Part II

Biodegradable Multifunctional Additives For Lube Oil

Chapter I

Background of the Present Investigation

Today conservation of energy and materials is becoming a very importance issue. The main reason of energy loss in a mechanical system is the friction but this can be minimized by lubrication. Thus, it is very essential to develop the lubrication performance. A good combination of base oil and additives is the key to develop this process. Again the natural reservoir of petroleum crude oil decreases day by day and thus price of oil is increases rapidly.[1]For most lubricated applications, the conventional choice is a mineral oil based lubricant, because of its well known properties. However due to their natural toxicity and non-biodegradable nature, [2, 3] they pose a constant warning to ecology and immense ground water reserves. These oils pollute the air, soil, and drinking water and influence human and plant life to a great extent. Therefore, strict specifications on various environmental issues such as biodegradability, toxicity, safety, health and emissions are required in certain specific areas.[4] Thus the requirement of environmentally suitable lubricants is increasing along with the public concerns for a pollution-free environment.[2, 3] Due to an increasing concern over the environmental issues, the lubricant companies have been trying to prepare biodegradable lubricants with quality better to those based on petroleum oil.[5] The use of renewable raw materials can appreciably contribute to a sustainable development,[6] typically interpreted as 'acting responsibly to meet the requirements of the present without compromising the capability of future generations to meet their own needs'.[7] In ages of exhausting fossil oil stocks and an increasing emission of green house gases it is apparent that the consumption of renewable raw materials is one crucial step towards a sustainable development. In particular, this can perennially provide a raw material basis for daily life products and avoid extra contribution to green house effects because of CO_2 emission minimization. Furthermore, the use 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 commonly applied renewable raw materials such as polysaccharides (mostly cellulose and starch), plant oil, wood, sugars and others used in the chemical industry for nonfuel applications. Products obtained from these renewable sources have diverse applications in pharmaceuticals, packaging materials, coatings or fine chemicals etc. Nowadays plant oils are the most essential renewable raw material for the chemical industry and are extensively used as raw materials for cosmetic products, surfactants, and lubricants.[8]

The vegetable oils are a potential source of environmentally benign (eco-friendly) lubricants[9-14] because of its biodegradability, renewability, and excellent lubrication performance. A majority of vegetable oils consist of mainly two broad chemical categories: monoesters and triesters. The main constituents of most vegetable oils are triglycerides, which are produced by three fatty acid chains connected to glycerol by ester groups. A small portion of vegetable oils are monoesters of long-chain fatty acid and fatty alcohols of diverse chemistry.[13,14] The vegetable oil triglycerides containing fatty acids are all of similar in length (14–22 carbons chain) with varying levels of unsaturation.[13,15,16] The majority of vegetable oils have separate regions of non-polar and polar groups in the same molecule. Due to the presence of polar groups in vegetable oil, they are amphiphilic in nature and therefore they can be used as both boundary and hydrodynamic lubricant.[11, 17] There are many advantages of using vegetable oils such as low volatility caused by high molecular weight triglyceride molecule, fine boundary lubrication characteristics because of the polar ester group and high viscosity index value, high solubilising power for polar contaminants and additive molecules, and cheaper than synthetic oils.[4, 10, 12, 18-24]

About 90% to 95% of the total weight of triglycerides (**figure. 2a.**) accounts for fatty acids and their composition is characteristic of 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 physical and chemical properties of vegetable oils are mostly affected by the stereochemistry of the double bonds present in the fatty acid chains, their degree of unsaturation and the length of the carbon chain of the fatty acids.

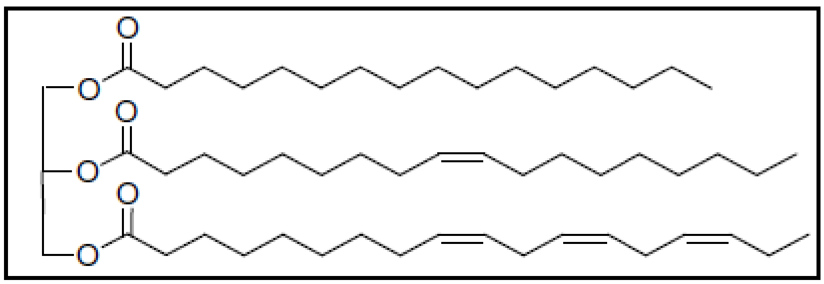

Figure 2a: General structure of triglyceride ester present in vegetable oil

The structure of triglyceride is also accountable for the inherent disabilities of vegetable oils as lubricant. For a lot of reactions, the fatty acids containing unsaturated double bonds 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 results quick degradation, deposit formation and thickening in use. The poor thermal and oxidative instability of plant oils is due to the presence of unsaturation (double bond) in the fatty acid chain and the "-CH group" of the alcoholic part.[10,38] The susceptibility towards oxidation of a vegetable oil is due to the quick reactions at the double-bonded functional groups.[39] Hence higher the level of unsaturation, higher the sensitivity of oil towards oxidation.[23,24] Oxidative degradation results to an increased viscosity that restricts the useful life time of vegetable oil based fluids.[30] It is also noticed that vegetable oils show poor corrosion protection.[42] Cloudiness and solidification become apparent in vegetable oil at low temperatures upon prolonged exposure to low temperature (–10 to 0°C).[40,41] Another problem is the susceptibility of the ester functionality present in the triacylglycerol structure to hydrolytic breakdown.[43] As a results, contamination with water in the form of emulsions must be prohibited. Poor thermal and oxidation stability along with poor low-temperature flow properties bound their potential application as lubricants in industry.[44] Vegetable oils exhibit particularly effective boundary lubricity additives. A boundary lubricity additive functions by its ability to adhere to the metal surface. This property is because of the high polarity of the entire vegetable oil which allows strong interactions with the lubricated surfaces. Polar compounds, for example synthetically prepared esters or naturally occurring triglycerides are especially efficient at this function due to their capability to orient a polar head group of the molecule onto a metal surface. This polarity produces a strong affinity to the metal by one end of the molecule and allows a non-polar hydrocarbon to extend out and provide a barrier between metal surfaces. Boundary lubricity is affected by affinity of the lubricant molecules to the surface and also by possible reaction with the surface.

Conversion of alkene groups of the aliphatic chains of fatty acid of vegetable oil to other functional groups that can provide a better oxidative stability, while reducing structural homogeny of the oil by attaching alkyl side chains would improve temperature performance.[45] Numerous modern technologies have been accepted to solve the issues concerning the application of plant oils in lubricants. Some of them are additive treatment, genetic and chemical modification.[19]

Vinci et al.[46] have suggested a thermo-oxidatively stable base lubricant based on methyl-12-hydroxystearate, a derivative of the castor oil with 70% renewable carbon content. Joseph and Sharma[47] studies shows that the thermo-oxidative stability of vegetable oils (when used as lubricant base oils at temperatures around 120°C) can be enhanced by the mixture of aminic and phenolic type antioxidants. Mendoza et al.[48] developed a formulated some additives based on sunflower oil for hydraulic systems of agricultural tractors, they can be considered with a biodegradability of 89%, substantial improvement of pour point up to -29°C (considering the pour point of sunflower base oil of -3°C). Again, the additive considerably improved the oxidation stability of the sunflower base oil. The microweldings formation has not been observed with this formulated oil and satisfies the requirements of the reference mineral fluids for extreme pressure tribological tests. Regueira et al.[49] has investigated the compressibility and viscosity properties of vegetable oils for their application as hydrolytic fluid and lubricants. From their study, it is manifest that chemically modified vegetable oils have prominent scope for use as base oils.

The lubricant characteristic has been trying to develop biodegradable lubricants with improved technical characteristics than usual lube oil additives and research in this direction is opening up a new opportunities. Franco et al has reported a new biolubricant formulation having high oleic sunflower oil which was blended with polymeric additives e.g. Sunflower oil bio fuels, polymeric additives e.g. ethylene vinyl acetate (EVA) and styrene-butadiene-styrene copolymers.[50] This lubricant formulations improved the kinematic viscosity values and viscosity thermal susceptibility. In recent times, the application of triglycerides molecules in polymer science was reviewed with a focus on cross-linked systems for resin and coating applications with the conclusion that triglycerides molecules are anticipated to play a major role during the 21st century to produce polymers from renewable sources.[51] Other than these cross-linked polymers, linear polymers can also be obtained from plant oils.

US patent no. 4873008 has presented a lubricating compositions based on jojoba oil. The compositions provide better-quality lubrication performance as antifriction, anti-wear and load-carrying properties. US patent no. 5229023 disclosed synthesis and evaluation of a group of lubricant additives comprises telomerized vegetable oils that have high viscosity and improved oxidative stability. US patent no. 4152278 discussed about tribological performance of some vegetable wax ester. Again US patent no. 4970010 has disclosed a group of sulfurized, phosphite derivatives of vegetable oils with superior lubricating properties. US patent no. 4925581 disclosed a procedure for sulfurizing meadowfoam oil which is soluble in a mineral oil and claimed the application of such meadowfoam oil derivatives as lubricant additives.US patent no. 6534454 B1 discussed regarding biodegradable vegetable oil compositions for lubricant. The compositions consist of at least one triglyceride component, an antioxidant comprising an amine or phenol derivatives.

Erhan et al.[12] has described superior oxidation and low temperature stability of vegetable oil based lubricants by means of different kind of sunflower oil and soybean oil. Biresaw et al.[11] has reported frictional properties of some triglyceride vegetable oils. Boshui et al.[52] studied the effects of two fatty acidic diethanolamide borates as additives on biodegradability and lubricity of an unreadily biodegradable paraffinic lubricating oil. Ghosh et al.[53] studied the multifunctional (VM, PPD and AW) greener additives performance for lubricating oil which contains copolymers of rice bran oil, peanut oil and β-pinene with isodecyl acrylate.

Generally, vegetable oils have been used to improve the tribological performance of base oils. Except that application of them as viscosity modifier (VM) and pour point depressant (PPD) is not so well known. That means the additive performances of only vegetable oils are not very hopeful in lubricant industry. So to use of them as LOA the author has polymerized citral oil with alkyl poly acrylate, rice bran oil with 1-decene and poly acrylate which combined high viscosity properties of vegetable oil with excellent low temperature flow property of poly alkyl acrylate and good anti-wear property in a single entity, in addition to considerable biodegradability.

In an era of mounting oil prices, global warming and other environmental issues (e.g. waste) the change from fossil feedstock to renewable resources can significantly contribute to a sustainable development in the future. The synthesis of monomers as well as polymers from plant oils has already got some industrial application and current developments in this area offer promising new opportunities.

References

References are given in BIBLIOGRAPHY under Chapter I of Part II (PP 160-165).