

INVESTIGATION OF TRIBOLOGICAL BEHAVIOUR OF VEGETABLE OIL AS AN ALTERNATIVE LUBRICANT FOR MAINTENANCE APPLICATIONS

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ABSTRACT: *The lubricant manufacturers invest between 1 and 5% of their sales in research and development depending on their field of activity. Extended oil change intervals show that more focus is on advanced quality lubricants (lifetime lubrication), which help to reduce lube consumption. About 1% of the total mineral oil consumption is used to formulate lubricants. Everywhere the production, application, and disposal of lubricants have to cover the best possible protection of our nature and the environment in general and of the living beings in special. The desire for environment adapted lubricants has begun to play an increasingly important role in many industrial applications particularly in the last two decades in view of contamination of soil and water and possible extinction of natural oil resources, which is caused by lost lubrication, leakage and accidents.*

Vegetable oils are potential candidate for lubrication of the future owing to their better biodegradability than petroleum based oils. However, the technical deficiencies associated with vegetable oils in terms of thermal, oxidative and viscosity-temperature properties have to be overcome before they are considered for specialty high performing lubricants. The present study deals with the current status of lubricants in relation to international developments and to identify future needs particularly of vegetable oils, considering various aspects as availability, processing, tribological and chemical behavior, testing, applications and economics. The feasibility of suitable non edible (castor) oil is also discussed.

Keywords: *Lubricants, Vegetable oil, Tribological behavior, Castor oil, Four-ball tester.*

1. INTRODUCTION

Tribology has a role to play in ameliorating the live of the rural poor in India. However, any hitech solutions evolved must be capable of being adapted to rural environment and therefore, involve scaled down technologies that are of low cost, operable and maintainable at village level, and maximal use of natural resources. One of the areas of scope in this regard is the possibility of utilizing agricultural produce including agro wastes to manufacture lubricants that are biodegradable & thus are environment friendly. [1]

There is growing concern regarding the environmental impact and associated costs of lost petroleum based fluids. The National Oceanic and Atmospheric Administration (NOAA) estimates over 700 million gallons of petroleum enter the environment each year, over half of which is through irresponsible and illegal disposal. Industry experts

estimate that 70% to 80% of hydraulic fluids leave systems through leaks, spills, line breakage and fitting failure. Petroleum is persistent and toxic. It damages living organisms including plants, animals and marine life for many years. In addition, the Coast Guard, EPA and local governments are increasing the range of responsibility of lubricant releases including significant fines and clean up costs. [2].

1.1 Current Concern: Environment and Ecosystem along with Product Quality

Product quality has acquired a new meaning today, infact a two dimensional aspect-Quality related to performance & quality related to benign nature of products towards environment and ecosystem after use. The punch line for most of the lubricant manufacturers today is "Transcending from customer demand to customer delight". Thus enforcement for biodegradable and eco-friendly lubricants is a

necessary requirement these days. The Eco-labeling scheme for lubricants categorizes the various lubricants into two categories:

Vegetable oil base with biodegradability limit of 90 and 60% respectively [11] Switzerland imposed the first regulations of biodegradable 2-stroke engine oils on lakes. European similar regulations have been applied to chainsaw oils, remolding and hydraulic oils. Fiscal incentives like VAMIL regulations have been applied in Netherlands. Then first eco-label environmental award for lubricants was the Blue Angel describing chain saw lubricants in Germany in 1988 followed by Blue Angel for concrete mould release oils in 1991 and for hydraulic fluids in 1996 [12]. Some other countries also promote eco-labels, for example: Painter Hundertwasser (Austria), Blossom symbol (Europe), White Swan (Nordic Countries), Green Cross/Green Seal (USA), Mapple Leaf (Canada), Ecomark (Japan), Green Tree (Hungary) [4].

2. POTENTIAL FOR BIO-LUBRICANTS

2.1 Tribo-chemical Properties

By their chemical nature, vegetable oils are triglycerides, where the building blocks are glycerol and typically three fatty acids, as shown on Figure 1. The fatty acids are often of different length and structure and they determine the physical-chemical properties and behavior of vegetable based lubricants. The more saturated the fatty acids are, then higher is the freezing point and the more resisting to oxidation. The ester bond between then glycerol and fatty acid impacts several properties making vegetable oils better in reducing friction and wear compared to mineral oils [13], [4].

3. TRIGLYCERIDE

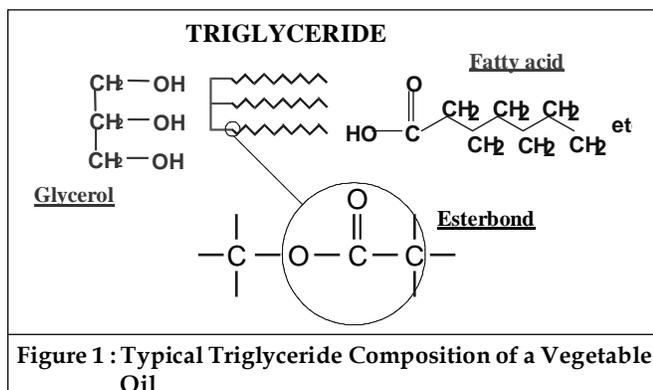
Igartua (1999) compared the properties of some vegetable oils (sunflower, soyabean & rapeseed) with

those of a mineral oil of same ISO grade using four ball test and Stribeck machine. The results showed that vegetable oils have better extreme pressure and anti wear characteristics and good friction reducing tendency in boundary lubrication. The shear strength proportionality constant for all three oils is lower than mineral oil; this can be an advantage for use in hydraulic system. The increase in acidity index and viscosity increase at 20°C w.r.t time is maximum for rapeseed oil followed by sunflower, soyabean & mineral oil. Vegetable oils gave thicker film at 40°C, and as thick as mineral oils at 80°C, and thus can be used for full film lubrication. The toxicity tests were also in favor of vegetable oils. [4]

Ioan (2002) investigated the tribological behavior of rapeseed oil using a sliding tribo model. The results showed a lower coefficient of friction for rapeseed oil as compared to the motor oil grade M 15 W/40 super 2. [15]

Adhvaryu *et al* (2004) did the friction and wear measurement on vegetable oil through ball on disk test and found that the friction coefficient (COF) is largely dependent on the concentration of vegetable oil and their derivatives in hexadecane. Results indicate that the COF sharply decreases with increase in oil content and levels off at higher concentration. Rate of decrease in COF is largely influenced by oil structure & their ability to form thin film at the point of metal contact. It has also been observed that friction coefficient & wear rate are dependent on the adsorption energy of the lubricant. [13].

Experimental studies as discussed by Seireg dealing with the investigation of some of the physical properties of lubricants on the contact temperature and were in heavily loaded Hertzian contacts under sliding conditions. Tests were done with a heavy-duty oil (SAE 80W-90), a high viscosity residual compound, a vegetable oil, and a water miscible fluid. It was observed that viscosity does not appear to be the significant property of the lubricant temperature rise and wear rate. [8]



3.1 Improvement in Properties Through Modification of Base Oil

Durak (2004) investigated the effects of addition of rapeseed oil (RSO) as an additive to mineral based lubricant. It was found that RSO as additive decreases the friction coefficient at high journal speeds, and even at moderate loads and the oil containing RSO performed a higher reduction in coefficient of friction at room temperature (25°C) than at higher temperature (100°C). The study clearly showed that RSO could be used as an additive of

friction modifier at room temperature and even at higher temperature. [17]

Durak and Karaosmanoglu (2004) investigated the effect of Cottonseed oil (CSO) addition to base oil on the friction coefficient, in the journal bearing under static loading at ambient room temperature (25°C). Tests were performed using base oil (SAE 20W50) alone and lubricating oil at concentration ratios 2.5, 5 and 10 volume % additive as CSO at five different speeds and three different loads. The experimental study clearly showed that CSO could be used as an additive of friction modifier. [6]

Adhvaryu *et al* (2004) studied the tribochemical properties of thermally and chemically modified soyabean oil by blending with amine phosphenate and antimony dithiocarbamate additives. Synthesis of chemically modified soyabean oil (CMSBO) gave two oils (CMSB1 & CMSBO2), having different degree of polarity and extent of substitution of fatty acid chain. Results showed that functional properties like oxidation, low temperature fluidity, and viscosity-temperature relation are improved by chemical modification. For thermal modification the normal refined oil was heated and stirred under N₂ gas purge at 330°C, soaked for 15 minutes and cooled gradually. The higher viscosity of TMSBO does not improve the lubricating properties significantly as there is no change in the polar functional group. Antimony additive reduces friction/wear and improves the strength & thermal conductivity of material. [13]

Maleque *et al* (2003) reported that fatty acid of palm oil methyl ester composition can provide effective boundary lubrication due to presence of a polar structure, which dissipates non-polar molecules or base lubricant and act as an anti wear and friction modifier for the commercial mineral based lubricating oil. Earlier research indicates the use of borate esters as friction modifier and anti wear additive due to their non-volatility and pleasant odor. But the borate esters are susceptible to hydrolysis resulting in liberation of oil insoluble & abrasive boric acid. [17]

Yunus *et al* (2003) conducted the chemical synthesis of palm oil trimethyl propane esters via transesterification of palm oil methyl esters (POME) with trimethyl propane (TM_P). The influence of the main operating variables, namely, temperatures and pressures, molar ratio of palm methyl esters to TMP, catalyst amount was studied and analyzed. The effects of temperature (80°C to 140°C) and reduced pressure (0.1, 10, 50, 100 and 500 mbar) were investigated and found to have a significant impact on the reaction. On the contrary, the amount of catalyst (%W/W) and molar ratio of POME to TMP had little influence on

the conversion but affected the overall yield of the reaction. The results confirmed the potential of palm oil TMP esters as biodegradable base stock for lubricant production. [7]

Lea (2002) reported that esters derived from vegetable oils offer the advantages of vegetable oils without their disadvantages and can be used for racing & competition oils. [12]

Adhvaryu *et al* (2001) explored the effectiveness of using deoxidized soyabean oil (ESBO) over soyabean oil (SBO) & high oleic soyabean oil (HOSBO) in certain high temperature lubricant applications. HOSBO was obtained by genetic modification of SBO, which showed improved thermal & oxidation stability over SBO due to elimination of multiple conjugated unsaturations in fatty acid (FA) chain of SBO. Antioxidant used was an alkylated phenolic compound, which was blended into vegetable oils at 40°C in various concentrations. The results showed that viscosity of ESBO at 40°C is higher than other oils & gives enhanced lubricity. This is attributed to its higher molecular weight and more polar structure. The deposit-forming tendency of ESBO was also found to be lower than SBO & HOSBO due to removal of multiple unsaturations in fatty acid chains. ESBO showed maximum improvement in oxidation stability at lower additive concentration. [16]

Greetham (1999) examined the suitability of copper compounds as additives for vegetable oils by an accelerated oxidation stability micro reactor and suggested that Cu dihydrocarbyl thio or dithio phosphates, carboxylates & phenates can be suitable additives. Copper and antimony additives are less expensive but the compounds chosen should be oil soluble for oxidation inhibition to be effective.

Choi *et al* (1997) investigated the anti wear (AW) performance of a newly synthesized additive, dibutyl 3-5-di t butyl 4-hydroxy benzyl phosphate (DBP) in olive and soyabean oils. The new additive showed constant wear rate without the transition in spite of increasing sliding velocity and higher AW performance under severe conditions compared with conventional additive. The new additive showed the dual function of hydrogen scavenging and protective film formation.

Mahendra (1997) studied the tribological characteristics of compounded oils containing Tallow. Friction and wear experiments were carried on a conventional four ball machine. Tallow was blended up to a concentration of 15% with paraffinic mineral oil as base. The results showed that Tallow in low concentration acted as an anti wear component in compounded oils in all experimental conditions.

However, an increase in Tallow concentrations has shown some prowear effect. It has been found to reduce the friction at higher load conditions.

Begland and Sommers (1982) conducted bench wear tests on four-ball wear tester on Diesters of dodecanedioc acid (DDDA). The results suggested that DDDA could be useful as a low level (5-10%) blending component in automotive lubricants. It not only brings about friction and wear reduction when added to petroleum oils but also leads to reduction when added to other synthetic base oil such as adipate diesters and polyalphaolefins.

3.2 Biolubricant Market and Applications

Until the nineteenth century lubricants had been manufactured using mainly, even exclusively vegetable oil and animal fats. When the internal combustion engines appeared, these "classical" lubricants were gradually replaced by mineral oils. The main cause of this change is the stability in time of the latest ones, for both stocking and functioning as compared to other lubricants [12].

Cost varies with specific application. But in general plant-based lubricants are 2 to 2.5 times more expensive than mineral oils and higher as much as synthetic lubricants. The price differential between plant-based and mineral oil lubricants is attributable both to the higher raw material cost of vegetable base oils and to more costly additives. According to Mark Miller, CEO of Torresolve, vegetable base oils are in the range of \$1.90 to \$2.30 per gallon (soy oil at the lower end the U.S. and canola at the higher), whereas petroleum base oils cost \$1.20 to \$1.40 per gallon. The additives Torresolve uses with vegetable uses with vegetable oils are approximately five times the cost of those used for petroleum-based lubricants.

Purchase price, however, is not an accurate measure of overall cost. Because vegetable oil-based lubricants evaporate less quickly and adhere better to metal surfaces, end users often use fewer products per application. Other cost benefits associated with vegetable oils may include reductions in environmental and safety penalties in the case of spills, parts wear and maintenance costs and disposal fees. As is the case within many plant-based products, once factors such as these are considered, plant-based lubricants appear to be competitive in cost with petroleum oils [10].

In case of lubricants, there are two different types of applications i.e. open systems & closed system. Bio-lubricants are the most attractive choice for applications that have potential environmental contact through accidental leakage, dripping or

generating large quantities of after use waste materials requiring costly disposal [13] and other environmental sensitive areas like agriculture, forestry, mining, construction, waterway & harbors [14].

The Slovenian Tool and Die Development Centre has formulated two different biodegradable vegetable based lubricants for deep drawing of steel sheet metal (CTD2 & CTD3). Biodegradable vegetable formulated oil CTD3 had higher concentration of additives than formulation labeled CTD2. The base stock for both formulations was high quality rapeseed oil, which is lower in price but very similar in performance compared with the high sunflower oil. Major additive was Ester sulphonate that acted as a corrosion inhibitor with additional emulsifying properties. Oleic fatty acid in small quantity was added as a lubricity improver. Ammonium soaps were used as emulsifiers. [9]

Sivasankaran *et al* (1988) examined the suitability of unmodified Jojoba oil compared with conventional formulations and also some blends based on jojoba oil, in two-stroke gasoline engine lubricating oil formulations in detail. The results showed that viscosity falls within SAE 20 range Jojoba oil was seen to have a better anti wear property than even Neutral 300 which is often used as a base stock in two stroke lubricant formulation. Piston tightening test and wear deposit forming tendencies were also assessed in short duration engine test.

The Fuels and Lubricants Technology team of the Army Tank-Automotive Research, Development and Engineering Center (TARDEC) is developing two parallel programs: (i) hydraulic fluid recycling, & (ii) development of environmentally safe hydraulic fluids and greases. [6]

Lee (2002) reported that around 40 years ago London bus and other vehicle companies were using castor oil based liquids in their rear axles thereby obtaining major advantage in consumption of fuel owing to the excellently low coefficient of friction. In Germany one major manufacturer has built a new diesel engine line commissioned in 1996 which uses only ester based cutting fluids hydraulic fluids and gear oils. [12]

Johnson (1999) observed the functionality of Canola oil as four-cycle motor oil. Canola oil and its high oleic fatty acid blends were evaluated in bench trials that included Timken test, seizure tests, etc., and small engine trials in automotive applications. The tests resulted in a reduction in the oil and fuel consumption, engine operating temperatures and engine wear. It was also observed that the addition

of a hydroxyl fatty acid source provides a motor oil superior to conventional petroleum oil.

4. SUITABILITY OF CASTOR OIL AS AN ALTERNATIVE LUBRICANT

Castor oil is obtained from the seeds of Castor tree, *Ricinus communis*. The seed has oil content of 50%. The world annual production of castor seed is 460000 Tonnes. The leading producers of castor seed are India, Brazil, China, Russia and Thailand with India producing around 270 thousand tones annually. Castor plant starts yielding beans 3 to 4 months after planting, and the yield is also high, up to 10 tones of beans/ha. It is perennial or annual plant and can be grown in tropical/subtropical regions and even at higher latitudes. Castor oil enquires from most of the



Figure 2 : (A) Castor Seeds

(B) Castor Oil

vegetable oils by having higher viscosity. Specific gravity and hydroxyl value and a greater solubility in alcohol. Also it is more soluble in glacial acetic acid at ordinary temperatures and less soluble in petroleum solvents than other vegetable oils. Among the vegetable oils, castor oil has the most unusual physical and chemical properties. This is because castor oil contains 85% of a hydroxyl unsaturated long chain acid called ricinoleic acid. The oil itself has therefore various uses. Castor seeds contain a toxic material resin, which makes the residue from the extraction of the oil unsuitable for feeding purposes. Besides the resin, the seed contains allergens. The AOCS standards for castor oil are given in Table 1.

Table 1
APCS Standard for Castor Oil

Specific gravity, 15 ^o /15 ^o C	0.9580.968
Refractive index at 25 ^o /25 ^o C	0.9450.965
Refractive index at 25 ^o C	1.4731.477
Saponification value	176-187
Iodine value, wj's	81-91
R-M value	Below 0.5
Acetyl value	144-150
Hydroxyl value	161-169
Unsaponifiables (%)	Below 1.0

Castor oil is dextrorotatory due to the asymmetric carbon atom in ricinoleic acid. Castor oil mixes in any proportion with absolute alcohol & will dissolve in about two volumes of 90% alcohol at 15^oC. On the other hand, it is so nearly insoluble in excess of petroleum ether that as little as 0.5% causes turbidity in the solvent at 15^oC. The flash point (229^oC.) and fire point (449^oC) of castor oil are also high that prevent in the combustion chamber.

5. CONCLUSION

Owing to growing concern on the environment, vegetable oils are finding their way into lubricants for industrial and transportation applications. They have the attractions of being natural, renewable, non-toxic, non-polluting and cheaper than synthetics, and provide scope for rural employment. In general, synthetic lubricants cost four to eight times higher than the mineral oil based lubricants. Vegetable oil-based lubricants are 50% cheaper than synthetic oils. Nevertheless, they are plentiful in supply and can be used as biodegradable lubricant base stocks. The properties of castor oil are quite encouraging to use them as lubricants for high/low temperature and high-speed applications after suitable modification through additivisation. Despite their enormous potential to be cost and performance competitive to mineral-based fluids, research and development in these biofluids are needed to overcome their innerent shortcomings such as oxidative and thermal stability.

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