Part III

Biodegradable lube oil additives

Chapter 1

Brief introduction of present investigation

It is well known that petroleum crude oil reserves are decreasing while the risk of exhaustion of the existing reserves and oil prices is increasing at a rapid pace.[1] Conventional mineral lubricant are usually environmentally unacceptable due to their low biodegradability and toxicity.[2,3] These oils contaminate the air, soil, and drinking water and affect human and plant life to a great extent. Therefore, strict specifications on various environmental issues such as biodegradability, toxicity, health and safety, and emissions are required in certain specific areas.[4] Thus, the demand for environmentally acceptable lubricants is increasing along with the public concerns for a pollution-free environment.[2,3] Because of an increasing concern over the environmental issues, the lubricant industries have been trying to formulate biodegradable lubricants with quality superior to those based on petroleum oil.[5]

The use of renewable raw materials can significantly contribute to a sustainable development,[6] usually interpreted as ‘acting responsibly to meet the needs of the present without compromising the ability of future generations to meet their own needs’.[7] In ages of depleting fossil oil reserves and an increasing emission of green house gases it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development. In particular, this can perennially provide a raw material basis for daily life products and avoid further contribution to green house effects due to CO2 emission minimization. Furthermore, the utilization of renewable raw materials, taking advantage of the synthetic potential of nature, can (in some cases) meet other principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products.[6]

Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (mainly cellulose and starch), sugars, wood, and others. Products obtained from these renewable are as diverse as pharmaceuticals, coatings, packaging materials or fine chemicals, to only name a few. Today plant oils are the most important renewable raw material for the chemical industry and are heavily used as raw materials for surfactants, cosmetic products, and lubricants.[8]

Due to a combination of biodegradability, renewability, and excellent lubrication performance, vegetable oils are a potential source of environmentally favourable (eco friendly) lubricants.[9-14] A majority of vegetable oils consist of mainly two broad chemical categories: triesters and monoesters. Most vegetable oils are triesters (triglycerides), which are glycerol molecules with three long chain fatty acids attached at the hydroxy groups via ester linkages. A small fraction of vegetable oils are monoesters of long-chain fatty acid and fatty alcohols of different chemistry.[13,14] The fatty acids in vegetable oil triglycerides are all of similar length (14–22 carbons long) with varying levels of unsaturation.[13,15,16] Most vegetable oils have separate regions of polar and non-polar groups in the same molecule. The presence of polar groups in vegetable oil makes it amphiphilic, thus allowing it to be used as both boundary and hydrodynamic lubricant.[11,17]

Vegetable oils have 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 and additive molecules, and cheaper than synthetic oils.[4, 10, 12, 18-24]

The triglycerides (tri-esters of glycerol with long chain fatty acids, **figure. 3.0.**) consist varying composition of fatty acids depending on the plant, the crop, the season, and the growing conditions.[25] The word ‘oil’ hereby refers to triglycerides that are liquid at room temperature. The most important parameters affecting the physical and chemical properties of such oils are the stereochemistry of the double bonds of the fatty acid chains, their degree of unsaturation as well as the length of the carbon chain of the fatty acids.

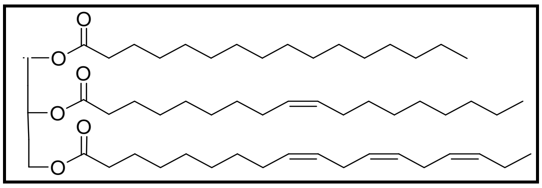

Figure 3.0. General structure of triglyceride ester present in vegetable oil

The triglyceride structure is also responsible for the inherent disabilities of vegetable oils as lubricant. For many reactions, unsaturated double bonds in the fatty acids act as active sites. There are two major problems associated with vegetable oils as functional fluids offer low resistance to thermal oxidative stability[12, 26-34] and poor low-temperature properties,[28,29,33,35-38] which leads to rapid degradation, thickening and deposit formation in use. The thermal and oxidative instability of plant-based oils is due to the structural "double bond" elements in the fatty acid and the "-CH group" of the alcoholic components.[10,38] The poor oxidative stability of a vegetable oil is because of the rapid reactions at the double-bond functional groups.[39] A variety of vegetable oils contains high amount of unsaturated fatty acids and is susceptible to oxidation. The greater the level of unsaturation, the more susceptible the oil becomes to oxidation.[23,24] Oxidative degradation leads to an increased viscosity that limits the useful life span of vegetable oil based fluids.[30] Cloudiness and solidification become apparent in vegetable oil at low temperatures upon prolonged exposure to low temperature (–10 to 0°C).[40,41] Vegetable oils also show poor corrosion protection.[42] The ester functionality present in the triacylglycerol structure renders these oils susceptible to hydrolytic breakdown.[43] Therefore, at every stage, contamination with water in the form of emulsions must be prevented. Low oxidation and thermal stability along with poor low-temperature properties, however, limit their potential application as industrial lubricants.[44] Vegetable oils exhibit particularly effective boundary lubricants as the high polarity of the entire base oil allows strong interactions with the lubricated surfaces. Boundary lubrication performance is affected by attraction of the lubricant molecules to the surface and also by possible reaction with the surface.

Transformation of alkene groups of vegetable oil to other stable functional groups can improve the oxidative stability, whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve temperature performance.[45] Several modern technologies have been adopted to solve the issues regarding the application of plant oils in lubricants. Some of them are genetic modification, additive treatment, and chemical modification.[19]

Joseph and Sharma[46] found that the mixture of phenolic and aminic antioxidants may be applied to boost the thermo-oxidative stability of vegetable oils when used as lubricant base oils at temperatures around 120 ◦C. Vinci *et al.*[47] have proposed a thermo-oxidatively stable base lubricant based in methyl-12-hydroxystearate, a derivative of the castor oil with 70% renewable carbon content. Mendoza *et al.*[48] developed a formulated sunflower base oil for hydraulic systems of agricultural tractors with a biodegradability of 89%, an improved pour point of -27 ◦C (being -3 ◦C for the sunflower base oil) and an improved oxidation stability (its oxidation induction time is 71 min instead of 8 min for the base oil). This formulated oil avoids the formation of microweldings and fulfils the requirements of the reference mineral oil for extreme pressure tribological tests. Regueira *et al*[49] has studied compressibility and viscosities of vegetable oils for their use as hydrolytic fluid and lubricant. From the above literatures, it is evident that chemically modified vegetable oils have eminent scope for use as base fluids.

Another aspect is use of green sources as lube oil performance additives instead of using them as base oils or base fluids. The lubricant identity has been trying to formulate biodegradable lubricants with better technical characteristics than conventional lube oil additives, and research in this direction is opening up new opportunities. Franco et al has reported the use oil sunflower oil bio fuels, polymeric additives e.g. ethylene vinyl acetate and styrene butadiene copolymer in lubricant formulation.[50] Recently, the application of triglycerides in polymer science was reviewed with a focal point on cross-linked systems for coating and resin applications with the conclusion that triglycerides are expected to play a key role during the 21st century to synthesize polymers from renewable sources.[51] In addition to these cross-linked systems, linear polymers can also be obtained from plant oils.

US patent no. 5229023 discloses synthesis and evaluation of vegetable oil based lubricating additive that can be used as viscosity improver and thermal stability enhancer. US patent no. 4873008 has explained the synthesis and use of jojoba oil based additive. US patent no. 4970010 has described a group of sulfurised derivatives of vegetable oils with better lubricating properties. Again US patent no. 4152278 describes anti wear and tribological performance of some vegetable wax ester. US patent no. 6534454 B1 discussed about biodegradable vegetable oil composition for lubricant. US patent no. 4925581 claimed the application of meadowfoam oil and meadowfoam oil derivatives as lubricant additives.

Erhan *et al*[12] has reported excellent oxidation and low temperature stability of vegetable oil-based lubricants using different kind of soybean oil and sunflower oil. Biresaw *et al*[11] has described friction properties of some triglyceride vegetable oils. Impacts of two fatty acidic diethanolamide borates as additives on biodegradability and lubricity of an unreadily biodegradable mineral lubricating oil were studied by Boshui *et al*[52] which showed tribological activity.

In most of the cases vegetable oils have been used to improve tribological performance and thermal stability of base oils. But use of them as viscosity modifier and pour point depressant is not very popular. As is already described additive performances of sole vegetable oils are not very encouraging. So to use then as LOA the author has polymerised different vegetable oils with alkyl poly acrylate, which combined high viscometric performance of vegetable oil and excellent low temperature flow ability of poly alkyl acrylate in a single system, along with considerable biodegradability.

In an age of increasing oil prices, global warming and other environmental problems (e.g. waste) the change from fossil feedstock to renewable resources can considerably contribute to a sustainable development in the future. The synthesis of monomers as well as polymers from plant fats and oils has already found some industrial application and recent developments in this field offer promising new opportunities.

Microwave irradiation is a well-known method for heating and drying materials for private households and industrial applications and is utilized in many greener protocols. Both organic and inorganic reactions undergo an immense increase in reaction speed under microwave irradiation compared with conventional heating. Significant improvements in yield and selectivity have also been observed as a consequence of the fast and direct heating of the reactants themselves. Furthermore, high-pressure synthesis is easily accessible for reactions performed in closed vessels, facilitating the use of low boiling solvents and thereby paving the way to environmentally benign reaction conditions. With this view in mind the author has undertaken the synthesis of the present vegetable oil-based lube oil additive under microwave condition.

References

References are given in BIBLIOGRAPHY under Chapter I of Part III (PP 219-223).