PART-3

CHEMICALLY MODIFIED VEGETABLE OILS AS LUBE OIL ADDITIVES AND AS A POTENTIAL LUBE BASE STOCK

PART-3/CHAPTER-1

BACKGROUND AND OBJECTIVE OF THE PRESENT INVESTIGATION

Ever growing lubricant industry requires a continuous flow of oil sources but unfortunately, the most frequent source of base stock or base lubricant is generated from petroleum crude and its sources are limited and gradually decreasing. Despite that mineral, lube has some serious disadvantages like

- They possess poor biodegradability and release toxic chemicals as residue in the environment.
- They have poor tribological and rheological properties.
- Sources are limited and non-renewable [5].

Synthetic lube base stock is considered to be an alternative but they have some serious issues, like-

- They are expensive compared to mineral lube[4].
- They are associated with more environmentally hazardous.
- Biodegradability is not promising.
- They are less miscible with mineral lube, hence can't work together.

Additives that are produced from petroleum resources such as polyacrylate as rheo improver and zinc-diethyl dithiophosphate (ZDDP) as tribo improver brings serious hazards to the environment as they possess heavy metal, and sulfur [1-2]. Friction modifier, molybdenum dithiocarbamate complexes used as solid lubricants, releases heavy metals and sulfur compounds, and their activity decreases with fluid aging [3]. Therefore, research interest in bio-based lubricant additives is also increasing. Although lubricants derived from vegetable oils are more costly than mineral lubricants, they are a promising alternative to synthetic and mineral oil-based lubricants because they have a high flash point, high viscosity index, better friction properties, high biocompatibility, and low aquatic toxicity [5-7]. With its long fatty acid chain and polar end groups, the structure of vegetable oil thus contains an oleophilic and oleophobic part in their structure, hence, these oils are suitable as a base stock for easily blending different kinds of environmentally acceptable additives, and are used as both boundary and hydrodynamic lubricants[3]. Additives prepared from vegetable oils showed excellent tribological and rheological properties as we observed in our previous chapters where additives prepared from castor oil, rapeseed oil,rice-bran oil exhibit excellent results in this regard. Research in this field of preparing alternate lube base stock and additives was also done.

1. Erhan et al.(2008-2014) patented the use of poly (hydroxy thioether) vegetable oil derivatives as antiwear additives for environmentally friendly industrial oils in automotive applications. Different methods of making fatty acid ester derivatives from unsaturated fatty acids through the formation of their epoxides have also been described by Erhan et al. [9-11].
2. Doll et al.(2014) patented a novel process of preparing chemically modified triglycerides by the reaction of epoxidized triglyceride oils or alkyl esters thereof with phosphorus-based acid hydroxide or esters. The phosphorus-containing triglyceride derivatives so produced have a found utility as antiwear/antifriction additives for industrial oils and automotive applications [12].
3. Biswas et al.(2014) patented a method of preparing nitrogen-containing fatty acid derivatives by reacting epoxidized fatty acids, their esters, or triglyceride oils with amines of cyclic or aromatic hydrocarbons. These fatty acid derivatives

are used as antiwear/antifriction additives for industrial oils and automotive applications[13].

4. Heise, G.L.; Sharma, B.K.; Erhan, S.Z.(2015) synthesized & analyzed the antiwear additive performance of Boron containing vegetable oil U.S. Patent 9156859 B2[14].
5. Ghosh, P, Karmakar, G; (2013-2015) investigated multifunctional additives based on soyabean oil, sunflower oil, and castor oil polymers[17-19].
6. Fox, N.J.; Stachowiak, G.W.(2007) perform a review work on vegetable oil-based lubricant[24].

Vegetable oils can't be used directly as lube because of their low thermal-oxidative stability, low volatility, and high viscosity compared to mineral lube This can be performed in two different ways: reactions at the carboxyl groups of fatty acids/esters/triglycerides of vegetable oils (transesterification) or reactions at the olefinic functionalities of the fatty acid chain. Different research activities in those areas are discussed below.

- **TRANSESTERIFICATION**

1. A significant reduction of wear scar diameter from the addition of 5% rapeseed oil methyl esters in diesel fuel was disclosed by Sukjit et al. [25]. It was reported that the lubrication performance of diesel base oils was improved when palm oil methyl esters are blended [26,27].

2. Masjuki and Maleque (1997) reported a low wear rate of steel ball bearing while adding palm oil methyl ester in the base oil lubricant [28].

3.Malavolti et al. have synthesized biodiesels through the transesterification of castor oil with various alcohols in the presence of trimethylchlorosilane (TMSCl) as an acidic mediator[29].

4.The potential use of castor oil methyl esters as lubricants, with their high viscosity, low pour point, and good lubricity, was explained by Madankar et al. [30].

Glycerol obtained can be used as water-based lube, or it has other utility in the diversified chemical field[31].

- **REACTION AT OLEFINIC PART OF VEGETABLE OIL**

Epoxidation of fatty acids/esters and their application as a bio lubricant: One of the most important steps in preparing a bio lubricant (base stock and/or additive) from vegetable oils is the epoxidation of its olefinic functionalities. Vegetable oils epoxide can be prepared using peracid([32-34]. Because of their higher reactivity, the oxirane rings of the epoxides can easily be opened by different reagents such as acids, alcohols, thiols, and amines to provide different value-added compounds such as lubricants (base stocks/additives), bio-plasticizers, and other industrially useful chemicals. The epoxidized vegetable oils/fatty esters are used to prepare antiwear/anti frictional additives for lubricants. Because of their higher solubility in vegetable oils.

1. Schafer et al. described the development of corrosion-protection additives from an epoxidized methyl ester of an unsaturated fatty acid and a sulphonic acid[35].
2. Rowland et al. disclosed different antifriction additives from an epoxidized ester of fatty acids to reduce lead corrosion in lubricants and fuels [36].

3. Hydroxy thioether derivatives of vegetable oils prepared by opening the epoxy rings of epoxidized soybean oil with common organic thiols are used as sustainable antiwear/anti frictional additives for lubricants [37-38].

The incorporation of sulfur in the triglyceride backbone introduces polar functionalities in the molecule which improved the adsorption power of the derivatives on the metal surface resulting in reduced wear and friction coefficient. Ester hydroxy derivatives of methyl oleate, obtained by opening the epoxy rings of epoxidized methyl oleate by different organic acids (propionic, octanoic, hexanoic, or 2-ethyl hexanoic acid) showed better pour point and cloud point values [28]. They also showed improved thermo-oxidation stability and tribological and lubricity properties when used as lubricant additives.

Some research-based on linseed oil was very interesting in this regard as Linseed oil has found various applications in the polymer industry as well as in the petroleum industry. In a study, linseed oil polyesteramide in combination with dehydrated castor oil was blended with polymethyl methacrylate to obtain a bioartificial polymer with improved mechanical and physical properties [40-41]. In another study, epoxidized linseed oil was used to prepare a natural viscosity increasing agent from polyvinyl chloride (PVC) and triethyl–lene glycol ester of gum rosin [42]. Epoxidized linseed oil is often used as lubricants or plasticizers and secondary stabilizers for halogen-containing polymers [43]. In a study, Linseed oil biodiesel was produced by the transesterification process and its effect was investigated on engine performance and exhaust emissions which showed that linseed biodiesel and fuel blends acted quite similar to the standard diesel fuel, but in the case of the former exhaust emissions was generally improved [44]. V A Markov et al. have established in their study that the physical and chemical properties of a mixture of 90% diesel fuel and 10% linseed oil are quite similar to petroleum diesel fuels characteristics and also application of this mixture as motor fuel minimized the emission of exhaust toxic components such as nitric oxides, carbon monoxide and unburned hydrocarbons [45]. P. P. Chahande has successfully prepared a novel polymeric surfactant that is biodegradable and eco–friendly as well, based on linseed oil, rosin, and sorbitol [46]. Birten Cakmakli et al. have prepared a series of biodegradable synthetic branched graft copolymers of linseed oil with methyl methacrylate and reported their potential application in tissue engineering due to their cell adhesion and development [47] S. M. Ashraf et al. have prepared a blend of polyvinyl alcohol and epoxidized linseed oil to use it as a plasticizer and corrosion-resistant coating film of good toughness, flexibility and low water absorption [40-41]

In this part of our study, we discussed the scope opportunity of using chemically modified linseed oil as additives or as lube base stock

In Chapter 1, we discussed Linseed oil-based biodegradable polymeric additives and their effectiveness as pour point depressant, viscosity index improver, and their shear stability in terms of permanent shear stability index (PSSI) has been evaluated. Polymers were proved to act as a good pour point depressant, viscosity index improver, and shear stability improver as well. The copolymers acted like better PPDs than the homopolymer whereas the latter showed better VI improving the property. Keeping in view the environmental issue, the results are quite inspiring. Apart from being biodegradable and eco–friendly, the linseed oil-based additives may be considered to be potential candidates to replace the traditional harmful organic chemical-based polymeric additives depending on the evaluated parameters. All the additives synthesized in this research illustrated excellent additive performances and, therefore, the outcome of this study can give a new dimension in the field of multifunctional additive research.

In chapter 2**,** the performance evaluation of chemically modified vegetable oil to be used as lubricant base stock. Linseed oil(LO), castor oil(CO), olive oil (OLO), Soyabean oil (SBO), sunflower oil(SFO) epoxide were discussed. The product prepared were characterized by FTIR and NMR spectroscopy. The reaction of epoxidized linseed oil with 2 ethyl hexanol, dodecanol,n octanol,1 decanol, and isodecanol in the presence of a catalytic amount of sulfuric acid gave rise to open-ringed products. Oxirene ring-opened products of linseed oil exhibit better low-temperature flow and high viscosity index. Ring opened product with isodecanol and 2 ethyl hexanol showed better results compared to others. ECO, EOLO, ESBO, ESFO rings were also opened through the same procedure using isodecanol and the product exhibits high viscosity index and excellent low-temperature flow in this case also. Ring opened product displays better Thermo Oxidative Stability compared to those vegetable oils from which they are synthesized. Better pour point, high viscosity index, better thermal-oxidative stability, and better antiwear property compared to conventional mineral lube make these products an alternative to the latter and more environmentally benign.

However, there are some limitations to using vegetable oils. The major component of vegetable oils is a triglyceride of long-chain fatty acids of mostly unsaturated carbon atoms. The double bonds of the fatty acid chains are not conjugated. They have low thermo-oxidative stability, poor bio-resistance, poor hydrolytic stability, and poor fluidity at lower temperatures [21–23]. Therefore, they cannot be used directly as lubricant-based stocks/additives. The presence of unsaturation in the chain makes vegetable oils fragile to oxidative degradation [24].

This ultimately results in an insoluble deposit formation in vegetable oils which increases oil acidity, viscosity, corrosion, and volatility. The production and processing cost of vegetable oil is another constrain. A Huge consumption of edible oil worldwide and low production of nonedible oil makes it difficult to replace mineral lube with modified vegetable oil-based lube. These limitations can, however, be mitigated by chemically modifying vegetable oils to reach the desired performance level without increasing the cost. Extensive research in this field is going on worldwide to produce lubricant base stocks or additives from vegetable oils [25–28].

REFERENCES

References are given in BIBLIOGRAPHY under "**Chapter-1 of Part-3**".