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Review

Vegetable oils as lube basestocks: A review

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The depletion of the world's crude oil reserve, increasing crude oil prices, and issues related to conservation have brought about renewed interest in the use of bio-based materials. Emphasis on the development of renewable, biodegradable, and environmentally friendly lubricants has resulted in the widespread use of natural oils and fats. Vegetable oils are promising candidates as base fluid for eco-friendly lubricants because of their excellent lubricity, biodegradability, viscosity-temperature characteristics and low volatility. In view of agriculture based Indian economy, there is a great potential of producing vegetable oil based lubricants, which has ecological compatibility in addition to technical performance. However, suitability of the vegetable oils for a specific application either needs chemical modification or may be used as it is with additive blending route in order to get basestocks as per specifications for a particular end use application.

Key words: Biolubricants, vegetable oils, biodegradable, renewable.

INTRODUCTION

In recent years, deliberate and accidental lubricant losses to the environment by means including evaporation, leakages, and spills have lead to major concerns regarding pollution and environmental health. About 5 to 10 million tons of petroleum products enter the environment every year, with 40% of that representing spills, industrial and municipal waste, urban runoff, refinery processes, and condensation from marine engine exhaust. Thus, strict specifications on biodegradability, toxicity, occupational health and safety, and emissions have become mandatory in certain applications. The enactment of these specifications, along with uncertainty in the petroleum supply for political and economic reasons, has stimulated the search for alternative energy sources. Vegetable oils, a renewable resource, are finding their way into lubricants for industrial and transportation applications (Nagendramma and Kaul, 2012; Padmaja et al., 2012; Arumugam et al., 2012; Quinchia et al., 2012; Singh, 2011; Quinchia et al., 2010; Campanella et al., 2010; Sharma et al., 2006). Waste disposal is also of less concern for vegetable oil-based products because of their environment-friendly and nontoxic nature. Synthetic lubricant base oils are also available and offer improved stability and performance characteristics over refined petroleum oils, but at a premium price. Most of the biodegradable synthetic oils are esters that offer superior thermal and oxidative stability.

India has a great potential of producing edible and non edible tree borne oils, which remain untapped and can be used as potential source for vegetable oil based lubricants with an objective of ecological compatibility in addition to technical performance. This paper will touch fairly wide cross-section of research and development issues pertaining to the replacement of non-renewable raw materials with bio-based materials in environment friendly lubricants selected based on their potential for combined environmental benefits and overall return to agriculture and contribute significantly to identify key research opportunities through which new biolubricants might come to replace mineral oil based lubricants.

BASESTOCK

Lubricants are complex formulated products consisting

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of 70 to 90% basestocks with the right physical characteristics, mixed with functional additives to optimize the physical properties in order to meet a series of performance specifications. The basestocks can be mineral, synthetic or re-refined apart from vegetable oils. Mineral oil bases are the most common. They consist predominantly of hydrocarbons but also contain some sulphur and nitrogen compounds with traces of a number of metals. Synthetic oils among others include polyalphaolefins (PAO), polyalkylene glycols (PAGs) and synthetic esters. PAOs are petrochemical derived synthetic oils that most resemble mineral oils. Polyalkylene glycols (PAGs) are polymers from petrochemical origin commonly made from ethylene oxide and propylene oxides. A major disadvantage of both PAOs and PAGs is their poor solubility with regard to additives. Since the additives themselves must also be biodegradable, this limits the additive types which can be used to formulate effective lubricants from PAOs and PAGs. Nowdays, some manufacturers are blending diesters with PAOs to form base oils which are biodegradable, have good solubility, resist oxidation, and have good temperature viscosity characteristics. Others are blending synthetic diesters with vegetable oils to provide similar results.

Synthetic esters form a large group of products, which can be either from petrochemical or oleo chemical origin. Esters can be categorized as: monoesters, di-esters, phthalate esters, polyol esters and complex esters. Triacylglycerol structure of vegetable oil makes it an excellent candidate for potential use as basestock (Salimon et al., 2010; Salimon and Salih, 2010; Zaher and Nomany, 1988). When using vegetable oils and/or esters to formulate lubricants, several specifications have to be considered. First technical specifications about suitability for the application are either as it is or with special attention to chemical modification to get basestocks with appropriate characteristics of the biolubricants and secondly taking into consideration that both the raw materials and additive have to be as harmless as possible, and this certainly in accordance with local legal requirements in matter of health and environment. Re-refined oil is used oil that undergoes an extensive refining process to remove contaminants to produce fresh base stock. These basestocks, irrespective of their origin, are then sold to blenders who add additive packages to produce lubricants.

ENVIRONMENT FRIENDLY LUBRICANTS AS BIOLUBRICANTS

In order to combine the environmental behavior and the technical properties of lubricants, a lot of countries have introduced so called “ecolebels”, or “ecologos” which give a sense of security to the users of environmentally compatible products. The eco-labeling system in Germany, The Netherlands, Nordic countries, Canada, Austria, France, Brazil, India, China, Japan, Spain, Thailand, UK, USA have issued criteria for lubricants. The parameters guided by the labeling criteria include toxicity, environmental impact (notably biodegradability), safety and renewability. Due to growing concern regarding the environmental impact and associated costs of lubricants, many lubricant companies have developed “environment friendly” lubricants or biolubricants. However, there is no universal definition used to determine environmental friendliness. Actually, biolubricants are nothing but the basestocks blended with additives/performance package aiming certain extent of rapid biodegradability and lower ecotoxicity as a deliberate and primary intention. However, no universal agreement exists on the origin and chemical composition of the biolubricants. Biolubricants are often but not necessarily based on vegetable oils. As the vegetable oils offer biodegradability and low toxicity, it is obvious that during the formulation of a biodegradable and low toxicity fluid, the additive must also be biodegradable and have low toxicity. Biolubricants display a neutral CO_2 balance and easily decompose in nature. The currently marketed vegetable oil based lubricants are an ecologically sensible alternative with performance characteristics and quality comparable to that of their conventional petroleum based competitors.

Biodegradable lubricants show less emission because of higher boiling temperature range of esters. They are totally free of aromatics, over 90 % biodegradable and non water polluting. Also the oil mist and oil vapor reduction lead to less inhalation of oil mist into the lung. Biolubricants have better skin compatibility, less dermatological problems as well as high cleanliness at the working place. The high wetting tendency of polar esters leads to friction reduction with at least equal and often higher tool life. Higher viscosity index can be an advantage when designing lubricants for use over a wide temperature range. This can also result in lower viscosity classes for the same applications combined with easier heat transfer. Higher safety due to higher flashpoints at the same viscosities can be obtained leading to cost savings on account of less maintenance, man power, and storage and disposal costs.

VEGETABLE OIL BASESTOCKS

Vegetable oils have a number of inherent qualities that give them advantages over petroleum oils as the feedstock for lubricants. Based on the fact that vegetable oils are derived from a renewable resource, they avoid the upstream pollution associated with petroleum extraction and refining in terms of usage. From a worker’s safety perspective, plant-based lubricants are more attractive than their petroleum counterparts because of their relative low toxicity, high flash point and low volatile-

Table 1. Vegetable oil production in developing countries.

Country	Million tons per annum
United States	11.0
Malaysia	9.6
China	8.9
Indonesia	7.1
India	6.5
Argentina	4.9
Brazil	4.6
Nigeria	1.9
Others	31.7

organic compound (VOC) emissions. The performance limitations of vegetable based lubricants stem from inherent properties of the vegetable oil basestocks rather than composition of additive package. Basestocks usually comprise nearly entirely predefine properties such as high biodegradability, low volatility, ideal cleanliness, high solvency for lubricant additives, miscibility with other types of system fluids, negligible effects on seals and elastomer and other less significant properties (e.g. density or heat conductivity). Basestocks are also a major factor in determining oxidative stability, deposit forming tendencies, low temperature solidification, hydrolytic stability and viscometric properties. On the other hand, parameters like lubricity, antiwear protection, load carrying capacity, corrosion (rust) prevention, acidity, ash content, color, foaming, de-emulsification (so called demulsibility), water rejection and a number of others are mostly dependent on the additives and/or impurities: contaminants. Therefore, when a given fluid is considered for its suitability as a lubricant, first of all the base stock-dependent parameters are evaluated. In addition to biodegradability, the characteristics to be given attention are cleanliness (particle count), compatibility with mineral oil lubricants and homogeneity during long term storage, water content and acidity, viscosity, viscosity index, pour point, cloud point, cold storage, volatility, oxidative stability (for vegetable oils also iodine value), elastomer compatibility and possibly other properties, depending on intended application. Water rejection, demulsibility, corrosion protection, ash content and foaming could also be tested if contamination of the additive-free oil is suspected.

Vegetable oils clearly outperform mineral oils in terms of volatility or viscosity index. Many of the other properties are similar between the fluids or may be manipulated with additives. However, low resistance to oxidative degradation and poor low temperature properties are major issues for vegetable oils to be taken care of. It has been established that methylene interrupted poly unsaturation is the key factor causing low oxidative stability of vegetable oils (Zaher and Nomany, 1988; Willing, 2001). Low temperature properties of vegetable oils are inferior to those of synthetics or even mineral oil basestocks. Low temperature properties to some degree can be characterized by determining the pour points. A similar test can also be used to determine the ability to remain liquid upon cold storage, which is often a concern in the case of vegetable-based lubricants. Oil purchases are made on the basis of availability, raw material price, manufacturing costs and utilization potential in addition to quality parameters. Four main vegetable oils dominate the industry accounting for about 82 to 85% of worldwide vegetable oil production. Soybean oil is 31 to 35%, palm oil 28 to 30%, rapeseed oil 14 to 15% and sunflower oil is 8 to 10% of global production. A large portion of vegetable oil production is in developing countries. The output in million tons per annum of various countries is given in Table 1.

In Indian context, a large potential of non edible oils remain untapped, which can be used as potential source for vegetable oil based lubricants. At the national level, 15 million hectares of wasteland could give about 20 MT of oil equivalent output. Non edible oilseeds can be grown along railway lines, wastelands, highways and fencing of various types. If we consider seeds like castor, jatropha, karanja, mahua, Tamanu etc., cost of the products can further be reduced. For mass cultivation, the long list of oilseeds can be narrowed down (Sahoo et al., 2002). India is the largest exporter of castor oil. It corners about 70% of the global castor oil trade. Given the preference for castor oil, particularly from the industrial sector, it is constantly in demand, which is estimated at about 220 000 tons per annum.

India consumes close to 25% of its production of which 1/4th is used in soap manufacturing while 1/5th is consumed by lubricants and derivatives industry. Paint and allied industry consumes nearly 35% of the domestic consumption. US are totally dependent upon imports to meet the industry and defense needs of castor oil. In the international market, castor oil is one of the most expensive vegetable oils. Despite India's dominant position in the global castor market, in the exports market the Indian castor produce doesn't drive the prices. However, a major part of the Indian castor oil is exported and the value addition takes place in the importing countries. It exports around 0.2 to 0.24 mn tons of commercial castor oil, 50 000 to 60 000 tons of castor seed extractions and 15 000 to 20 000 tons of castor seed. India supplies 70% of the world's requirements of castor oil (Singh, 2011).

The introduction of Simarouba glauca DC (a native of El Salvador first introduced in NBPGR station at Amravathi, Maharashtra in 1966), a versatile oilseed tree with a productivity potential as high as 2000 kg oil/ha/year and with an ability to establish well even in marginal/wastelands with degraded soils has given new hope for their use as renewable resource for biofuels and biolubricants (Sahoo et al., 2002). Seeds contain 60 to 65 % oil that is edible and the oil cake is an excellent source of N, P and K. The fruits provide sugar rich pulp for preparation of beverages or for juice. The bark and the leaves are of medicinal importance. The insect resistant lightwood is good for furnitures, toys and match industry. Mahua (*Madhuca indica*) is non-edible tree based seed oil, which has an estimated annual production potential of 181 thousand metric tonnes in India (Sahoo et al., 2002; Kaul et al. 2003) and can be an excellent source for biolubricants.

Vegetable oils consist primarily of long chains of carbon and hydrogen with terminal ends containing carbon, hydrogen and oxygen. This differentiates them from petroleum “hydrocarbons” which consist of chains and rings of carbon and hydrogen. Vegetable oils also differ from hydrocarbons as the carbons may or may not be “saturated” with hydrogen. The fact that vegetable oils make very good alternatives to petroleum hydrocarbons as the more saturated carbon behaves more like petroleum. Vegetable oils in some case out perform petroleum for example, bio-based motor oils in terms of friction reduction. However, they contain oxygen and some percentage of unsaturated carbon so they become more reactive and will polymerize, forming long chains of molecules. Most vegetable oils contain 18 carbon chains. The popular theory has long been that the longer the chain, the better the lubricant, but this may not be true in many cases. Longer chain acids like erucic acid (22 carbons) from rapeseed and crambe are not as good lubricating oil as canola (18 carbons). Canola also contains a small percentage of palmitic (16 carbon saturated) and stearic (18 carbon saturated) in its oil. The ability of these oils to aid lubrication is unknown because these fatty acids constitute small percentage of the oil. The use of palm oil in biolubricants requires a greater percentage of pour point depressant if used in temperate climates.

The market for biolubricants will be driven by environmental concerns, as well as by economics and performance issues. Vegetable oil based lubricants generally have lower performance characteristics than their petroleum based competitors, thus the initial market focus has been on “total loss” lubricants like chain bar and two stroke engine oils etc. taking advantage of the lower ecotoxicity and more favorable biodegradability characteristics of environment friendly lubricants. Despite the small current market, potential is large. Each application area has unique performance requirements. To expand market opportunities, one market segment that justifies more R and D is the huge motor and gear oil market, which accounts for about half of the total lubricant market. From a positive point of view this means that bioproducts still have an enormous market potential. However, reality looks different. Although the bioproducts are available on the market since at least five years, they have struggled from the beginning to compete with the well-established mineral oil-based products. Major technical performance barriers must be overcome to enable vegetable oils to be more widely competitive with mineral oils. In this area R and D effort plays a significant role as it has to be end use specific, environment specific and at the same time cost effective.

Price is a major barrier in the development of biolubricants as the oilseed prices are not competitive in comparison with the world market prices for many vegetable and mineral oils. However, due to instability in the price of mineral oils and the growing trade imbalances globally, use of indigenous renewable raw materials is an important logical step in view of severe predictions for the future. Biolubricants are generally between 1.5 to 5 times more expensive than mineral oils. Economical and environmental balance needs to be performed in order to minimize the higher price that is, economic cost versus true cost in terms of their advantages and hidden cost savings on account of less maintenance, manpower, storage and disposal costs. This explains why the market share of vegetable based biolubricants is only about 3 to 4% of the total use of lubricants and hydraulic fluids. A strong requirement is the necessity for rules and standardization for the classification of different raw materials, stability of price and supply of seed oils and a robust long term policy on industrial crops, allowing them to plan and set up investments.

Design of environment friendly lubricants seeks the basestocks to meet commercial, technical and environmental needs. The challenge for researchers in this field will be to improve certain characteristics of vegetable oils without impairing their excellent tribological and environmentally relevant properties. This implies the utilization and sustainment of the natural chemistry of vegetable oils to a high extent. A preliminary chemical evaluation of basestocks should detect defects that may cause problems during in-use operation. In order to control the behavior during use, it is necessary to control the hydrolytic stability, control of the physicochemical and environmental characteristics during use, compatibility with materials and seals, corrosivity and wear and friction properties, apart from the two main issues of operational temperature limitations and oxidative instability. The selection of the type of typical physico-chemical and friction and wear test depends also on the final application of the oil. Positively addressing these concerns has led to the development of new additive systems thus widening the choice of basestocks enabling even standard vegetable oil to meet the requirements for certain low temperature applications in addition to chemically modifying the vegetable base oil and genetically modifying the oilseed crop.

ADDITIVE REFORMULATION

A lubricant consists of base oil (usually 75 to 90%) and an additive package designed to improve performance characteristics such as oxidative stability, pour point and viscosity index (Brophy and Zisman, 1951; Miller and Anderson, 1957). In the past, it was assumed that additives designed for mineral oil lubricants perform similarly when used with vegetable oils. This led to the production of technically inferior plant-based lubricants. Many of the industry's negative opinions of plant-based lubricants stem from these early products. More recently, companies have started reformulating and/or designing additives specifically for vegetable oils with successful results. Purely plant-based additive packages are now available which produce a full line of total loss lubricants and hydraulic fluids (Jessica, 2000).

CHEMICAL MODIFICATION OF THE BASE OIL

Some of the rapidly biodegradable lubricants are based on pure, unmodified vegetable oils. The triacylglycerol structure of vegetable oil makes it an excellent candidate for potential use as a base stock for lubricants and functional fluids (Zaher and Nomany, 1988; Willing, 2001). Chemically, these are esters of glycerol and long-chain fatty acids (triglycerides). The alcohol component (glycerol) is the same in all vegetable oils. The fatty acid components are plant-specific, therefore, it varies and differs in chain length and number of double bonds, besides, functional groups may be present. Natural triglycerides are very rapidly biodegradable and are highly effective lubricants. However, their thermal, oxidation and hydrolytic stability are limited, their inferior low temperature behavior (Quinchia et al., 2010; Campanella et al., 2010; Sharma et al., 2006; Salimon et al., 2010) and other tribochemical degrading processes (Willing, 2001; Gardener, 1989; Gunstone et al., 1994; Jessica, 2000; Willing, 2001; Becker and Knorr, 1996) that occur under severe conditions of temperature, pressure , shear stress, metal surface and environment also restrict their use as lube basestocks in its natural form. Therefore, pure vegetable oils are used only in applications with low thermal stress. These include total loss applications like mold release and chain saw oils. Chemical modification is necessary to improve these performance limitations with the focus on eliminating bis allelic hydrogen functionalities in methylene interrupted poly unsaturation and optimal extent of structural alteration for improved low temperature performance. Chemical modification of vegetable oils is an attractive way of solving these problems. Biolubricants formulated from plant oils should have the following advantages derived from the chemistry of the base stock:

i. Higher lubricity leading to lower friction losses, yielding more power, and better fuel economy.
ii. Lower volatility resulting in decreased exhaust emissions.
iii. Higher viscosity indices.
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.

Present review focuses on modifications which are of significance to manufacture lubricant base fluids. The improvement of natural oils by plant cultivation or genetic modification will be mentioned briefly.

Modifications of the carboxyl group

One of the most important modifications of the carboxyl group of the fatty acid chain, performed on large scale is the transesterification of the glycerol esters or the esterification of the fatty acids obtained by cleavage of such esters, which are normally catalyzed with acidic or basic catalysts. Typical homogeneous catalysts are p-toluene sulphonic acid, phosphoric acid, sulphuric acid, sodium hydroxide, sodium ethoxide and sodium methoxide. In some cases, heterogeneous catalysts such as Sn-oxalate or cation exchange resins are used. Enzyme catalyzed reactions are also known (Zaher and Nomany, 1988; Becker and Knorr, 1996; Adhvaryu et al., 2000; Asadauskas and Erhan, 1999; Adhvaryu et al., 2003).

Transesterification (synthesis of esters)

The major components of vegetable oils and animal fats are Triglycerides. To obtain ester, the vegetable oil or animal fat is subjected to a chemical reaction termed transesterification as shown below in Figure 1. A number of transesterified and alkylated derivatives have been synthesized from available vegetable oils. It has been found that several esters of fatty acids of these vegetable oils have a high natural viscosity index, low pour points, and high thermo oxidative stability, and can meet the requirements as base fluid components for energy-efficient, eco-friendly, long-drain interval, multigrade oils. These oils have markedly lower viscosities at 40°C, higher load-carrying characteristics, and lower friction coefficients than the base fluids of currently marketed multigrade oils. A 50% blend with hydrorefined hydrocarbon oils could prove highly viable. It clearly establishes the potential for utilizing these esters, either alone, or in combination with mineral oils, for formulating cost-effective high-performance, energy-efficient, and environmentally friendly lubricants. Performance characteristics of these oils as engine oils, automotive gear oils, and 2 stroke oil with conventional additives and with alternative additives are under investigation in comparison to the most advanced hydrocarbon based

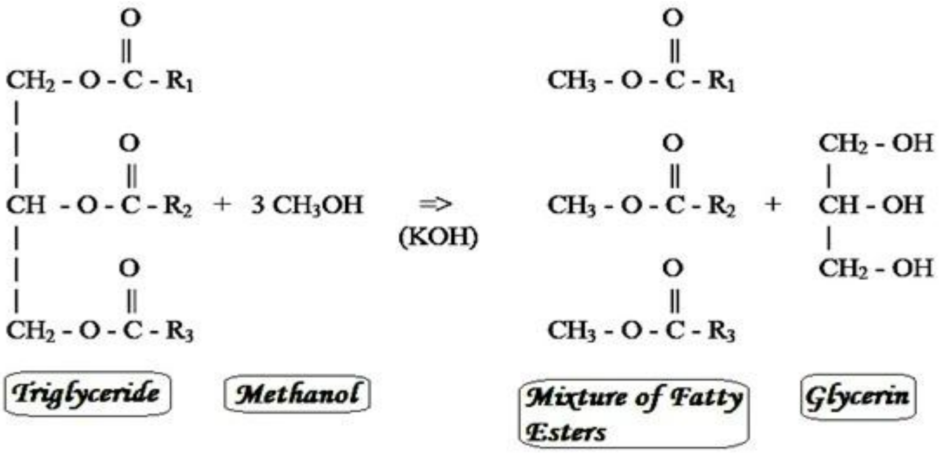

Figure 1. Transesterification of triglycerides. Anjana Srivastava, Prasad R. Sustainable and Renewable Energy Reviews, (4),111-133,(2000).

multigrade oil formulations of long-drain interval. Biodegradable organic polyesters derived from the transesterification/esterification of vegetable oils and branched neopolyols such as trimethylolpropan (TMP) and poly esters have been developed for various applications. Biodegradable TMP [2-ethyl- 2-(hydroxymethyl)-1,3-propanediol esters] of rapeseed oil fatty acids was synthesized via enzymatic and chemical methods. Sodium methylate (0.5% w/w) was employed as catalyst, and the reaction mixture was refluxed under a reduced pressure of 3.3 kPa. Approximately 99% conversion was achieved at 110 to 120°C in 10 h. Using 40% w/w Candida rugosa lipase, only 64% of the TMP was converted to triesters in 24 h at 5.3 kPa at 478°C. With immobilized Rhizomucor miehei (50% w/w), the highest conversion to the TMP triester was 90% and was achieved in 66 h.

Palm oil TMP esters containing 98% w/w triester can be successfully synthesized in less than an hour. The chemical transesterification of TMP with palm oil methyl esters was attainable under a reduced pressure with a 3.9:1 molar ratio and the use of sodium methoxide as a catalyst. The optimum molar ratio was established as 3.9:1, and the catalyst was required at less than 1.0% w/w, a quantity far less than the lipase required for enzymatic transesterification (40 to 50% w/w). The low-temperature properties of alkyl esters derived from tallow and recycled greases in neat esters and 20% ester blends in No. 2 low-sulfur diesel fuel were determined.

The properties studied included cloud point (CP), pour point (PP), cold filter plugging point (CEPP), low-temperature flow test (LTFT), crystallization onset temperature (Tc), and kinematic viscosity. The compositional properties of the alkyl esters determined included water, residual free fatty acids, and free glycerol content. In general, secondary alkyl esters of tallow shows significantly improved cold-temperature properties over normal tallow alkyl ester derivatives. Wu et al. prepared three monoalkyl fatty acid esters derived from tallow and grease by lipase-catalyzed transesterification and evaluated the esters as prospective diesel engine fuels. The low temperature properties of the esters, both neat and as 20% blends in No. 2 diesel fuels were evaluated. The properties investigated included CP, PP, CEPP, LTFT and crystallization onset temperature.

MODIFICATIONS OF THE FATTY ACID CHAIN

In the field of lubricant base fluids, reactions at the double bonds are used to increase the temperature and hydrolytic stability but somewhat lowers the viscosity index. Viscosity index increases with linearity whereas low pour characteristics gradually deteriorates. Furthermore, the polarity can be altered by the introduction of hetero-atoms such as oxygen or nitrogen. At present, less than 10% of the known reactions of fatty acid chains are industrially exploited (Campanella et al., 2010; Sharma et al., 2006; Salimon et al., 2010; Salimon and Salih, 2010; Becker and Knorr, 1996; Adhvaryu et al., 2000; Asadauskas and Erhan, 1999). Thus, there is a great potential for economic exploitation of vegetable oils and fats to have a new product line of biolubricants. Many of these modifications are highly promising, but at present, are still in the development stage. Industrial and academic research institutes are currently actively engaged in researching these areas. Selected modification processes of fatty acid chains which are of interest for the lubricants sector are as follows.

Selective hydrogenation

This process primarily serves to improve the melting point as well as the ageing behavior. Selective hydrogenation, in which the fatty acid residue is not fully saturated, is of greatest interest in the area of lubricant chemistry.

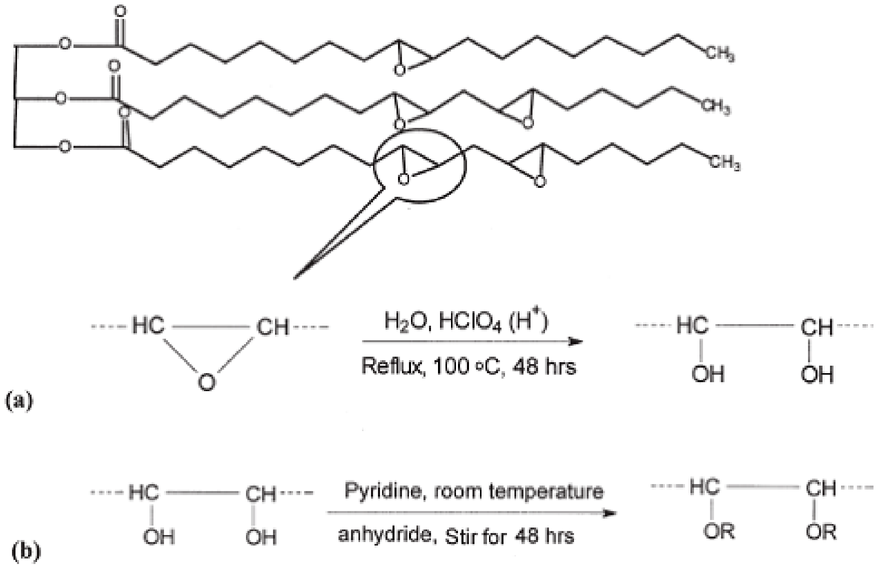

Figure 2. Epoxidation Reaction. Jumat Salimon1, Nadia Salih1 and Emad Yousif, Eur. J. Lipid Sci. Technol. 2010, 112, 519-530.

The stability of the oils can be significantly improved by selective hydrogenation of easily oxidisable compounds into more stable components. It transforms the multiple unsaturated fatty acids into single unsaturated fatty acids without increasing the saturation, necessary to avoid deterioration in low-temperature behavior.

Epoxidation

Epoxidation is one of the most important double bond addition reactions. In the case of unsaturated fatty acid esters, it is often performed *in situ* using the per formic acid method (Figure 2). This process is industrially performed on a large scale. At present the vegetable oil epoxides are used in polyvinyl chloride (PVC) and stabilizers. Furthermore, they are also used to improve the lubricity in lubricants. Due to their good lubricity and high oxidation stability in comparison to rapeseed oil, pure epoxidised rapeseed oil can also be used as a lubricant base fluid (Adhvaryu and Erhan, 2002). Sharma et al. (2006) carried out a series of structural modifications of vegetable oils using anhydrides of different chain lengths (Figure 3). The reaction was monitored and products were confirmed by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography, and thermogravimetric analysis (TGA). Experimental conditions were optimized for research quantity and for laboratory scale-up (up to 4 lb = 1.8 kg). The thermo-oxidation stability of these new lubricant base fluids was tested using differential scanning calorimetry and TGA. The chemically modified base fluids exhibit superior oxidation stability in comparison with unmodified vegetable oils. These base fluids in combination with suitable additives exhibit equivalent oxidation stability compared with mineral oil-based formulations. Epoxidised fatty components are reactive substrates for a number of interesting products. Ring opening of such epoxidised oils with organic acids or alcohols produce epoxy polyol esters and epoxy polyethers. These are widely used in polymer chemistry, e.g. in the areas of paints and dyes. The cleavage of the epoxy ring allows also the introduction of hetero-atoms and a whole series of functional groups. Work is going on to form a whole new series of oleo chemical products which can be used as lubricant base fluids, additives, etc. (Adhvaryu et al., 2000; Asadauskas and Erhan, 1999; Adhvaryu et al., 2003).

Estolides of oleic acid and saturated fatty acids

Estolides are a class of esters-based on vegetable oils and are synthesized by the formation of a carbocation at the site of unsaturation. This carbocation can undergo nucleophilic attack by other fatty acids, with or without carbocation migration along the length of the chain, to form an ester linkage. Figure 4 gives the schematics of the synthesis of oleic estolide esters. Estolides were developed to overcome some of the short-falls associated with vegetable oils, such as poor thermal oxidative stability and poor low temperature properties. Some deficiencies can be improved with the use of additives but usually at the expense of biodegradability, toxicity and cost. Mono-estolide esters and enriched saturated monoestolide 2-ethyl hexyl esters were

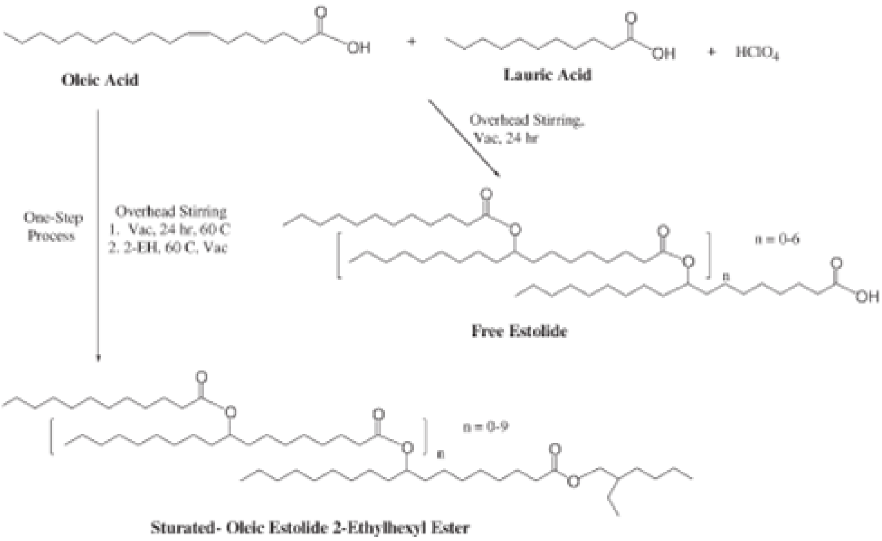

Figure 3. (a) Epoxy ring opening with formation of dihydroxy derivative; (b) reaction with anhydride to form diester derivatives. Brajendra K. Sharma Atanu Adhvaryu, Zengshe Liu*a*, and Sevim Z. Erhan*a,** JAOCS, Vol. 83, no. 2 (2006).

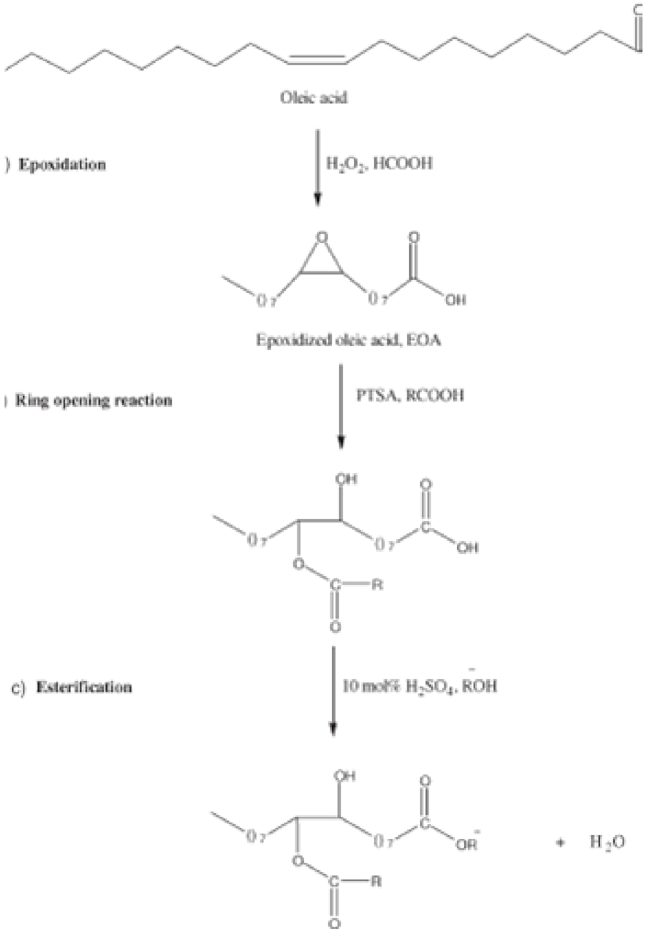

Figure 4. Schematics of the synthesis of oleic estolide esters. Jumat Salimon1, Nadia Salih1 and Emad Yousif, Eur. J. Lipid Sci. Technol. 2010, 112, 519-530.

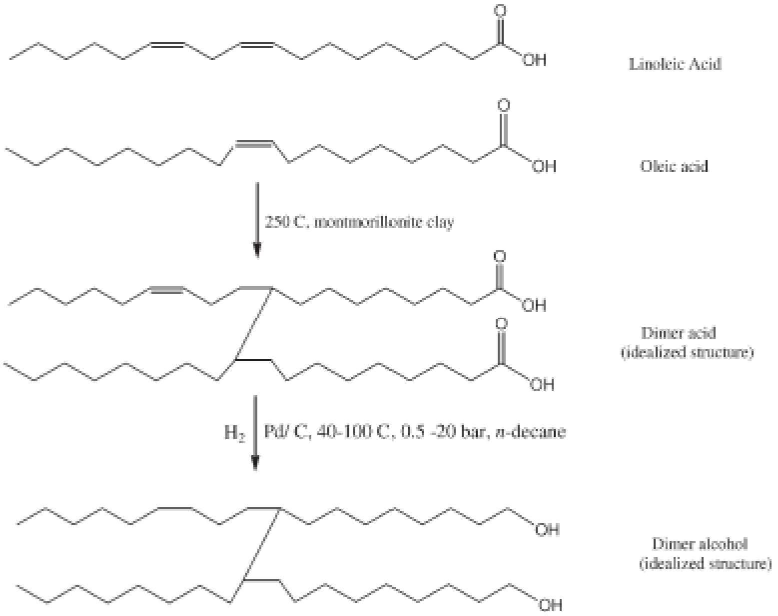

Figure 5. Dimerization of unsaturated fatty acids. Jumat Salimon1, Nadia Salih1 and Emad Yousif, Eur. J. Lipid Sci. Technol. 2010, 112, 519 to 530.

synthesized from oleic and saturated fatty acids using three different synthetic routes. The estolide numbers (ENs), the average number of fatty acid units added to a base fatty acid, varied and was dependent on synthetic conditions. The physical property data indicates that both chain length and EN affect low temperature properties. Tallow-oleic estolide 2-ethylhexyl (2-EH) esters were synthesized in a one-pot perchloric acid-catalyzed process from 90% industrial oleic and tallow fatty acids with varying ratios. Varying the ratio of tallow and oleic fatty acids along with the esterification process provided a functional fluid that may be used as a lubricant.

DIMERIZATION/OLIGOMERISATION

Another technologically feasible modification of the double bonds of unsaturated fatty acids is their dimerisation and oligomerisation involving two or more fatty acid molecules being attached to the residual alkyls. C18 fatty acids with one or more double bonds react with each other at temperatures of about 210 to 250°C in the presence of layered aluminosilicate catalysts (e.g. montmorillonite) forming a complex mixture of C36 dicarboxylic acids (dimeric fatty acids), C54 trimer fatty acids and C18 monomer fatty acids as shown in Figure 5. Industrially manufactured di- and trimeric acids are primarily used in hot glues, printing colors and epoxy hardeners. However, they may also be used in lubricants. It is assumed that the reaction to the dimeric fatty acids (C36) takes place via a Diels Alder-addition, whereby one fatty acid molecule (after double bond shifting) seems to have the function of the di ene and the other the function of the dienophile (Salimon and Salih, 2010).Parallel to this reaction other mechanisms can occur such as ene-reactions and reactions of carbo-cations, whereas other dimer products are formed. Additional by-products of the dimerisation are C18-monomeric fatty acids which consist out of a mixture of straight-chain, branched, saturated and unsaturated fatty acids. Hydrogenation of the double bonds in those compounds results in a solid acids whose branching points are mainly concentrated in the centre of the molecule.

BRANCHING OF FATTY ACIDS

Branched fatty acids are interesting base fluids for lubricants because of their extraordinary physical features. For example, the pour point of fatty acids and their derivatives is significantly lowered by branching. By adding sterically hindered branches, hydrolytic stability can also be increased. Their low pour point, low viscosity, high chemical stability and high flashpoint make saturated, branched fatty acids highly desirable base fluids in the lubricants industry and to the cosmetic, plasticizer, plastics, and defoamer industry. Branching of the fatty acids residues is initiated by C–C and C–O linkages. Below are some reactions that lead to the branching of chains:

a). One possibility of manufacturing alkyl-branched fatty acid derivatives is cooligomerization and introduction of an aldehyde group by hydroformylation opens up further opportunities of modifying fatty acid chains. For example the cooligomerization of ethene with C18:2-fatty acid derivatives homogeneously catalyzed over $RhCl_3 \cdot 3H_2O$ and produce yields of branched fatty acids of up to 95%. Besides simple addition, also multiple additions take place which occur only on the side chain. If methyl esters are used, consecutive reactions permit higher addition. The initially created 1:1 products can be conjugated and ultimately attract ethene. The cooligomerization of propene with conjugated C18 fatty acid methyl esters results in up to 92% yield of 1:1- and 2:1 products. Similarly to ethene addition, a second addition takes place at the existing branch. 3:1 propene products were not observed. A further hydrogenation of these cooligomerates over Pd/carbon catalysts generates the corresponding saturated derivatives which are also of interest to the lubricants industry.

b). Hydroformylation also allows the branching of unsaturated fatty acid chains and opens up further opportunities of modifying fatty acid chains. The reaction with methyl oleate, for example, results in an equimolar mixture of methyl-9-formylstearate and methyl-10-formylstearate with a yield of 90 to 99%. A rhodium-triphenylphosphine system is used as catalyst. Subsequent hydrogenation such aldehydes forms the corresponding alcohols.

c). The Friedel–Crafts alkylation is another possibility for synthesis of branched fatty acids and their derivatives. The reaction of oleic acids with isopropyl chloroform in the presence of $Et_3Al_2Cl_3$ forms a 1:1 mixture of the two regioisomers, 9- and 10-isopropyloctadecanoic acid with a yield of 72% (48, 49, 50, and 51). Isopropylation can also be performed with natural oils such as sunflower oil. They are of interest for the lubricants and cosmetics industries. However, such a process is not economically feasible because about two aluminium alkyl molecules have to be used per one molecule of fatty components. High-performance catalysts could transform alkylation into a technologically interesting reaction.

d). The Friedel–Crafts acylation is a reliable method for the functionalisation of unsaturated fatty substances. It allows the induction of a keto group in the side chain. Over Lewis acids such as $AlCl_3$, $SnCl_4$ or $ZnCl_2$, a mixture of unsaturated ketones is obtained. But, this process is not economically viable because of the high catalyst consumption.

e). Ene-reaction type represents a further modification possibility of the double bond and is suitable for the introduction of side chains with hetero functions such as –COOR, –OH, –CN in unsaturated fatty substances. Apart from a shift in position, the fatty substance double bond remains intact. A special case of ene-reactions are the carbonyl-ene reactions in which electron-deficient aldehydes as formaldehyde or glyoxylic ethyl ester can react as an enophile. Ene-additions of formaldehyde to vegetable oils take place by the formation of the corresponding di and tri-functionalized triglyceride.The use of further substances in the ene-reaction, such as maleic acid, glyoxylic acid ethyl ester and mesoxalic acid diethyl ester offer a further series of interesting products. Unfortunately in these reactions stoichiometric quantities of dimethyl aluminium chloride or ethylaluminium chloride are used. Other catalysts such as SnCl4, noble metal halides and boron trifluoride are under investigation.

f). Radical addition: Short branches can be introduced by addition of electrophilic radicals to the double bond thus; forming functionalized and branched fatty acids and their derivatives. An example of this type of reaction is the radical addition of acetone to oleic acid methyl ester. This reaction is catalyzed by manganese (III)-acetate. First, an acetonyl radical is formed which afterwards adds to the regioisomers 9-(10)-acetonylstearic acid methyl ester the product mixture yield is up to 72% (51, 56, 5). Following manganese (III)-acetate initiation further enolisable compounds such as acetic acid and malonic acid were added to fatty substances.

g). Acyloxylation: The addition of carboxylic acids to the double bonds of unsaturated fatty substances is known as acyloxylation. This is yet another method for modifying the double bonds of vegetable oils. This modification and the use of sterically hindered acids, improves the hydrolytic and oxidation stability of the fatty substances which is the reason why neo acids are often used (58, 59, 60). An example is the addition of pivalic acid to methyl oleate using a heterogeneous nafion/silica composite catalyst with a yield of 44% at a product selectivity of 93% .This type of reaction has yielded a number of new raw materials which represent a largely unexplored potential.

h). Metathesis reactions are applied in the petrochemical industry on large scale to vary the olefin chain lengths. Olefin metathesis is catalyzed by transition metal compounds (molybdenum, tungsten and rhenium). This reaction type can also be transformed to vegetable oil chemistry. A mixture of corresponding diesters and alkenes is formed from two carboxylic acid ester molecules. Self metathesis of oleic acid methyl ester using a tungsten (VI) chloride tetramethyltin catalyst system produces 9-octadecene and dimethyl 9-octadecenedioate-1, 18 in an equilibrium mixture. The co-metathesis of erucic acid or oleic acid methyl ester with short-chain olefins such as ethene (ethenolysis) or 2-butene produces unsaturated fatty acid methyl esters of chain lengths C10–C15 and the corresponding olefins. From the co-metathesis of oleic acid methyl ester and ethene methyl-9-decenoate is formed with a yield of >80% over $Re_2O_7 \cdot B_2O_3/Al_2O_3 \cdot SiO_2 \cdot SnBu4$ as catalyst.

The resulting fatty acid methyl esters such as methyl-9-decenoate and methyl-13-tetradecenoate are of interest for the manufacture of polyamides, polyesters, lubricants and for flavors and fragrances.

Modified cultivations of natural vegetable oils

Apart from a chemical modification, the oil industry is working together with plant cultivators to develop new oils whose fatty acid make-up is better suited for the demands of industrial applications as the industry is highly interested in tailor-made raw materials. Such natural structural uniformity of vegetable raw materials is utilizable input in the chemical processing. However, oleic acid or oleic acid esters still are the starting point of the chemical modifications. More than 90% technical oleic acid content would produce much fewer by-products than with present raw materials resulting in more efficient reaction and purer end-products. One cultivation success is high oleic sunflower oil (HOSO). The development of high oleic types of sunflower was first reported in 1976 and was further developed. At present HOSO is available with an oleic acid content of >90% and a very small stearic acid content of 1.0 to 1.5%. The extremely good physical and chemical properties of HOSO may lead to this vegetable oil being used in the non-food sector on a large scale. Even unmodified, it is suitable as base fluid for various biodegradable lubricants. Furthermore, it is a highly popular starting material for chemical modifications in other sectors of the chemical industry because of its outstanding purity. However, it remains a success in terms of crop yield and economical viability of their industrial applications. Apart from this, genetic modification is also being investigated (Srivastava and Prasad, 2000, 2002).

Conclusions

In view of stringent emission norms and environmental compliance, R and D activities in the area of development of renewable basestocks for lubricant formulation are rapidly increasing. Due to specific structure of vegetable oils, they combine good boundary friction lubricity and general wear protection along with stable viscosity-temperature behavior and very low evaporation. In addition, they have particularly good tribological properties apart from excellent biodegradability and low toxicity (Srivastava and Prasad, 2000). All in all, they are excellent raw materials for the formulation of bio lubricants. All their highly positive physical features are countered by a few major limitations, the most important of which is the inadequate ageing resistance of these products. As a result, they are either not, or only sometimes suitable for circulation lubricant systems. Vegetable oil-based products are perfect for total loss applications in which the lubricant inevitably enters the environmental cycle. The resulting high-performance lubricants are technologically at least as good, if not in some cases, much better than mineral oils.

The optimization of vegetable oils through chemical modification refers to specific technical properties such as hydrolytic stability, foaming, viscosity, evaporation, oxidation stability, etc. Resulting basestocks are subject to performance and cost constraints and are expensive to take over any worthwhile market share. However, vegetable oil availability is the key to overall cost of the product. India is the third largest oilseed producing country in the world with its rich agro ecological diversity ideally suited for cultivation of most oilseed crops. Thus, opportunities for expanding the market share of lubricants based on renewable raw materials are promising. The decisive factors for this development is environmental protection and, to a lesser extent, technical requirements. However, emergence of new oils will always be slow in their initial development due to small volumes and the conservative nature of the industry. This is likely to be one of the main reasons for surprisingly slow development of the industry in recent years.

Chemically modified renewable basestocks offer great potential for the development of biolubricants. Important modifications relate to the carboxyl group of fatty acids, e.g. esterification and fatty acid chain. In each case, the overriding objective is to realize application-relevant properties. Apart from the well-established processes, a number of fatty acid and fatty acid derivative reactions have been included which are still in the investigation stage. Successes in this area reduce the dependence on petrochemical raw materials and create new synthesis processes. The challenge for researchers in the field of biolubricants will be to improve certain characteristics of vegetable oils without impairing their excellent tribological and environmentally relevant properties. This implies the utilization and sustainment of the natural chemistry of vegetable oils to a high extent.

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