or no effect on cultivation or prices of the world's food. Such crops often can be cultivated on less fertile land [12]. Pakistan, being an agricultural country, has a great potential for increasing the cultivation of oil-yielding crops, which will also help in improving exports and economic growth [29]. Depending upon climate conditions, production, cultivation, and harvesting of oilseed crops in Pakistan can be classified into the categories mentioned in Table 2.

Crop seed oils contain 98% of triacylglycerides (triglycerides) which have saturated or mono-, di-, tri- or poly-unsaturated chains of various fatty acids and glycerol, as shown in Fig. 5.

Carboxyl groups of fatty acids attach with three hydroxyl groups of glycerol via ester linkages. Other than triacylglycerides, very small amounts of free fatty acids (0.1%), sterols (0.3%), tocopherols (0.1%) and diglycerides (0.5%) are also the part of vegetable oils [31].

About 350 indigenous oil-yielding crops are available throughout the world for extracting crop seed oils as

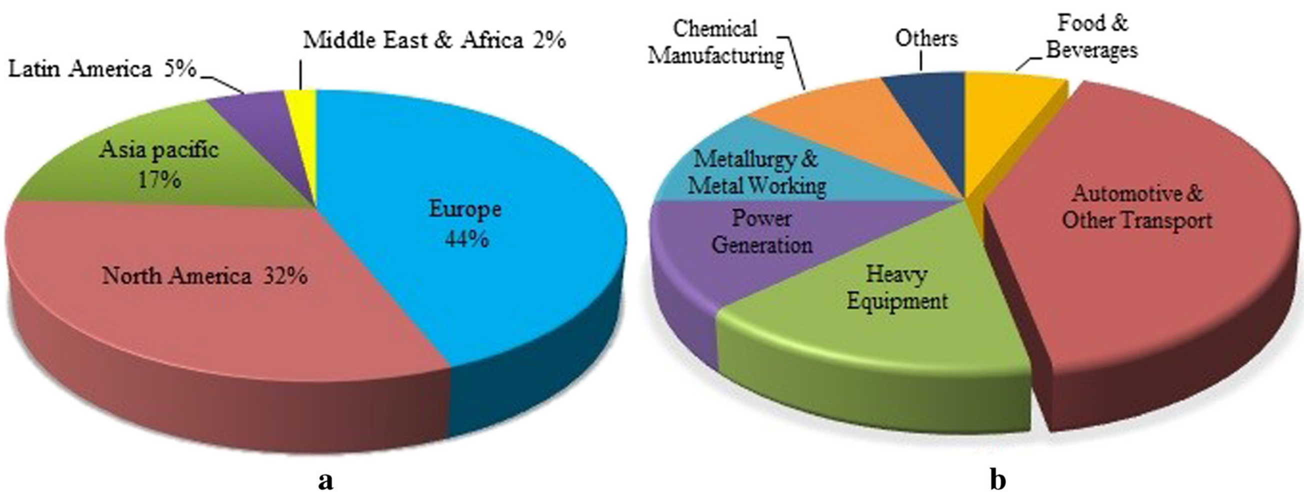


Fig. 2 FY 2017: Global Green lubricant utilization **a** by regions and **b** by applications [22]

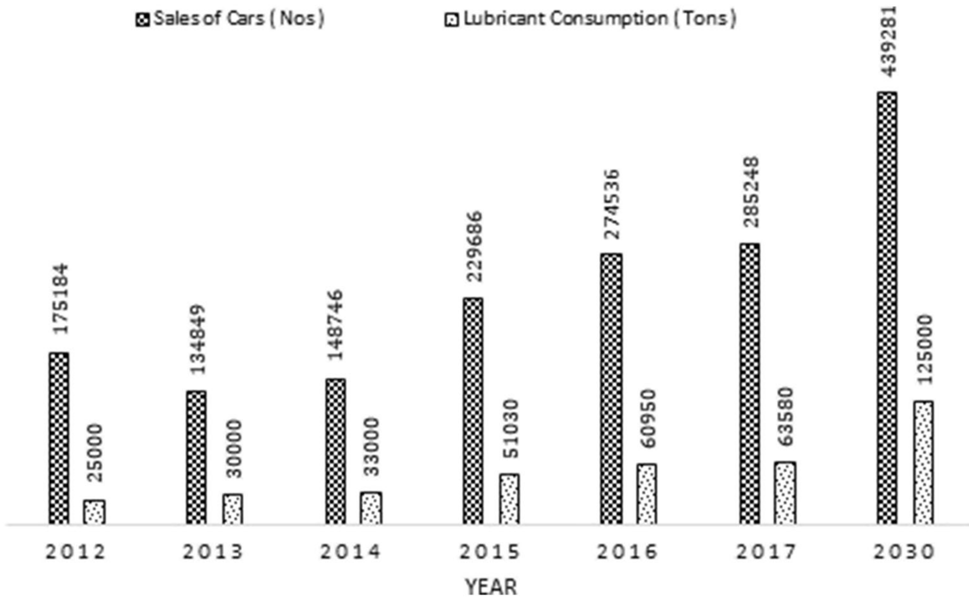


Fig. 3 Car growth and lubricant consumption by automobiles in Pakistan [23, 24]

feedstock for green lubricants. The popular feedstocks of the global market and their prospects in Pakistan, with their fatty acids compositions, are given in Tables 3 and 4.

Physicochemical characteristics of the different feedstock are influenced by the structural compositions of the triacylglycerides, i.e. the number of double bonds and carbon chain lengths in the fatty acids. In crop oils, saturated or unsaturated fatty acid carbon chains vary from C-06 to C-24. Minimum carbon chain length required for successful lubrication is C-9 [43] and lubricity is evaluated by Gibbs free energy of adsorption [44]. Poor pour point and high viscosity of crop seed oils are because of the high molecular weight (longer carbon chain) of triglyceride, which also helps in maintaining their thermal and structural stability [8, 26, 45]. Researchers reported pure crop oils are effective as boundary lubricant because the polar nature of ester group of triglyceride developed strong interaction with lubricating surfaces. In addition, these also have the capability to solubilize additives and contaminants. Increase in double bonds (high degree of unsaturation) improves the lubricity [44] and low-temperature properties but decreases oxidative-thermal stability and viscosity at high temperatures and loads [46]. Sevim Z. Erhan et al. reported that required thermo-oxidative stability at high temperatures can also be achieved by blending high-oleic crop seed oils with polyalphaolefin (PAO) as a diluent, while employing zinc diamyl dithiocarbamate (ZDDC) and antimony dialkyldithiocarbamate (ADDC) as chemical additives [47].

Pure crop seed oils cannot be used directly in industry and IC engine applications for prolonged times due to lower thermo-oxidative stability. However, chemical modification of crop seed oils containing more monounsaturated fatty

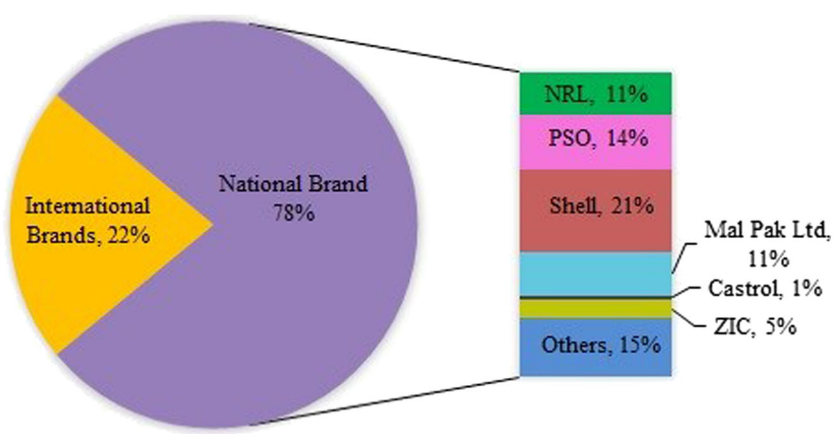


Fig. 4 FY 2018: Lubricant market share by different brands in Pakistan [25]

Table 1 General classification of green-lubricant feedstocks

Green-lubricant Feedstocks			
Vegetable Oils		Other Sources	Chemically Modified Vegetable Oils
Edible Oils Sunflower, Corn, Soybean, Rapeseed, Palm, Safflower, Canola, Coconut, Olive, and Refined Castor	Non-Edible Oils Karanja, Neem, Jatropha, *Calophyllum inophyllum* oil	Solid fats, Waste materials (cooking oils), Tallows and Algae	E.g Modification by i) Transesterification ii) Epoxidation iii) Hydrogenation

acids, like high oleic or palmitoleic acid, have a good balance for thermo-oxidative stability, low pour point and viscosity for high-temperature applications [4, 45, 47, 48]. Transesterification, epoxidation or hydrogenation are some recognized chemical modification methods for converting crop oil into effective green lubricant [32, 33, 49]. So it is important to grow crop's seed, having a high percentage of oleic (C18:1) and palmitoleic (C16:1) acids, by genetic modification. Varieties of soybean, palm, sunflower, rapeseed, and camelina have been produced by genetic engineering to get the desired fatty acid compositions [50–53]. Genetically and chemically modified crop seed oils, having high thermo-oxidative stability, are currently being utilized in a few fields [54].

Table 2 The potential of oil yielding crop seeds in Pakistan [30]

Oil Yielding Crop Seeds in Pakistan	Yield potential (kg/ha)
Conventional	
Moringa	500
Corn	1000
Sesame	1200
Eruca sativa L. (Taramira)	900
Coconut, Rocket Seed	500
Non- Conventional	
Safflower (Carthamus)	1000
Sunflower	4000
Soybean	1000
Groundnut	4000
Industrial Crops	
Cotton Seed	460
Castor (*Ricinus communis*)	2000
Rapeseed/ Mustard Seeds	3500
Linseed	2500
Wild Crops	
Olive Tree	100
Neem Tree	1200
Jatropha	2750

Production Technology of Green Lubricants

Pour point and thermal stability of crop seed oils can further be enhanced by transesterification of polyol (NPG/TMP/PE) and methyl ester [52, 55, 56], by epoxidation [28, 57–59], which converts C=C bonds into oxirane rings and by selective hydrogenation [60–62], which eliminates polyunsaturated C=C bonds. Transesterification is considered suitable when crop seed oils contain high oleic acid (**C18:1**) content and their acidic value is less than or equal to 1 (FFA < 0.5%) [63]. As we know FFA = 0.5% * AV.

Transesterification with alkaline catalysts produces soaps when reacting with excess FFA. Presence of soap causes difficulty in separating ester and glycerin. Hence, FFA (AV) should be low. The acid value of vegetable oils can also be reduced by acidic catalyzed esterification [64]. Here we discuss only the transesterification, because it is most suitable for genetically improved crops rich in oleic acid. Many green lubricants produced by transesterification use NPG, PE and TMP polyol. However, TMP is most preferable because of its low melting point. This method not only improves thermo-oxidative stability [65], but also reduces wear and friction at extreme pressure by eliminating H-molecule at the beta C-position of a triglyceride of the crop seed oil substrate. TMP ester (green lubricant) made by the transesterification process is suitable for high temperature and pressure applications, such as automotive engines [66].

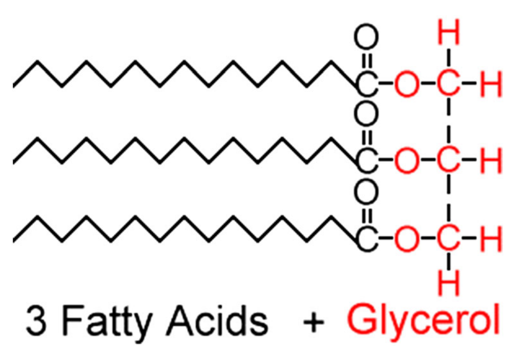


Fig. 5 Triglyceride structure of crop seed oils

Table 3 Globally used common green-lubricant feedstocks with fatty acids composition [32–35]

Crop seed oils ↓	Major Producers ↓	Fatty Acids (FA) Composition Cxx:y ** (%) →															
		C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1oleic	C18:2	C18:3	C18:1:OH	C20:0	C20:1	C22:0	C22:1	C24:0
Edible Oils																	
Palm Oil	Malaysia, Indonesia	–	–	–	1.12	42.70	–	4.55	39.37	10.62	0.21	–	0.39	0.17	0.58	–	0.06
Sunflower Oil	Europe, Russia, Ukrain, Argentina	–	–	–	–	6.18	–	2.16	26.12	65.52	–	–	–	–	–	–	–
Mustard Oil	EU, US, Canada, Australia, China, India	–	–	–	0.1	2.6	0.2	0.9	7.8	14.2	13	–	0.8	5.3	1.5	45.7	2.5
Rapeseed Oil		–	–	–	–	4.8	–	1.8	62.7	19.5	8.6	–	1.7	–	–	1	–
Olive Oil	Spain, Italy, Greece	–	–	–	–	11.7	0.8	3.0	77.9	7.2	–	–	–	–	–	–	–
Soybean Oil	US, Argentina, Brazil, China, India	–	–	–	–	11.28	–	2.70	24.39	56.28	5.34	–	–	–	–	–	–
Canola Oil	EU, Canada, Australia, China, India	–	–	–	–	3.0	–	3	60	30	7	–	–	–	–	–	–
Corn Oil	US, China, Brazil Argentina, Mexico	–	–	–	–	10.6	–	2	26.7	59.8	0.9	–	–	–	–	–	–
Coconut Oil	Indonesia, India, Sri-Lanka, Philippines	9.5	4.5	51.0	18.5	7.5	–	3	5	1	–	–	–	–	–	–	–
Cottonseed Oil	China, Pakistan, US, Australia, Brazil	–	–	–	0.77	21.87	0.47	2.27	16.61	56.35	0.33	–	0.26	0.28	0.36		0.12
Safflower/ carthamus Oil	India, US, Mexico	–	–	–	0.10	6.70	0.08	2.40	11.5	79	0.15	–	–	–	–	–	–
Moringa Oil	India, Sudan, South Africa, Latin America,.	–	–	–	–	5	2.7	0.8	85	2.3	–	–	4.2	–	–	–	–
Sesame Oil	United Republic of Tanzania, Myanmar, China, India, Japan, Sudan	–	–	–	–	10	–	4	47	39	<1	–	<1	<1	–	–	–
Non-Edible Oils																	
Jatropha Oil	Malaysia, Indonesia, Nepal, India, Thiland	–	–	–	1.4	15.6	–	9.7	40.8	32.1	–	–	0.4	–	–	–	–
Karanja Oil		–	–	–	–	11.65	–	9.7	40.8	32.1	–	–	0.4	–	–	–	–
Neem Oil	China, Europe	–	–	–	0.26	14.9	0.1	20.6	43.9	17.9	0.4	–	1.6	–	0.3	–	0.3
Calophyllum Oil	Malaysia, Indonesia, Hawaii, Australia, India, Philippines	–	–	–	–	17.9	2.5	18.5	42.7	13.7	2.1	–	–	–	–	–	2.6
Rubber Oil		–	–	–	2.2	10.2	–	8.7	24.6	39.6	16.3	–	–	–	–	–	–
Pongamia pinnata Pierre/Karanja Oil	Australia, India, Japan, Malaysia, Australia, Pacific islands	–	–	–	–	10.6	–	6.8	49.4	19	–	–	4.1	2.4	5.3	–	2.4
Castor oil	China, Brazil, India, Cuba	–	–	–	–	0.86	–	1.01	2.63	4.10	0.36	90.24	0.45	0.35	–	–	–

C xx:y ** shows a fatty acid chain with xx = no’s of carbon atoms and y = no’s of double bonds

Table 4 Major feedstock availability in Pakistan with fatty acids composition

Crop seed oils ↓	Production Rate of Oil in Pakistan (FY 2017-18) ↓ [30]		Fatty Acids (FA) Composition (%) →														Ref
	(Tons)	(%)	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C18:1: OH	C20:0	C20:1	C22:0	C22:1	C24:0	
Edible Oils																	
Cottonseed Oil	386,000	76.74%	–	–	22-26	–	2-5	15-20	49-58	1	–	–	–	–	–	–	[36]
Mustard/ Rapeseed Oil	66,000	13.12%	Tr	Tr	2-5	Tr	1-2	20-30	10-20	5-10	–	<2	5-10	<1	20-45	–	[37]
Sunflower Oil	40,000	7%	–	Tr	6	Tr	5	20-48	40-60	Tr	–	–	–	–	–	–	[38, 39]
Canola	11,000	2%	–	–	3-4	–	1-3	55-60	20-30	5-10	–	–	–	–	–	–	[33, 40]
Jatropha Oil	–	< 1%	–	1.4	15.6	–	9.7	40.8	32.1	–	–	0.4	–	–	–	–	[33]
Corn Oil	–	< 1%	–	1-2	8-12	–	2-5	19-49	34-62	Tr	–	–	–	–	–	–	[1]
Neem Oil	–	< 1%	–	0.2-0.26	14.9	0.1	20.6	43.9	17.9	0.4	–	1.6	–	0.3	–	0.3	[34]
Castor Oil	–	< 1%	–	–	1-3	–	2-3	4-5	2-8	Tr	80-90	Tr	Tr	–	–	–	[33, 34]
Sesame Oil	–	< 1%	–	–	10	–	4	47	39	<1	–	<1	<1	–	–	–	[41]
Moringa Oil	–	<1%	–	–	6.5	–	6.0	72.2	1.0	<1	–	4.0	2.0	7.1	–	–	[42]

Source: Pakistan Oilseed Development Board (PODB), Pakistan Bureau of Statistics. FY: 2017-18

Tr = Traces, C12:0 = Lauric Acid, C14:0 = Myristic Acid, C16:0 = Palmitic Acid, C16:1 = Palmitoleic Acid, C18:0 = Stearic Acid, C18:1 Oleic Acid, C18:2 = Linoleic Acid, C18:3 = Linolenic Acid, C18:1: OH = Ricinoleic Acid, C20:0 = Arachidic Acid, C22:0 = Behenic Acid, C22:1 = Erucic Acid, C24:0 = Lignoceric Acid

Chemical Modification of Crop Oils into TMP Based CSOME

Synthesis of chemically modified green lubricant from methyl ester as a starting material is the most efficient method, and it also expands the methyl ester business in the eastern European market [67]. Chemical modification of crop seed oils into TMP-CSOME (green lubricant) by transesterification involves the following steps.

Pre-Transesterification Treatment to Reduce FFA

Initially, it is necessary to determine the acid value (mg KOH/g) of crop seed oils, which indicates the amount of FFA. If the acidic value is greater than 1%, then an esterification process (pre-transesterification treatment) should be performed [68]. During this process, crop seed oils (triacylglycerol) are treated with alcohols (methanol/ ethanol) in the presence of acidic catalysts such as H_2SO_4, HCl, H_3PO_4 and sulfonic acid [69]. Usually, the crude crop seed oil is preheated to about 45-50 °C in a flask and then mixed with methanol and stirred for a few minutes. After that, acid is poured into it at atmospheric pressure and reaction continues for at least 30 min with constant stirring at 50 °C. On completion, product is transferred into a separating funnel and left for 10-24 h, then two layers appear. The upper layer has excess alcohol along with acid and impurities. A lower layer having CSO with very low FFA is separated and used for further transesterification processing.

Transesterification of Crop Oil into Methyl Ester

During the production of CSOME, the low FFA triglyceride of crop seed oil (CSO) reacts with alcohol to yield fatty acid alkyl esters. In methanolysis, methanol, as alcohol, reacts with triglyceride. Stoichiometrically, one mole of CSO (triglyceride) requires three moles of methanol, as shown by Eq. (1). Transesterification is a reversible reaction, but catalyst (alkaline) and an excess amount of methanol accelerate the conversion of reactants into methyl esters.

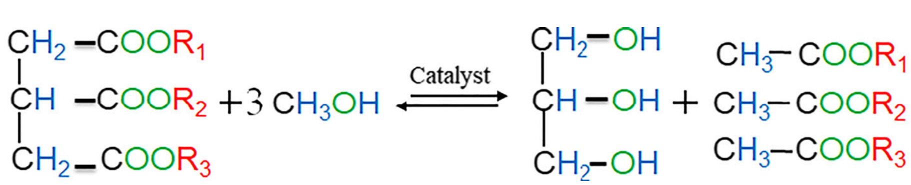
In conventional transesterification, CSO is pre-heated at 100 °C to ensure the evaporation of any water content, then it is transferred to a batch glass reactor and the temperature is sustained below the boiling point of methanol (65 °C). The optimized quantity of catalyst dissolves in methanol and is poured into the glass reactor. The reaction proceeds for 1-2 h with continuous stirring. Upon completion, the mixture is transferred to a separating funnel at room temperature for 10-24 h. After the prescribed time two layers appear, methyl ester, along with excess alcohol and unreacted triglyceride, remains in the top layer, and glycerol remains in the bottom layer. Both layers are removed from the funnel by sedimentation. The obtained top layer of fatty acid methyl ester is heated at 80 – 100 °C to remove methanol. It is then washed with hot water (80 °C) to remove glycerol, methanol, and catalyst. Anhydrous Na_2SO_4 is used to dry the remaining water and, finally, purified CSOME is obtained after filtration [70]. The percent yield of CSOME is calculated by using Eq. (2).

$$\text{CSOME\%yield} = [\text{weight (g) of CSOME} / \text{weight (g) of oil in the sample}] \times 100\% \tag{2}$$

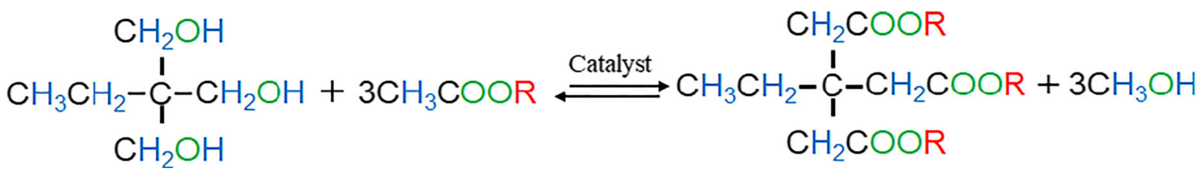
New advanced microwave-assisted transesterification (MAT) can also be utilized for ester production. It activates the alcohol molecules and ions by a magnetic field that changes continuously, increasing the reaction rate and yield within a short time [71]. In MAT, the microwave unit has a magnetic stirrer bar and non-contacting infrared constant temperature system. CSO is preheated in the microwave up to the required temperature. Then the mixture of methanol and catalyst is fed into the flask through the condenser. The reaction mixture is irradiated under reflux at optimal reaction times, ranging from 2 to 7 min [72].

Transesterification of TMP with CSOME

Transesterification of TMP with CSOME is carried out in a rotary vacuum evaporator with a round flask to produce CSO-TMP ester, as shown in Eq. (3). At least 20 mbar of vacuum pressure is required for maximum yield of the product.



(1) (1)



(3)

Green lubricant is prepared by transesterification of TMP with CSOME as summarized in Fig. 6.

Factors that Affect the Transesterification

The following key factors should be considered carefully to obtain the maximum yield of esters by the transesterification process.

Effect of Molar Ratios of Reactants

The alcohol-to-crop-seed-oil (triglyceride) molar ratio affects the conversion efficiency and production cost. Theoretically, alcohol-to-triglyceride molar ratio is 3:1. However, in most cases, the molar ratio is greater than the stoichiometric ratio to stimulate the reaction towards completion, so its optimum value should be determined to minimize the production cost. Further increase in molar ratio beyond the optimum value yields little improvement in the conversion efficiency and makes ester recovery difficult. Moreover, it also decreases ester yield and viscosity due to its dilution effect [70].

Effect of Catalysts

Correct catalyst type and optimum concentration accelerate the reaction. The concentration of acid catalyst (like H_2SO_4, HCl, H_3PO_4 and sulfonic acid) in esterification process usually varies between the ranges of 0.25–2% by volume fractions of the crop seed oil used in the reaction. Addition of acid above the optimum value darkens the color of the product.

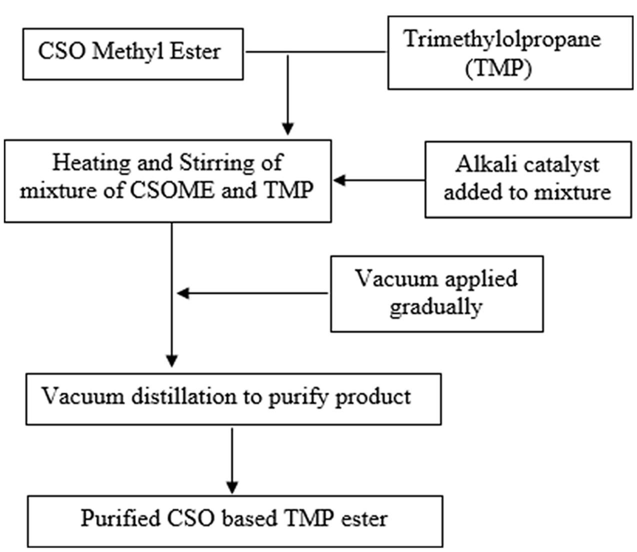


Fig. 6 Synthesis Process of CSO based TMP ester (Green lubricant)

Homogeneous alkali catalysts (such as NaOH, KOH, and sodium methoxide) in the transesterification process were varied from 0.5–1.5% by weight of the crop seed oil. The reaction did not accelerate with the insufficient concentration of catalyst, while an excess amount of catalyst beyond the optimum value caused emulsion (gel) formation and ultimately increased the viscosity [73]. Gel formation increases the difficulty in glycerol separation and ester and decreases the ester's yield.

Heterogeneous base catalysts are getting more attention than homogeneous ones for economic reasons. They are reusable and can easily be modified to include desired characteristics in such a way that even water content and FFA do not adversely affect the transesterification process. Different types of heterogeneous catalysts such as porous zirconia, titania, KOH with MgO or CaO [74, 75] alumina/silica-supported K_2CO_3 silica [76] zeolites [77] can be efficiently used in esterification and transesterification reactions [78].

The transesterification of TMP with CSOME is a relatively slow process, so sodium methoxide (homogeneous) and calcium methoxide (heterogeneous) catalysts are used to speed up this reaction [79].

Effect of Reaction Temperature

Temperature also affects the conversion efficiency. At room temperature, efficiency is very low, but it increases rapidly as with the rise in temperature up to the optimal value. Overly-high temperature during acidic esterification, increases the production cost and darkens the color of the product. During alkali transesterification of CSO, the temperature should be below 65 °C to avoid evaporation of methanol and saponification of the FFA of glycerides with alkali catalyst. For TMP, methyl ester reaction temperature varies from 100 to 250 °C.

Effect of Reaction Duration

During the reaction, constant and continuous stirring accomplish perfect contact between the crop seed oil and the reactant. Ester production rate slightly increases with the increase in reaction time. Usually, 30-180 min are adequate for esterification and conventional transesterification processes, and 2-7 min are required in microwave-assisted transesterification.

Table 5 gives details of feedstock for green-lubricant production along with influencing factors and operating conditions.

Microwave assisted transesterification appears to be a good upgrade to speed up the production method.

Physicochemical and Lubricity Properties of Green Lubricants

Acid Value (AV)

Acid value (mg KOH/g) of a crop seed oil indicates the quality and amount of FFA in the oil. A low acid value is required to protect the metal parts of the machine or engine from corrosion. The acid value of anhydrous crop seed oil should be less than 1 for alkali-catalyzed transesterification to avoid soap formation [88]. The acid value of high FFA-containing crop seed oil can be reduced by the esterification process. During esterification, crop seed oils are treated with alcohols in the presence of acidic catalysts [69]. AV can be determined using the AOCS Cd 3d-63 method or by the titrimetric method under ASTM D 664.

Viscosity & Viscosity Index

Oil-resistance against flow/ fluidity is called viscosity. High viscosity means long fatty acid C-chain length and establishment of thicker lubricant film. High viscosity plays a very vital role in increasing the lubricity of green lubricants [89]. For industrial applications, the viscosity range should be 5–15 cSt at 100 °C. Generally, kinematic viscosities of polyol esters range between 5-225 cSt @ 40°C and 2-20 cSt @ 100°C. Polypropylene can be used as a viscosity enhancer

The **viscosity index (VI)** reflects variation in viscosity because of temperature changes. Low VI indicates that viscosity will change as temperature varies, and vice versa. High viscosity is required in a good lubricant, as it can maintain oil film thickness over a wide range of temperatures. Lubricants with low VI become less stable at high temperature as oil film gets thinner and less viscous. The VI also depends on the molecular structure length of the fatty acids. It increases as linear C-chain length and un-saturation level increase, but branching in the structure decreases [90] the VI [91]. For instance, castor oil has higher viscosity and VI than highly refined mineral oil because of the hydrogen-bond of the hydroxyl monounsaturated triglycerides [19].

Some additives, like decyl acrylate polymers and isooctyl acrylate polymers, can be used to enhance the VI of green lubricants. Polyol esters (NPG, TMP, and PE-based chemically structured green lubricants) shows high viscosity. Polyol esters are recommended for drilling fluids [90], hydraulic fluids, catapult oil and engine oils. Usually, viscosity and VI are measured at 40 °C and at 100 °C by viscometer under kinematic viscosity methods ASTM D445 and ASTM D2270, respectively.

Flashpoint/ Fire Point

Flashpoint is the minimum temperature required to heat the green lubricant before it vaporizes. It demonstrates the instability range and safe working temperature of the oil. Fire pointreflects the minimum temperature at which the green lubricant catches fire from an external flame. Flash and fire points should be high in order to minimize fire risk during lubricant leakage. Flashpoints of crop seed oils are high, correlating with very low volatility and vapor pressure, thus reducing hazards during practical usage [53]. Both can be measured by Cleveland open cup apparatus, as per ASTMD 92 / ASTM D93, or by using a tag closed tester under ASTM D5679.

Thermal / Oxidative Stability

Thermal stability gives information about the degradation rate of the green lubricant at elevated temperatures. It should be superior or similar to the maximum limit of temperature in any particular application [92], and is measured by thermogravimetric analysis.

Oxidation causes polymerization and increases the viscosity and acid content of the green lubricant. Consequently, metal parts become corroded, sludge is produced and decreases the lubricant's overall efficiency. Oxidation starts because of the double bonds present at the beta carbon-position in the structure of fatty acids, as shown in Fig. 7.

Thermal-oxidative stability of crop oils is strongly influenced by fatty acid composition and its structure. Shorter FFA chains and a high proportion of saturated fatty acids in a crop oil increases its oxidative stability, but is not favorable for low-temperature behavior. Coconut oil has high oxidative stability because it contains 90% saturated fatty acids [93]. While poly-unsaturated crop seed oils readily oxidize at room temperature, only crop oils containing mono-saturated fatty acids (such as oleic acids, C18:1) have comparatively good oxidative stability at high temperature.

A very small percentage of anti-oxidants, such as pyrogallol [94], ascorbic acid, BHT (butylated hydroxytoluene), PG (propyl gallate), MTBHQ (mono-tert-butyl-hydroquinone), BHA (butylated hydroxyanisole), and naturally occurring tocopherols [45], can be used to overcome this problem. Chemically modified feedstock (polyol esters) have much better thermal-oxidative stability at high temperature and rigorous conditions. Their response is good towards antioxidants and also resists aging processes better than mineral oil [86]. The following methods can be performed to determine the oxidation stability of crop seed oils.

Table 5 Production methods for green-lubricant synthesis

Reactants		Molar Ratios Alcohol: CSO or CSOME: Polyol	Catalyst	Reaction Conditions	Yield (%)	References
Crop Seed Oil/ Glycerides/ Methyl Ester (ME)	Alcohol/ Polyol (TMP)					
Low FFA CSO by Esterification						
Crude rubber seed oil (CRSO)	Methanol	6: 1	H_2SO_4 (0.5% by *v*/v fraction of CRSO)	Acid esterification: 50 °C, 30 min P_{atm} (Atmospheric P)	99%	[73]
Glyceride (Rubber seed oil with less than 2% FFA)	Methanol	9: 1	NaOH (0.5% by weight of RCO)	Alkali esterification: 45 ± 5 °C, 30 min	99%	[73]
CSO Methyl Ester by Transesterification						
Soybean oil	Methanol	6: 1	NaOH (1%)	MAT, 333 K, 3 min	97.7%	[71]
Soybean oil	Methanol	12: 1	Heterogeneous: MgO/Al2O 3	CT, 180 °C, 1 h	92%	[80]
Rapeseed oil	Methanol		Heterogeneous: CaO/MgO	CT, 64.5 °C,	92%	[81]
Rapeseed oil	Methanol	9: 1	Heterogeneous: $Ba(OH)_2$	MAT, methanol reflux, 15 min,	97-98%	[82]
Jathropa oil	Methanol	7.5:1	KOH (1.5%)	CT, 65, 1.5 h preheating +1 h RT	99.8%	[68]
Jathropa oil	Methanol	7.5:1	KOH (1.5%)	MAT, 65, No-preheating +2 min RT	97.4%	
Cotton Seed oil	Methanol	6: 1	KOH (1.5%)	CT, 333 K, 30 min	91.4%	[72]
Cotton Seed oil	Methanol	6: 1	KOH (1.5%)	MAT, 333 K, 7 min	92.4%	
Cotton Seed oil	Methanol	6: 1	Sodium Methoxide ($NaOCH_3$ = 0.97%)	CT, 63.8 °C, 2 h and 797 rpm	98.3%	[70]
Canola oil	Ethanol	6: 1	KOH (1%)	CT, 70 °C, 2 h	>90%	[83]
TMP Methyl Ester (Green lubricant) by Transesterification						
Jathropa oil	TMP	4: 1	H_2SO_4 (2%)	CT, 150 °C, 3 h	98.6%	[84]
Palm kernel oil ME	TMP	3.9: 1	$NaOCH_3$ (Sodium Methoxide)	CT, 20 mbar, 120 °C. time < 1 h	98%	[84]
Palm oil ME	TMP	10: 1	$NaOCH_3$	CT, 1-1.5 mbar, 110 °C	98%	[85]
Rapeseed oil ME	TMP	17.1:5.3	$NaOCH_3$ (0.5%)	CT, 3.3 kPa,110 °C, 8 h	99%	[84]
Olive oil ME	TMP	Olive ME = 50 g, TMP = 6.7 g	Calcium methoxide = 3 g	CT, 95 °C, 20 h	85.1	[86]
Jatropha oil methyl ester	TMP	4: 1	Sulfuric acid (1%)	CT, 483 K, 5 h, 25 kPa	91.5%	[87]

CT Conventional Transesterification, *MAT* Microwave assistant transesterification, *RT* Reaction Time

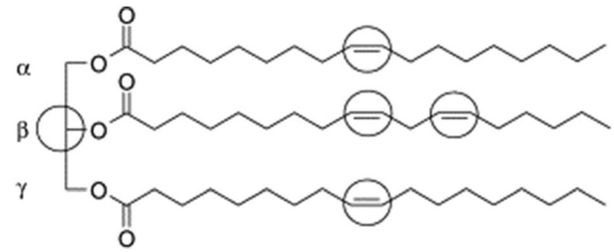


Fig. 7 Critical oxidation sites in triglyceride structure of crop oils

i) **Pressure differential scanning calorimetry (PDSC) method**

In the PDSC method, oxidation stability is determined by onset temperature (OT) during oxidation induction time (OIT) of isothermal experiments. The low value of OT suggests low oxidation stability. the PDSC method consists of a computerized thermal analyzer. The OT is calculated directly from the plot (exotherm) drawn between heat flow and temperature for each case [47].

ii) **Rotary bomb oxidation tests (RBOT)**

In the RBOT test, a sealed vessel containing crop seed oil and copper catalyst rotates axially in an oil bath set at 150 °C and 90-psi, as per ASTM D-2272. The pressure of the rotary bomb is also monitored and RBOT time is noted when the pressure of the rotary bomb reaches 25.4 psi [47].

iii) **Long-term oven oxidation stability test**

This is the most commonly utilized test; it can be used for any type of pure, additized, blended or chemically modified vegetable oil. In this test, CSO is poured into glass vials and put into the oven at 85 °C for 28 days. Change in the weight of CSO and total acid number (TAN) are determined at 0 and 28 days to find oxidative stability. The total acid number of crop seed oils remains in the range of 0.17–0.38 mg KOH/g, but in the absence of anti-oxidant it increases to 2–3 mg KOH/g after 28 days [47].

Pour Point (Low-Temperature Properties)

Pour point indicates the lubricant's fluidity at low temperatures. It is an important characteristic, especially in winter and for cold weather countries. A good lubricant has a low pour point so that it can provide lubrication, even at extremely low temperatures. Usually, crop oil loses fluidity below −10 °C when it remains in cold weather for a long time [33].

A long chain of FA and a high degree of unsaturation in fatty acids chains favors the low temperature and anti-wear characteristics of vegetable oils, but it is not favorable for oxidative stability [47, 95]. Rapeseed oil has the lowest pour point, at −21 °C [86]. Sevim Z. Erhan (2006) has improved the pour point (PP) of soybean oil by adding 20% PAO (polyalphaolefin) as a diluent, having PP of −57 °C. A small amount of butylated hydroxyl toluene can be used as a pour point depressant [64]. Isobutyl oleate, 2-ethylhexyl oleate, di-isodecyl adipate, trimethylolpropane trioleate, and pentaerythritol tetraoleate are also used as pour point depressants [96].

Green lubricants produced from methyl oleate, TMP triundecenoate, and canola biodiesel have pour points of −51 °C, −36 °C, and − 66 ,°C respectively [96]. Numerous chemically modified feedstock have very low pour points, −30 to −70 °C, and gives good lubrication during cold starting and protects engines parts from damage. DSC (Differential scanning calorimetry) calculates the pour point under ASTM D97.

Tribological Properties

About 15% to 20% of fuel energy is wasted in overcoming frictional forces in IC engines. A lubricant having low COF (coefficient of friction) can reduce this energy wastage [97]. The polar heads of the saturated and monounsaturated fatty acids form a monolayer film with metal surfaces, and stick away from the non-polar end. As a result, the coefficient of friction is reduced. Polyunsaturated fatty acids prevent the close packing of carbon-chains, weakening the monolayer film and increasing COF and wear rate. Avocado oil presents very good anti-frictional and anti-wear performance, better than other crop seed oils [98].

Green lubricants show better anti-wear properties than mineral oils [13, 99]. Lovell et al. discovered that boric acid powder as an additive in crop seed oil improves friction and wear performance [100]. Agarose as an additive also improves the coefficient of friction. The four-ball tester machine measures the tribological properties. The coefficient of friction is measured under ASTM D 5183-05, and wear scar diameter by ASTM D4172-94.

All the lubricity and tribological requirements of commercially available petroleum-based lubricants and bio-based lubricants are given in Table 6. Table 7 shows that physicochemical properties of pure crop seed oils can be improved by chemical modification.

Table 6 Reference green lubricants requirement according to applications [8, 101]

Reference Lubricant Name	Type of Feedstock	Applications Area	Lubricants Requirement/ Properties							
			Kinematic Viscosity mm^2/s (cSt):		Viscosity Index (VI)	Flash Point (°C)	Pour Point (°C)	Oxidative Stability/ *BD(21 days)	Coefficient of Friction (COF)	Wear Scar (mm)
			@ 40 °C	@100 °C						
BIOSYNT 40 V	Synthetic oil (Petroleum-based)	Universal Greasing Oil for all kind of mechanical equipment in the home or workshop like a bicycle, sewing machine, guns, rusty locks, etc	48	–	–	>300	−35	>80 BD(CEC)	–	–
BIOGEL	Refined rapeseed oil	Food Grade Lubricants used in food processing industry	32	–	–	>110	<−20	>98 BD(CEC)	–	–
PROBECO	Saturated and unsaturated fatty Acids	Food industry: Dough separation, Grease	35	–	–	>220	−33	>90 BD(CEC)	–	–
BIOGEL SE	Synthetic oil	Marine, Bearings, Rail curves, Wire ropes, Grease & General	38	–	–	>110	<−20	>90 BD(CEC)	–	–
EcoSEP	–	Demoulding & Release Agent Corrosion inhibitor	7-12	–	–	200	−20	>95 BD(CEC)	–	–
LUBECO™ BK70/ BK70 S	–	Conservation oils in sea transportation operation, Corrosion inhibitor	70	–	–	>200	−35	>90 BD(CEC)	–	–
Bar & Chain Oil 100	Rapeseed oil based lubricant	Chainsaws	100	–	>200	>250	<−20	>98 BD(OECD)	–	–
Bar & Chain Oil 150		Power saws and cutting equipment	150	–	>200	>250	<−20	BD >99 BD(OECD)	–	–
Bar & Chain Oil 220		Power saws and belt conveyors.	220	–	>200	>250	<−20	BD >98 BD(OECD)	–	–
Saw Blade & Guide Oils. ISO VG 40	FFL: Mineral-based	Heavy-duty applications for high lubricity, extreme conditions with wear & corrosion protection.	40	9.1	>210	>230	−30	>98 BD(OECD)	–	–
BIO 2 T Oil	Synthetic oil	2 stroke Engine oil, chainsaws, brush cutter and trimmer etc	45	Min 7.5	140	>90	−47	>90 BD(CEC)	–	–
BIO 4 T-SAE 30		4 stroke Engine oil, Agricultural equipment		11.2	150	220	−35		–	–
BIO HO 46	Rapeseed oil based lubricant	Bio Hydraulic Oil (HO)	46	–	>220	>250	−34	>90 BD(CEC)	–	–
Premium ISO VG 46	Saturated synthetic ester	Hydraulic Oil (HO) Marine Applications	46	–	>180	>220	−57	>90 BD(CEC)	–	–
Premium ISO VG 68			68	–	>180	>220	−57	>90 BD(CEC)	–	–
ISO VG 150	Highly refined vegetable synthetic ester.	Wire Rope Biolube lubricants used in mining, forestry, marine, construction, transport, and all other industries	150		140	>230	−45	>70 BD(OECD)	–	–
ISO VG 460			460		150	>230	−40	BD >70 BD(OECD)	–	–

Table 6 (continued)

Reference Lubricant Name	Type of Feedstock	Applications Area	Lubricants Requirement/ Properties							
			Kinematic Viscosity mm^2/s (cSt):		Viscosity Index (VI)	Flash Point (°C)	Pour Point (°C)	Oxidative Stability/ *BD(21 days)	Coefficient of Friction (COF)	Wear Scar (mm)
			@ 40 °C	@100 °C						
ISO VG 32	Rapeseed or high oleic sunflower oil based Lubricant	Industrial hydrostatic and hydrodynamic machines	>28.8	>4.1	>90	204	−6	>90 BD(CEC)	–	–
ISO VG 46	Rapeseed or high oleic sunflower oil based Lubricant	Industrial hydrostatic and hydrodynamic machine	>41.4	>4.1	>90	220	−10 to −6	>90 BD(CEC)	–	–
ISO VG 68	Rapeseed or high oleic sunflower oil-based Lubricant	Industrial hydrostatic and hydrodynamic machines, gear oil	>61.4	>4.1	>198	226	−6	>90 BD(CEC)	–	–
ISO VG 100	Rapeseed or high oleic sunflower oil based Lubricant	Industrial machinery oil, gear oil	>90.0	>4.1	>216	246	−6	1670.3 min	0.1230	0.181
Paraffin VG 95	FFL: Mineral based	Mechanical Systems	95	10	102	–	–	–	–	–
Paraffin VG 460	Synthetic lubricant from high oleic sunflower oil	Gear Oil	461	31	97	–	–	–	–	–
R 150	FFL: Mineral based	–	150.04			195		931.16 min	0.1033	0.164
SAE20W40	FFL: Mineral based	Motorcycle engine oil for extreme conditions	105	13.9	132	200	−21		0.117	0.549
75 W 90	FFL: Mineral based	Automobile	120	15.9	140	205	−48	–	–	–
75 W 140	FFL: Mineral based	Automobile	175	24.7	174	228	−54	–	–	–
80 W 140	FFL: Mineral based	Automobile	310	31.2	139	210	−36	–	–	–
AG100	High oleic sunflower oil or synthetic ester	Aerosol Grease	216	19.6	103	244	−18	–	–	–

*BD = Biodegradability (%) as per OECD 301B or CEC-L-33-A-93, FFL = Fully formulated lubricant

Table 7 Physico-chemical properties of different types of green lubricants [32, 46, 52, 55, 86, 96, 102]

Green lubricants Properties	AV	Kinematic Viscosity mm²/s (cSt): @ 40 °C	Kinematic Viscosity mm²/s (cSt): @ 100 °C	Viscosity Index (VI)	Flash Point (°C)	Pour Point (°C)	Oxidative Stability For oils: hr. @110 °C by Rancimat [13]	Coefficient of Friction (COF)	Wear Scar (mm)
Unmodified (Native) crop seed Oils Properties									
Palm	0.54	52.4	10.2	186		−5	4 h @ 110 °C	–	–
Sunflower	0.41	40.05	8.65	206	252	−12	0.9 h @ 110 °C	–	–
Canola	–	38.5	8.5	207	162	−18	–	–	–
Corn	–	35.4	–	–	251	−2.8	2.2 h @ 110 °C	0.4458	
Olive	1.17	39.44	8.39	196.6	–	−15.1	**Δν (%)** = +97.5, **ΔAc** = +4.14 and 7.5 h @ 110 °C	0.0778	–
Soybean	0.61	28.86	7.55	246	325	−9	2.1 h @ 110 °C	0.4059	–
High Oleic Soybean	0.12	41.34	9.02				–		
Coconut		24.8	5.5	169	325	21	35.4 h @ 110 °C	0.101	0.601
Rapeseed	1.40	45.60	10.07	180	240	−12	7.5 h @ 110 °C	–	–
Jatropha	3.20	35.4	7.9	205	186	−6	2.3 h @ 110 °C	–	–
Castor	1.40	220	19.72	220	250	−27	1.2 h @ 110 °C	–	–
Moringa	–	44.88	–	–	204	–	28.27 min	0.0835	0.15
Lesquerella	–	119.8	14.7	125	–	−21	–	0.045	0.857
Rice Bran	–	40.6	8.7	169	318	−13	0.5 h @ 110 °C	0.073	0.585
Chemically Modified (by Transesterification) Crop Seed Oils									
Palm ME +TMP + Na-methoxide	–	47.1	9.0	176	–	−2	355 °C Degradation temp	–	–
High Oleic Palm ME+ TMP + Na-methoxide	–	45.5-50.7	9.2-10	183-200	–	−37 to −9		–	–
Sunflower+ Octanol	–	7.93	2.74	226	–	−3	23 min (RBOT)	–	–
Fe-Zn double metal cyanide complexes									
Canola ME +TMP + Na-methoxide	–	40.5	7.8	204	–	−66	OIT = 0.74 h	–	0.223
Rapeseed ME+ NPG/TMP/PE + immobilized Lipase	–	17.4, 38.2, 35.1	4.7, 8.4, 7.9	209, 205, 207	–	−19.5, −18, −19.1	**Δν (%)** = +136.5, **ΔAc** = +6 **Δν (%)** = +90.1, **ΔAc** = +2.9 **Δν (%)** = +145.7, **ΔAc** = +7.5	–	–
Olive Oil ME+ TMP + Calcium methoxide	0.55	36	8.32	218.3	–	−13	**Δν (%)** = +72.1, **ΔAc** = +2.15	–	–
Rapeseed oil + TMP + Calcium methoxide	0.24	35.34	7.99	209.2	–	−15.5	**Δν (%)** = +100.7, **ΔAc** = +3.29	–	–
Rapeseed ME+ 2-ethylhexanol+ immobilized Lipase	–	7.8	2.7	224	–	−31.3	**Δν (%)** = +147.1, **ΔAc** = +7.7	–	–
Jatropha ME+ TMP + Na-methoxide	–	42.57	9.37	183	–	−6	325 °C Degradation temp	–	–
Jatropha+TMP+ Na-methoxide	–	43.90	8.71	180	–	−6	–	–	–
Waste cooking oil ME+ TMP + KOH	–	38.6	8.44	204	240	−8		–	–

ME Methyl ester, Δν: percentage of viscosity change, ΔAc: acid number change, *OIT* Oxidative induction time, *RPVOT* Rotating pressure vessel oxidation test

Table 8 Legislation and regulation's concerns of green lubricants

Sr #	Concerns/ Purpose	Legislation and Regulations
1	Fit for utilization	Include health and safety measure.
2	EU Directives	Biocidal products, recycling, and criteria for disposal of oils and lubricants.
3	Water Management Act	Toxic effects of lubricants and their threats to the aquatic system
4	Restrictions on Hazardous Substances (RoHS)	Chemical hazards
5	Globally Harmonized System	Registration for toxic chemicals, evaluation, regulation, authorization, and restriction on the use of chemicals
6	Eco-labels	Ecological concerns. Ecotoxicity of materials:
7	Life Cycle Analysis	Synthesis of product and its sustainability
8	Bio-Preferred	Green and renewable procurement

Laws and Regulations for Green Lubricants

Green lubricants are receiving public attention because of environmental and health issues caused by the evaporation, loss, leakage, and spillage of mineral lubricants. Therefore it is the responsibility of legislators and regulatory authorities to take measures for protecting the ecosystem from harmful effects of lubricants and to expand the market share of environmental friendly green lubricants as mentioned in Table 8.

In many European countries, governments have taken strict actions in their policies for limiting the use of mineral-based lubricants. They stimulate the use of renewable, non-toxic and biodegradable resources for green-lubricant synthesis and application in sensitive areas like forestry, agriculture, mining, shipping, marine, sawmills, heavy industry, pulp and paper mills, transportation, motorcycle chains, etc. They also introduce many projects and policies to support research and development activities by giving subsidies in different areas and developing a legislative framework to expand the green-lubricant market.

Table 9 represents the laws, regulations, and policies of different countries for promoting green lubricants.

Conclusion and Future Recommendations

Growing demands for energy, increasing prices of mineral oil, as well as environmental and health concerns, have directed a lot of research and development in the field of lubricants. Physico-chemical property reviews showed that lubricity and tribology of lubricants depend on fatty acid composition of base oil. Increase in C-C chain length (up to C18-C22) increases the viscosity and lubricity of green lubricants. Unsaturated fatty acids play a significant role in improving lubricity with a decrease in friction and wear rate. Poly-unsaturated fatty acids are favorable for low pour points, but increase oxidative instability. Saturated FA increases oxidative stability as well as wear rate. Mono-saturated fatty acid (oleic acid C18:1 or erucic acid C22:1) content is more desirable for improving both thermal-oxidative stability, pour point and lubricity. Crop oils with high oleic acid (C18:1) content showed low COF and wear rate. Thus, crops should be cultivated according to the required fatty acid composition for any specific application.

Chemically modified green lubricants have good thermo-oxidative stability, low-temperature characteristics and improved tribological characteristics. Therefore, for high oleic acid oils, TMP-based transesterification is most suitable. Upgraded microwave-assisted transesterification increases yield and production rates of methyl ester by decreasing reaction time. High oleic transesterified TMP-based green lubricant has shown superior physio-chemical and tribological properties at extreme conditions that are comparable with commercially available lubricants. Addition of some suitable additives can also make them a competitive automotive lubricant.

Cottonseed oil has a high percentage of linoleic acids (C18:2) and oleic (C18:1) acids, but its potential as a feedstock for green lubricant production has not been explored. Its fatty acid composition shows that TMP-based transesterification process can produce a promising green lubricant from cottonseed oil for high temperature and pressure applications to replace the conventional petroleum-based lubricants. Cottonseed oil can also be utilized as an emerging green lubricant feedstock for the global market. Moreover, cottonseed oil, mustard oil, sunflower, corn and moringa oils are extracted from the indigenous crops of Pakistan, while cottonseed oil is available abundantly. Dynamic climatic conditions and huge uncultivated areas of Pakistan also support the cultivation of crops mentioned in the Table 2.

Therefore, strong collaboration between agriculture and biotechnological sectors is necessary for increasing the production rate of high oleic indigenous crop oils as green lubricant feedstock. As a result, feedstock cost could be diminished and green lubricants could prove a favorable solution for the global green lubricant market as well as for Pakistan's crippled energy economy in the automotive sector.

Table 9 Laws and regulations for green lubricants [103, 104]

Countries	Laws and regulations	Policies
Europe	EU regulation 67/548 EWG	Deals with the synthesis of cooling lubricants
	EU Biocidal Products Directive (BPD)	This regulation is for metalworking fluid (MWF) utilization. EU Directive ensures that all commercially available hazardous chemicals are registered and properly documented with toxicity and bio-toxicity levels. This policy is adopted in Europe for all chemicals supplied in bulk or smaller quantities since 2018
	EC/ 1999/ 45 Directive	It ensures that oils should be biodegradable, renewable and nontoxic to an aqueous environment
	EU DSD 67/548/EEC	It sets the criteria for potential hazards of the green lubricants in the aquatic environment.
	European waste oil legislation	It restricts the development of chlorine-free lubricants
	Used oil disposal laws. Directive 75/439/EEG.	In the EU, all used oils are characterized as hazardous waste. The directive tells about the collection, processing, and re-refining methods.
	European Eco-label (EEL): The Flower Nordic Ecolabel: the Nordic Swan	Gives recognition and acceptance to green lubricants by mentioning biodegradation and toxicity criteria since 2005
	European Committee for Standardization (CEN) **develop CEN/TC 19** WG33: *For bio-based lubricants*	A European standard PREN 17181 (11) was developed to find aerobic biodegradation of lubricants by carbon dioxide production CEN/TR 16227:2011- *Recommend terminology of bio-based lubricants* EN 16807: 2016 - Develop criteria and requirements of *bio-based lubricants*. EN 16785-1 - Find bio-contents.
Germany	German TRGS 611	Production of water-miscible cooling lubricants.
	"Market Introduction Program (MIP) Biolubricants and Biofuels" managed by the German Agency of Renewable Resources	This program works for substituting mineral oil-based lubricants with green lubricant, specifically for hydraulic fluids. It ensures the reimbursement of costs if more than 50% mass content of lubricant derived from renewable resources
	Blue Angel Label Legislation	A labeling system for green lubricant
Austria	Made a 'Law' to ban the use of lubricants derived from mineral oil.	Especially for chain bar saws applications. Only bio-based lubricants are allowed
Switzerland	Regulations to measure the effects of lubricants on the environment.	It prohibits the use of mineral-based lubricants in watercourses and forests. Bio-based lubricants have a labeling system
Sweden (Gothenburg)	Swedish Standards: "Ren Smo rja" (Clean Lubricants) project with the collaboration of municipal authorities, consultants, and industries	It sets environmental criteria and standards for grease and hydraulic fluids. Labeling schemes are adopted and all taxes are exempted on green lubricants
USA	Great Lakes Water Quality Initiative (GLWQI).	GLWQI works to maintain the water quality by putting a ban on zinc compounds utilization in the Great Lakes Basin of USA
	Executive Order 12873 (EO 12873)	EO 12873 was implied since 1998 and implementing the regulations on environment-friendly oils and military lubricants from recycled oils
	Executive Order 02-03: Sustainable Performs by State Agencies	This practice cares about future generations needs and minimizes the threats to resources like clean water.
	US Environmental Protection Agency's (EPA) develop the following regulations. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)-based regulations. Federal Clean Water Act. 40 CFR 110 (Discharge of oil)	The EPA has established water quality and its requirements in accordance with the criteria for the discharge of harmful oils and lubricants into US navigable waters or adjacent shorelines. It allows a maximum of 1000 barrels discharge of oil into US water. The VGP says that "All vessels entering US waters must use an Environmentally Acceptable Lubricants (EAL) in all oil-to-sea interfaces, unless technically infeasible" from 19 to 12- 2013

Table 9 (continued)

Countries	Laws and regulations	Policies
USA	Vessel General Permit (VGP)	
	Farm Safety and Rural Investment Act of 2002	The Ministry of Agriculture has proposed guidelines for the labeling of bio-based products since 2002.
	Toxic Substance Control Act (TSCA)	These four federal regulations help in promoting the growth of the green lubricant market and highlight cost & environmental issues
	Resource Conservation and Recovery Act (RCRA)	
	Comprehensive Environmental Response Compensation and Liability Act (CERCLA)	
	Superfund Amendments and Reauthorization Act (SARA)	
Itlay	Regulation on tax policy	.Mineral oils and their products are subject to a tax.
Portugal	In 1991, a regulation imposing the use of bio-lubricant was introduced.	It ensured the usage of bio-based 2- stroke engine oil for outboard boat engines
Belgium	Legislation	All kind of machinery or operations happening near navigable waters are using a bio-based lubricant.
Netherlands	The Dutch Ministry of Spatial Planning, Housing, and the Environment had adopted a policy and program of action for green lubricants in 1996.	Tax incentives affecting green lubricants are operated under the Dutch VAMIL to protect the environment.

Moreover, Pakistan should develop legislation, rules, and regulations for green lubricant synthesis so that the green lubricants sector can participate actively in the economic growth of the country.

Continued cooperation between government, farmers, researchers, genetic engineering, green lubricant manufacturers and the end-user is required to ensure the cultivation of cheaper and potential feedstock, according to required fatty acid composition. It is also necessary that organizations like ISO, EU, EN, and ASTM provide complete guidelines on feedstock requirements and performance criteria for environment-friendly sustainable green lubricants, along with their pros and cons.

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