PART-III

MULTIFUNCTIONAL VEGETABLE OIL POLYMER AS A LUBRICATING OIL ADDITIVE

CHAPTER-I

BACKGROUND OF THE PRESENT INVESTIGATION

Mineral oil and synthetic oil from petrochemical are principally used as base oil in present lubricant industry. Petroleum is vital to the maintenance of industrialized civilization. The major volume products of the petroleum industry are fuel oil and gasoline. Also petroleum is the raw material for many chemical products including pharmaceuticals, fertilizers, solvents, pesticides, and plastics. The petroleum resources are exhausting rapidly and one of the main problems of the 21 st century is the imbalance between the rate of production of petroleum oil from older inland oil fields with the rate of finding new reserves.

As the days past, due to depleting finite resources of petroleum crude oil, there remains growing risk of exhaustion of the existing reserves and oil prices.[1] Petroleum products are poorly degradable[2] and cause severe environmental hazards when released.[3]The spilling of mineral oil causes negative effect on the land and water reserve which severely affects the agricultural growth. With an increasing emission of green house gases, petroleum oils pollute the air, soil, and drinking water and affect human and plant life to a great extent.[4]

Therefore, strict specifications in certain specific areas are necessary on various environmental issues such as toxicity, biodegradability, health, and safety[5] which leads to a better investigation based on greener technology. The utilization of natural and renewable raw materials, can sometime meet the principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products[6]. Thus they can considerably contribute to a sustainable development wherever and whenever possible. Due to the increasing depletion of crude oil reserves, prices of crude oil, the environmental hazard caused by mineral oils, increasing global concern for a pollution-free environment and extreme demand of lubricants the industries are driven to find out more variety of effective eco-friendly lubricants with quality quite superior to those based on petroleum oil.[7,8,9] One of the easily available and commercially viable biodegradable, less toxic lubricants and lubricating additives are vegetable oils. Vegetable oils, the most significant renewable raw material for the chemical industry[10] are extensively used as a potential source of eco-friendly lubricants.[11-16] In the chemical industry most extensively used renewable raw materials for nonfuel applications are plant oils, polysaccharides (mainly cellulose and starch), wood, sugars, and others. These are ideal as lubricant because they are biodegradable [16-20] and have net zero greenhouse gases.

There are several vegetable oils derived from various sources. These include oilseed oils - soybean, cottonseed, sunflower oils, pea-nuts; and others such as palm oil, palm kernel oil, castor oil, coconut oil, rapeseed oil and others. They also comprise the less commonly known oils such as rice bran oil, patua oil, niger seed oil, piririma oil and numerous others. Their yields, different compositions and by extension their physical and chemical properties determine their usefulness in various applications aside edible uses. Among them Palm oil, cottonseed oil, olive oil, peanut oil, and sunflower oil etc are classed as Oleic – Linoleic acid oils seeing that they contain a relatively high proportion of unsaturated fatty acids, such as the monounsaturated oleic acid and the polyunsaturated linoleic acid.[21-22] They are characterized by a high ratio of poly unsaturated fatty acids to saturated fatty acids. Presence of high proportion of unsaturation favours the synthesis of polymer which leads to the formulation of lube oil additives.

Engine lubricants formulated from vegetable oils have the following advantages deriving from the base stock chemistry:

i. Higher Lubricity resulting in lower friction losses, and hence more power and better fuel economy. [23]

ii. Higher viscosity indices.[23]

iii. Lower volatility resulting in decreased exhaust emission.[23]

iv. Higher shear stability.

v. Higher detergency eliminating the need for detergent additives.

vi. Higher dispersancy.

vii. Rapid biodegradation and hence decreased environmental / toxicological hazards.[24]

The lubricant industry is always looking for new technology to improve product performance. The performance targets shift over time as market demands change and the industry continually reaches new levels. A new subset of performance criteria has now been introduced to the lubricant market, namely, environmental performance. During the last couple of decade's environmental awareness has risen considerably. The lubricants industry has developed many specification and regulations to define what an environment friendly biodegradable lubricant product is and the performance specifications it must meet. Biodegradable means sample to be consumed by microorganisms and return to compounds found in nature. The most common lubricant specification for biodegradability is >60% biodegradation in 28 days by Organisation for Economic Cooperation and Development (OECD) 301 (4) or ASTM methods. Biodegradable lubricants have been in the market for some time; but it was not until recently, through a combination of government regulation and consumer demands, that an available marketplace for products with high levels of environmental performance has arisen.

Vegetable oil are principally triesters or triglycerides of long chain fatty acids (both saturated and unsaturated) combined with glycerol (Figure 2(a)). The fatty acids are all of similar length (14–22 carbons long) with varying levels of unsaturation.[15, 25, 26] Most vegetable oils have separate regions of polar and non-polar groups in the same molecule. Due to presence of polar groups in plant oil which makes it amphiphilic, allowed it to be used as both boundary and hydrodynamic lubricant.[10,27] The vegetable oils have been charecterised as having many favourable natural properties including renewability, biodegradability[28], and nontoxicity with excellent tribological properties.[29,30] They have also many advantages such as low volatility due to high molecular weight triglyceride molecule, good boundary lubrication characteristics due to the polar ester group and high viscosity index, high solubilising power for polar contaminants. [9, 12, 14, 31-39] There are also some examples where vegetable-based oils have been utilised as lubricating oils as an substitute to petroleum-based base oils.[15, 40, 41]

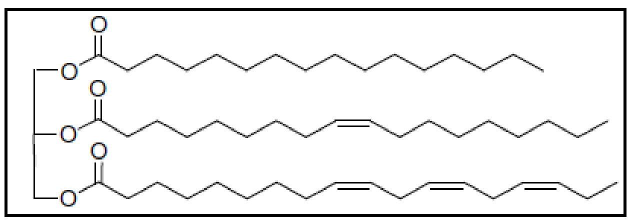

Figure 3.0. General structure of triglyceride structure present in vegetable oil

However the vegetable oils also possess some inferior qualities such as low oxidative and hydrolytic stability, high temperature sensitivity in tribological behavior, poor cold flow properties, higher cost, and gumming effect[42-44] etc. Among them, the two vital problems are poor cold flow properties[45, 46, 47, 48-51] and low resistance to thermal and oxidative stability.[14, 52-57] Low oxidation and thermal stability along with poor low-temperature properties, however, limit their potential application as industrial lubricants[58]. The main reason for the thermal and oxidative instability of plant oils is the “double bond” elements in the fatty acid part and the “-CH group” of the alcoholic components.[12, 53,51,59,60] The greater the level of unsaturation, the more susceptible the oil becomes to oxidation.[36, 37] Oxidative degradation results an increased viscosity that limits the useful life span of vegetable oil base fluids.[54] Also Cloudiness and solidification become apparent in vegetable oil at low temperatures upon prolonged exposure to low temperature.[61, 62] The triglyceride structure is also responsible for the inherent disabilities of vegetable oils. So, their use as base fluids in the formulation of industrial lubricants is very limited. Therefore petroleum based lubricants are still leading in the market. Chemically or genetically modified vegetable oils[51, 63] are now used to formulate environmentally benign lubricants. But their application as a base fluid is still not prevalent due to economical reasons and their insufficiency to meet bulk demands.

Although acrylate based additives of many different types have been developed to serve the needs of modern lubricants[64], they are very harmful for the environment. The vegetable oils can be used as additives[65-67] in the design of biolubricants, and their application as ecofriendly[30] multifunctional additives not only increases the lifetime of engines but also increases its field application. Therefore, though the biolubricating oil may act as an effective alternative to conventional lubricants, they are associated with certain advantages[11-14, 16, 68-70] and disadvantages.[14,52-56,47,48-50] These disadvantages need to be addressed before commercializing the production of biolubricants. Conversion of alkene groups of vegetable oil to other stable functional groups can improve the oxidative stability,[12,71,72] whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve low temperature performance of the plant oil.[73]

Numerous modern technologies have been used to solve the matters regarding the application of plant oils as lubricants. These include additive treatment, genetic modification and chemical modification.[32] So, if the thermal stability and fluidity at low temperature of the oil can be effectively increased by chemical modification.[74] then their use as an additive into the lube oil will not only add or improve performance but will also maintain its cost effectiveness. However, low thermal stability and low resistance to thermal oxidative still remains a key drawback of using plant oil in lubricants.[12]

There exist several references on the use of modified vegetable or plant oils as base oil or lube oil additive.

Sony and Agarwal presented a survey report based on biolubricants containing plant oils as base fluids for their excellent lubricity, biodegradability, viscosity-temperature characteristics and low volatility[75].Maleque et al. reported an article that explains a case study on biodegradable vegetable oil based lubricating oil additives with specific properties and application and uses palm oil methyl ester as an additive.[65]

Durak and Karaosmanoglu showed that cottonseed oil could be used as an additive of friction modifier very well.[76] Lathi and Mattiasson reported a novel process for the production of biodegradable lubricant base stocks from epoxidized vegetable oil with a lower pour point.[77]

Asadauskas and Erhan in 1999 reported that addition of 1% pour point depressant depressed pour points down to -33°C for canola and -24°C for high-oleic sunflower oils.[50] Mendoza et al.[78]developed a formulated sunflower base oil for hydraulic systems of agricultural tractors with a biodegradability of 89 %, an improved pour point of -270C (being -30C for the sunflower base oil) and an improved oxidation stability. This formulated oil avoids the formation of microweldings and fulfils the requirements of the reference mineral oil for extreme pressure tribological tests.

Hwang et al.[59] produced soybean oil-based lubricants by reacting epoxidized soybean oil (ESBO) with various alcohols (methanol, 1-butanol, 2-butanol, 1-hexanol, cyclohexanol, 2, 2- dimethyl-

1-propanol, and 1-decanol) in presence of sulfuric acid. The modification of ESBO improved the oxidative stability and pour point property. Erhan et al.[14] has reported excellent oxidation and low temperature stability of vegetable oil based lubricants using different kind of soybean oil and sunflower oil. Impacts of two fatty acidic di ethanol amide borates as additives on biodegradability and lubricity of an unreadily biodegradable mineral lubricating oil were studied by Boshui et al.[79] which showed tribological activity.

Nassar et al. prepared homopolymer of jojoba oil and its six copolymers with different alkylacrylate, and α-olefins. The prepared polymers were evaluated as viscosity index improvers and pour point depressants for lubricating oil.[80]

Ghosh et al.[81] prepared some copolymers of sunflower oil with different mass fraction of decyl acrylate, methyl methcrylate and styrene and evaluated their property as VI, PPD in base oils. Later, the author reported biodegradable homopolymers of sunflower oil and soybean oil and evaluated their performance as Viscosity Index Improver (VII) and Pour Point Depressant (PPD) for lube oils.[82] In another work,[83] the author carried out synthesis of homopolymer of sunflower oil by two different ways - thermal method and microwave irradiation method using benzoyl peroxide as initiator. Performance evaluation of the polymers as PPD, Viscosity Modifier (VM) and anti-wear additives in two different base oils was carried out. The author extended their research for some biodegradable Soybean oil polymers.[84] The work comprises the synthesis of its copolymers with methyl acrylate, 1-decene and styrene. Performance evaluations of the polymers as PPD, VM and anti-wear in different base oils (mineral oil) were indicated.

Some patents are also there regarding vegetable oil or plant oil used as base oil or lube oil additives. U. S. Patent No. 4873008 has explained the synthesis and use of improved lubricant base composition comprising ingredients selected from jojoba oil, sulfurized jojoba oil, and a phosphite adduct of jojoba oil. U. S. Patent No. 6534454 B1 describes about biodegradable vegetable oil composition for lubricants.

U. S. Patent No. 4970010 A discloses the use of vegetable oil and vegetable oil derivatives as lubricant additives. U. S. Patent No. 5229023 discloses synthesis and evaluation of telomerized vegetable oil based lubricant additives which can be used as thermal oxidative stability enhancers and viscosity improvers.

U. S. Patent No. 4152278 describes anti-wear, friction modifier and extreme pressure lubricant additives of some wax ester prepared entirely from acids obtained from hydrogenated vegetable oils.U. S. Patent No. 5888947 A describes vegetable oil lubricants principally derived from castor or lesquerella and the vegetable wax from jojoba or meadow foam oil for internal combustion engines.

In the International Conference on Chemical Processes and Environmental issues (ICCEEI'2012) held on July 15-16, 2012 at Singapore, the synthesis of pour point depressant from sunflower oil has been discussed. Thus there exists an ample opportunity to work on this area in order to develop environmental benign lube oil additives with better performance than the conventional synthetic chemical based additive.

As reported earlier the use of vegetable oils has been used mostly to improve tribological performance and thermal stability of base oils. But their use as pour point depressant and viscosity modifier is not very common. As is already described, additive performances of sole vegetable oils are not very encouraging. So to use them as bio lubricant, the present work comprises the copolymerisation of alkyl acrylates or α-olefin with vegetable oil in order to utilize renewable resource and to induce biodegradability into the conventional Lube Oil Additive (LOA) to make an attempt to solve environmental issues related to petroleum lubricants to some extent.

References

References are given in Bibliography under Chapter-I of Part-III (Page No. 197-206).