Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.143

Vegetable oil-based additives for lubricant formulations

Brajendra K. Sharma *&* ***Sevim Z. Erhan****, United States Department of Agriculture, Agricultural Research Service Eastern Regional Research Center, Wyndmoor*

Raj Shah*,* ***Blerim Gashi*** *&* ***Nicole Turner****, Koehler Instrument Company*

Gobinda Karmakar *&* ***Pranab Ghosh****, Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal*

Introduction

With increasing environmental concerns, the use of commercial petro-based lubricants which are harmful to the eco-system is gradually being replaced by environmentally benign lubricants prepared from vegetable oils (VO) or other natural resources. Although VO or animal fats had been used as lubricants since ancient times, due to certain limitations such as poor thermo-oxidative and hydrolytic stability, they have been replaced by mineral oil/synthetic based lubricants. However, in the 21st century, VO and natural oils have overcome these limitations and come into focus for the formulation of bio-lubricants due to the rapid depletion of non-renewable resources and increased pollution from them. They can be used for both boundary and hydrodynamic lubrication due to their amphiphilic character (polar ester group and non-polar hydrocarbon chain). The global biolubricants market size is projected to grow from 2 billion USD in 2020 to 2.4 billion USD by 2025, at a compound annual growth rate (CAGR) of 4.1% between 2020 and 2025 [1]. The dominant market position of the biolubricants segment can be attributed to their high biodegradability, lower toxicity, excellent temperature-viscosity relationship, high flash point, and superb lubricity. The growing environmental awareness and adoption of stringent regulations have increased the acceptance of plant-based oil-derived biolubricants. Various regulations such as the vessel general permit in the US and EcoLabel in Europe have made it mandatory to use biolubricants or environmentally accepted lubricants in shipping vessels, which is driving the market.

Vegetable oils are main;y comprised of triglycerides of long-chain fatty acids having different degrees of unsaturation. Thus they have different chemical structures and different properties when compared to mineral oil [2]. The limitations of VO such as a lack of viscosity range, their compatibility with different chemical compounds, low thermo-oxidative stability, poor pour point and gumming effects restrict their direct use as biolubricants (base oil/additive). These limitations can be mitigated by different chemical treatments and/or blending with suitable additives. The use of additives in a base fluid is crucial to improve the overall performance of lubricating oils thereby increasing the lifespan of engines. The additives generally improve thermo-oxidative stability, pour point, antiwear performance, and viscosity index of the lubricating oils. They may be synthetic, semi-synthetic, and/or biobased. The commercially used additives are generally petro-based synthetic (e.g., acrylate-based polymers, polycaprolactones, polyesteramides, aliphatic copolyester). They exhibit satisfactory performances but are non-biodegradable and slightly toxic to the biosphere [3-5]. Organic additives like zinc dithiophosphate (ZDDP), a well known class of organophosphate additive, molybdenum di-thiocarbamate (Mo-DTC). are widely used as efficient antifriction additives in turbine oil lubricants but produce harmful emissions. According to the Environmental Protection Agency, within lubricant additives, the following are considered harmful priority chemicals: acenaphthene, acenaphthylene, benzo(ghi)perylene, fluorene, phenanthrene, and pyrene.

The synthesis of bioadditives is an emerging area of research in the lubricant sector considering several environmental hazards associated with commercial petroleum-based additives, the performance of lubricants, and the lifetime of engines. Currently, the advantages of renewable resources will provide satisfactory lubrication to applications in the machinery industry without compromising the effects of lubricant performance. The suitability of vegetable oils and other natural resources as lubricant base oils or additives is constantly being evaluated in the field of tribology. Within the next decade, advancements in the application of biobased additives in the formulation of biodegradable lubricants will become more significant as legislatures have become more proactive for ecosystem protection. In addition to pure VO, waste cooking oils and other bio-resources like microalgae oil, plant-based materials like cellulose, lignin, chitosan, and bio-based ionic liquids are also being investigated as starting materials to prepare efficient bio-additives. There are many reports of chemically modified VO or other bio-based materials being used as additives in the formulation of environmentally acceptable lubricants.

The application of soybean oil, sunflower oil, castor oil, rice bran oil, palm oil, olive oil, and jojoba oil-based additives for lubricants have been reported [6-12]. Recently palmitoylated lignin was reported to be used as an antioxidant additive in castor oil [13] and showed better performance compared to butylated hydroxytoluene, a commonly used petroleum-based antioxidant. In another work, the advantages of vegetable oil-based antioxidant additives like tocopherols, propyl gallate, and ascorbyl palmitate were disclosed over synthetic additive (4, 4'-methylenebis(2,6-di-tert-butylphenol) [14]. The experimental results reveal that the antioxidants, even at low concentrations, defer the onset of oxidation or slow the oxidation rate, thus improving the thermal stability of the vegetable oils studied. Oils from microalgae after chemical treatment have been recently reported to be used in the formulation of biolubricants [15]. In this context the synthesis and utilisation of new bio-based multifunctional additives towards the formulation biolubricants is explored.

Synthesis of bio-based additives from VO/waste cooking oils and other natural resources:

Many green additives have been synthesised from VOs, like soybean oil, palm oil, and sunflower oil due to their high availability. However, non-edible vegetable oils with lower degrees of unsaturation such as neem, castor, mahua, karanja, jatropha, and linseed have an advantage in producing additives for biofuel/biolubricants. Recently additives were synthesised from less expensive sources such as waste cooking oils and other natural oils like microalgae oils. The quality and performance of an additive depends largely on the physical properties of the oils (especially degree of unsaturation) and their chemical derivatives. The derivatives of natural oils which are used as multifunctional additives for biolubricants should have higher viscosity index, flash point, thermo-oxidation stability, shear stability, lubricity, and lower pour point and cloud point. ASTM International methods are applied to evaluate these properties.

Common approaches to synthesise additives from VO are transesterification, hydrolysis, conversion of the olefinic functional groups into epoxides, cyclic carbonates, incorporation of different nano-particles in the backbone of VO, polymerisation (homopolymerisation and copolymerisation with suitable comonomers), preparation of polymer composites by reinforcing different organic and inorganic nanofillers in the vegetable oil polymer matrix, formation of ionic liquids, derivatisation of vegetable fatty esters into fatty amines, fatty amides, fatty alcohols.

Transesterification

In transesterification, the VO triglyceride esters are converted into fatty acid alkyl esters and glycerol by reacting with smaller alcohols like methanol, ethanol, or propanol in presence of a base or acid catalyst [16]. These fatty acid methyl esters (FAME) or ethyl esters have great importance in the lubricant industry. They are also the key components of biodiesel, biolubricant, and bio-additives. The FAME of canola oil was used as an excellent lubricity additive for biodiesel [17]. FAMEs can be easily further transesterified with longer chain alcohols, polyols like TMP, pentaerythritol etc. which have enhanced additive performances [18]. Garlapati et al. reported the use of transesterified Olax scandens oil as biobased additive in petroleum oil [19]. The blends showed better engine performance, higher flash points, and higher lubricity. The fatty acid alkyl esters are also easily converted into fatty amines, amides, alcohols, polyols, epoxides, or other essential compounds (by various reactions like oxidation, hydrogenation, metathesis, isomerisation, etc.) that can be used as additives for lubricants.

The type of catalyst used in the transesterification reaction may be homogeneous, heterogeneous, or enzymatic. Although the selection of catalyst i.e. acid or base, depends on the quality of the feedstock, the use of homogeneous alkali catalysts (KOH/NaOH) is very common. In the base-catalysed process, the fat and oils must be of good quality with least amounts of free fatty acids (FFAs). In the case of low-quality oils (i.e.: non-edible or spoiled VO, waste cooking oils, grease, animal fats that contain a significant amount of FFAs) base catalysts cannot be used in the transesterification process because of the formation of a soap-like material. In such a case, the FFAs present in the feedstock should be converted into esters first by an acid catalyst to obtain a mixture of fatty acid alkyl esters and triglycerides. The esters in the second step are then transesterified with suitable longer chain alcohol catalysed by a base to obtain fatty acid esters.

For conversion of high-FFA unrefined palm oil, the acid-catalysed process in combination with high temperature is required to break down thick yellow grease. Moreover, due to the corrosive nature of acids, costly acid-resistant reactors will have to be used. Recently, the use of heterogeneous solid catalysts, photocatalysts, enzyme catalysts, and non-catalytic transesterification in subcritical and supercritical conditions is gaining popularity due to disadvantages of homogeneous catalysts like high energy consumption, corrosive nature (acids are more corrosive than base catalysts) and difficulty in their recovery [20].

Hydrolysis

In the hydrolysis of vegetable oil, the triglyceride esters of fatty acids are converted into FFAs using catalysts like acid, base, or enzymes. The rate of the hydrolysis depends upon the type/quantity of catalyst, temperature, type of VO, and other such factors. These FFAs then can be esterified with alcohols of different chain lengths to produce biolubricants. This method can be used to produce biodiesel/biolubricant from low-quality VO (waste cooking oils, animal fats, etc.) as an alternative to the transesterification process and provides the possibility of overcoming many problems associated with the recovery of the by-product glycerol. The FFAs obtained from hydrolysis are easily converted into fatty amides, amines, alcohols, or ionic liquids that are used as multifunctional additives for lubricants. Gusain et al. prepared tetrabutylammonium ionic liquids having fatty acid anions of variable chain length and unsaturation (caprate, laurate, myristate, palmitate, and oleate) which improved the tribological properties of mineral base stock significantly [21]. It is also reported that the tetrabutylammonium ionic liquids having various anions, viz., stearate, oleate, and linoleate improved the friction and antiwear properties when added to polyol ester lube base oil, for the steel surfaces [22].

Preparation of fatty amides and amines

Amines and amide derivatives of oils have versatile applications in different industries including friction modifiers or antiwear additives in engine oils. The amides are prepared by catalytic aminolysis of fatty acids/esters with ammonia or primary/secondary amines. For the preparation of amines, the fatty esters/acids are aminolysed with ammonia followed by dehydration and hydrogenation with suitable catalysts. These additives have better environmental footprint than the commercial ZDDP-type antiwear additives.

Partially neutralised fatty amine salts were used as friction modifier for lubricants especially for internal combustion engines. Soybean oil-based fatty amide was used as a rheology modifier additive in coatings. The chemistry of tribology of fatty amines on steel surfaces was mentioned by Nalam et al. [23]. Amide derivatives of non-edible high free fatty acids containing triglycerides of waste cooking oil, karanja oil, and jatropha oil using Li doped CaO-Ca(OH)2 heterogeneous nano-catalyst are used as diesel fuel additives and have been found to improve the cetane number from 52.6 to 56.1 and lubricity from 460 to 247 μm of diesel fuel [24].

Epoxidation and carbonation of fatty acids/esters

Epoxidation, an important pathway towards improving the oxidation stability, is generally carried out by reaction of the fatty esters/acids with a peroxy acid (peracetic, performic, m-chloroperbenzoic acid) in presence of a catalyst. The extent of reaction depends on several experimental conditions like temperature, type of peracid, catalyst, solvent, stoichiometry, time, contacting patterns (batch/ semi-batch mode/ azeotropic distillation) etc. These epoxidised derivatives are used to prepare base stock and antiwear/antifriction additives having considerably better performance than conventional petroleum-based lubricants. The opening of oxirane rings of the epoxy fatty esters/acids with different nucleophiles (alcohols, thiols, amines, acids) in presence of catalysts also produce versatile products that are used as biolubricant base stocks/additives, bio-plasticisers, and other industrially useful chemicals [25-28]. Epoxy derivatives of oils may be converted into cyclic carbonate derivatives by reacting with CO_2 in presence of catalysts [29]. These carbonate derivatives are also used to prepare lubricant additives and other essential value-added materials. These have the advantage of consuming and utilising atmospheric CO_2. The synthesised compounds showed potential application as industrial lubricants or fuel additives. Fig. 1 shows epoxidation and carbonation reactions of VO.

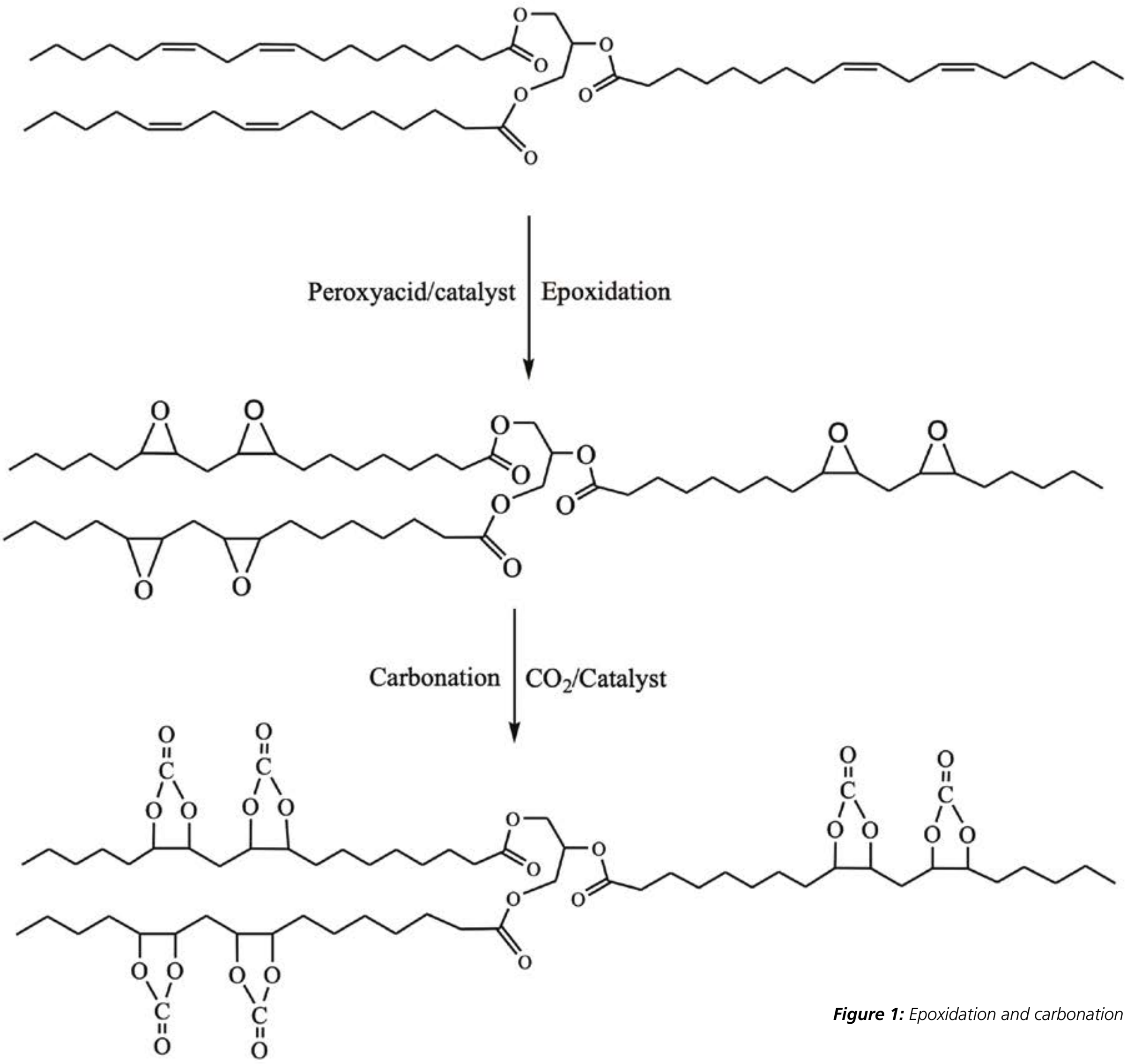

Figure 1: *Epoxidation and carbonation of VO.*

Polymerisation

Polymerisation is a potential way to improve oxidation stability of VO. Polymerised plant oils have extensive application as additives/base stocks in the formulation of biolubricants. The polymerisation of vegetable oil fatty esters/acids can be performed using methods including cationic, free radical, ring-opening, metathesis, condensation. There are many examples of lubricant additive manufacturing by free radical polymerisation [2, 3, 6, 7, 10]. The polymers synthesised using this method are highly branched having very high molecular weights. The atom transfer radical polymerisation (ATRP) method is followed to obtain polymers having narrow molecular weight distribution and low polydispersity index required for specific applications [30]. The macrostructure of the polymers, upon which their potential as biolubricants (additive/base stock) depends, is determined also by the types of monomers and the conditions of polymerisation including reaction time, heating method (thermal, microwave), temperature, and control of the reaction (living polymerisation/atom transfer radical polymerisation). It was found that the antifriction performance increases due to incorporation of polar functionalities in VO skeleton. Homopolymer of VO and their copolymers with different functional monomers such stearyl methacrylate, methyl methacrylate, different alkyl acrylates (methyl/decyl/dodecyl acrylates), different α-olefins (α-pinene, 1-dodecene, 1-hexadecene, 1-octadecene) were reported as efficient multifunctional additives in biolubricants. Copolymers of sunflower, soybean, castor or waste cooking oils with stearyl methacrylate act as pour point depressants, viscosity index improvers, and rheology modifiers for the N-150 base oil [31]. The backbone of stearyl methacrylate makes the copolymer a better pour point depressant due to extensive crosslinking and branched network. Homopolymers of rice bran oil and its copolymers with dodecyl acrylate, styrene, and stearic acid have potential multifunctional performance especially as antiwear agents [32]. All these polymers were synthesised by free radical polymerisation method using benzoyl peroxide or AIBN initiator. Thermal and microwave irradiation both methods have been applied to synthesise the polymers. Few polymers were synthesised by ATRP method also to produce additives having desirable performances.

The addition of different organic or inorganic nanofillers during polymerisation has noticeable impact towards increase in additive performance and thermal stability [33,34]. It was reported that organic nano particles such as nanocellulose, nano graphene, carbon nanotube and different inorganic and metallic nano particles like zinc, boron, and iron. significantly enhanced antifrictional properties when introduced in

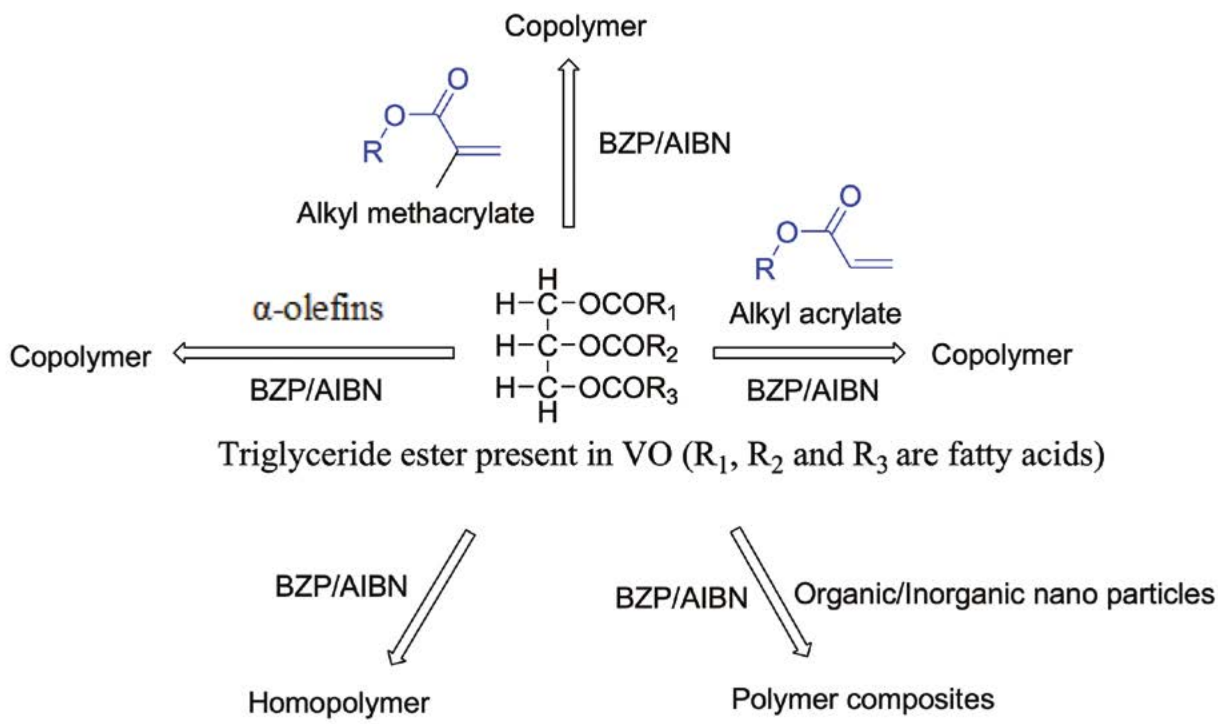

Figure 2: *Polymerisation and preparation of polymer composites of VO.*

the macro-structure of a vegetable oil based polymer. But due to problems associated with the dispersibility of metallic nanomaterials in bio-based oils, organically modified/layered nano metals have become very popular recently. The nano particles introduced in the macrostructure of the polymers help the lubricant to bind with the metal surface more strongly and therefore reduce friction significantly. These polymerisation reactions are shown in Fig 2.

Additives from natural resources other than VO:

Different natural substances other than vegetable oils like microalgae oil, lignin, curcumin, chitosan, cellulose are used as natural additive for lubricants. The red microalga Dixoniella grisea have potentiality to reduce friction in tribosystem [35]. Palmitoylated lignin and curcumin were used as antioxidant additive [13] in VO/waste cooking oils.

The lignin fractions obtained from straw, birch wood after palmitoytation exhibited excellent antioxidant performance compared to butylated hydroxytoluene (BHT), when blended with castor oil. Azomethinefunctionalised chitosan showed efficient tribological performance when added to paraffin base oil [36].

Amidation of biophenols with 4-aminodiphenylamine produce highly efficient multifunctional additives for bio-base fluids like rapeseed oil, coconut oil and epoxy soybean oil [37]. They increase thermo-oxidative stability, reduce friction and wear regardless of the saturation degree of VOs. Four-ball test demonstrated that the additives decreased the wear and friction up to 18% and 25% in rapeseed oil and coconut oil respectively.

Conclusion

The above discussion gives a brief account of various vegetable oil-based additives in lubricant formulations. Although the use of chemically modified plant oils as the base stock in lubricant formulation is not new, the use of biobased additives has recently attracted considerable attention as a green approach to produce the same and avoid several environmental hazards of petroleum-based additives.

The biobased materials often offer better performance such as higher viscosity index, better wear performance, and higher flash point compared to commercial petro-originated additives.

Developed countries have already started to use biolubricants commercially. The global biolubricant market is gaining momentum very rapidly. Research is still ongoing to develop new, greener and more economical methodologies for manufacturing biolubricants (base oil and additive) from vegetable oils.

*** Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.*

www.ars.usda.gov
www.nbu.ac.in/dept/chemistry.aspx

References

[1] Salih, N.; Salimon, J. A Review on Eco-Friendly Green Biolubricants from Renewable and Sustainable Plant Oil Sources. ***Biointerface Res. Appl. Chem***. 2021, 11 (5), 13303 – 13327.

[2] Karmakar, G.; Ghosh, P.; Sharma, B.K. Chemically modifying vegetable oils to prepare green lubricants. ***Lubricants*** 2017, 5, 44.

[3] Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil. J. Chem. Eng. Data, 2011, 56 (10), 3752–3758.

[4] Johnson, D. W.; Hils, J. E. Phosphate Esters, Thiophosphate Esters and Metal Thiophosphates as Lubricant Additives. ***Lubricants*** 2013, 1, 132-148.

[5] Boyde, S. Green lubricants. Environmental benefits and impacts of lubrication. ***Green Chem***. 2002, 4, 293-307.

[6] Karmakar, G.; Ghosh, P. Green Additives for Lubricating Oil. ***ACS Sustainable Chem. Eng***. 2013, 1, 1364–1370.

[7] Ghosh, P.; Hoque, M.; Karmakar, G. Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant. ***Polym. Bull***. 2017, DOI 10.1007/s00289-017-2047-6.

[8] Sapawe, N.; Hanafi, M. F.; Samion, S. The Use of Palm Oil as New Alternative Biolubricant for Improving Anti-Friction and Anti-Wear Properties. ***Mater. Today: Proc***. 2019, 19 (4), 1126-1135.

[9] 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. ***Ind. Crops. Prod.*** 2015, 65, 328–333.

[10] Ghosh, P., Upadhyay, M. Isodecyl acrylate - olive oil copolymers as potential biodegradable additive for lubricating oil. ***J. Polym. Res***. 2016, 23, 100.

[11] Owuna, F.J. Stability of vegetable based oils used in the formulation of ecofriendly lubricants – a review. ***Egypt. J. Pet***. 2020, 29, 251-256.
[12] Tulashie, S. K.; Kotoka, F. The potential of castor, palm kernel, and coconut oils as biolubricant base oil via chemical modification and formulation. ***Therm. Sci. Eng. Prog***. 2020, 16, 100480.
[13] Jedrzejczyk, M. A.; Bosch, S. V; Aelst, J. V.; Aelst, K. V; Kouris, P. D.; Moalin, M.; Haenen, G. R. M. M.; Boot, M. D.; Hensen, E. J. M.; Lagrain, B.; Sels, B. F.; Bernaerts, K. V. Lignin-Based Additives for Improved Thermo-Oxidative Stability of Biolubricants. ***ACS Sustainable Chem. Eng***. 2021, 9 (37), 12548-12559.
[14] Quinchia, L.A.; Delgado, M. A.; Valencia, C.; Franco, J. M.; Gallegos, C. Natural and Synthetic Antioxidant Additives for Improving the Performance of New Biolubricant Formulations. ***J. Agric. Food Chem***. 2011, 59(24), 12917–12924.
[15] Da Silva, A.P.T.; Bredda, E.H.; de Castro, H.F.; Da Rós, P.C.M. Enzymatic catalysis: An environmentally friendly method to enhance the transesterification of microalgal oil with fusel oil for production of fatty acid esters with potential application as biolubricants. ***Fuel*** 2020, 273, 117786.
[16] Jothiramalingam, R.; Wang, M. K. Review of Recent Developments in Solid Acid, Base, and Enzyme Catalysts (Heterogeneous) for Biodiesel Production via Transesterification. ***Ind. Eng. Chem. Res.*** 2009, 48 (13), 6162-6172.
[17] Dmytryshyn, S.L.; Dalai, A.K.; Chaudhari, S.T.; Mishra, H.K.; Reaney, M.J. Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties. ***Bioresour Technol***. 2004, 92(1), 55–64, 2004.
[18] 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. ***Egypt. J. Pet***. 2020, 29, 75-82.
[19] Garlapati, V. K., Mohapatra, S. B., Mohanty, R. C., Das, P. Transesterified Olax scandens oil as a bio-additive: Production and engine performance studies. ***Tribol. Int***. 153, 106653, 2021. doi:10.1016/j.triboint.2020.106653
[20] Belousov, A. S., Esipovich, A. L., Kanakov, E. A., Otopkova, K. V. Recent advances in sustainable production and catalytic transformations of fatty acid methyl esters. ***Sustain. Energy Fuels***. 2021, 5, 4512-4545.
[21] Gusain, R., Khan, A., Khatri, O. P. Fatty acid-derived ionic liquids as renewable lubricant additives: Effect of chain length and unsaturation. ***J. Mol. Liq***. 2020, 301, 112322.
[22] Gusain, R., Dhingra, S., Khatri, O. P., Fatty-Acid-Constituted Halogen-Free Ionic Liquids as Renewable, Environmentally Friendly, and High-Performance Lubricant Additives. ***Ind. Eng. Chem. Res***. 2016, 55(4), 856–865.
[23] Nalam, P. C.; Pham, A.; Castillo, R. V.; Espinosa-Marzal, R.M. Adsorption Behavior and Nanotribology of Amine-Based Friction Modifiers on Steel Surfaces. ***J. Phys. Chem***. C, 2019, 123 (22), 13672-13680.
[24] Kumar, D.; Park, C. H.; Kim, C. S. Sustainable heterogeneously catalyzed single-step and two-step amide derivatives of non-edible natural triglycerides as dual-functional diesel fuel additives. Ind. ***Crops. Prod***. 2020, 158, 113001.
[25] Lozada, Z. R.; Suppes, G. J.; Tu, Y.C.; Hsieh, F. H. Soy-Based Polyols from Oxirane Ring Opening by Alcoholysis Reaction. ***J. Appl. Polym. Sci***. 2009, 113(4), 2552 – 2560.
[26] Varshney, H.; Ahmad, A.; Rauf, A. Ring Opening of Epoxy Fatty Esters by Nucleophile to Form the Derivatives of Substituted ß-Amino Alcohol. ***Food Nutr Sci***, 2013, 4, 21-24.
[27] Sharma, B.K.; Adhvaryu, A.; Erhan, S.Z. Synthesis of Hydroxy Thio-ether Derivatives of Vegetable Oil. ***J. Agric. Food Chem***. 2006, 54, 9866–9872.
[28] Chan, C. H.; Tang, S. W.; Mohd, N. K.; Lim, W. H.; Yeong, S. K.; Idris, Z. Tribological behavior of biolubricant base stocks and additives. ***Renew. Sustain. Energy Rev***. 2018, 93, 145-157.
[29] Perez-Sena, W.Y.; Eränen, K.; Kumar, N.; Estel, L.; Leveneur, S.; Salmi, T. New insights into the cocatalyst-free carbonation of vegetable oil derivatives using heterogeneous catalysts. ***J. CO_2 Util***. 2022, 57, 101879.
[30] Karmakar, G.; Ghosh, P. Atom transfer radical polymerization of soybean oil and its evaluation as a biodegradable multifunctional additive in the formulation of eco-friendly lubricant. ***ACS Sustain. Chem. Eng***. 2016, 4, 775–781.
[31] Agarwal, P.; Chaudhary, S.; Porwal, J.; Singh, R.; Porwal, S. Evaluation of renewable feedstock-derived copolymers of stearyl methacrylate-co-triglyceride as multifunctional green additives in lubricant. ***Polym. Bull***. 2022, 79, 10.1007/s00289-021-03611-2.
[32] Talukdar, S.; Ghosh, P. Biodegradable vegetable oil polymer as a multifunctional lubricating oil additive. ***J. Macromol. Sci. A.***, 2019, 57. 1-6.
[33] Ren, Y.; Zhang, L.; Xie, G. A review on tribology of polymer composite coatings. ***Friction*** 2021, 9, 429–470.
[34] Bhuyan, S.; Sundararajan, S.; Lu, Y.; Larock, R.C. A study of the physical and tribological properties of biobased polymer–clay nanocomposites at different clay concentrations. ***Wear*** 2010, 268, 797–802.
[35] Gavalás-Olea, A.; Siol, A.; Sakka, Y.; Köser, J.; Nentwig, N.; Hauser, T.; Filser, J.; Thöming, J.; Lang, I. Potential of the Red Alga Dixoniella grisea for the Production of Additives for Lubricants. ***Plants*** 2021, 10, 1836.
[36] Murmu, M.; Sengupta, S.; Pal, R.; Mandal, S.; Murmu, N. C.; Banerjee, P. Efficient tribological properties of azomethine-functionalized chitosan as a bio-lubricant additive in paraffin oil: experimental and theoretical analysis. ***RSC Adv***. 2020, 10 (55), 33401–33416.
[37] Zhao, H.; Feng, J.; Zhu, J.; Yu, H.; Liu, Y.; Shi, P.; Wang, S.; Liu, S. Synthesis application of highly efficient multifunctional vegetable oil additives derived from biophenols. ***J. Clean. Prod***. 2019, doi: https://doi.org/10.1016/j.jclepro.2019.118274.