

# VEGETABLE OILS :POTENTIAL BIODEGRADABLE CANDIDATES FOR VARIOUS LUBRICATION REQUIREMENTS – A REVIEW

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## ABSTRACT

A review is made here to understand the application of vegetable oils as potential candidates for various lubrication requirements. The study highlights the contributions from more than twenty authors on vegetable based oils as emerging environment friendly lubricants and focuses on the various properties of vegetable oils that affects lubrication. Thus the work tries to address the future socio economic challenges of the world in general and our country in particular because of depleting mineral oil resources.

**KEYWORDS:** Vegetable oils, Biodegradable, Lubrication, Tribology, Oxidation

## 1. INTRODUCTION

Global warming and generally speaking the fight against pollution lead to an industry evolution of biodegradable lubricants. The new trend in industry is to develop lubricants that are as effective as mineral oil lubricants and environment friendly to

respect restrictions. For example, in automobile industry all over the world regulations are being made more and more severe as shown in table below concerning NO<sub>x</sub>, CO and particles emissions.

Table 1: Evolution of european regulations for vehicle diesel engine (mg/km) [1]

Norms	EURO 1 1992	EURO 2 1996	EURO 3 2000	EURO 4 2005	EURO 5 2009	EURO 6 2014
Nitrogen oxide (NO <sub>x</sub> )	-	-	500	250	180	80
Carbon monoxide(CO)	2720	1000	640	500	500	500
Hydrocarbom (HC)			-	-	-	-
HC + NO <sub>x</sub>	970	900	560	300	230	170
Particles	140	100	50	25	5	5

According to the U S National Oceanic and Atmospheric Administration (NOAA), 700 million gallons of petroleum lubricants is released into the ocean each year. Over half of that, 360 million gallons, is because of irresponsible maintenance practices as well

as routine leaks and spills. It puts the user under pressure of fines, cleanup costs and downtime. Hence all over the industry there is a positive trend for developing biodegradable lubricants [2]. Interactive European Network for Industrial Crops & their applications assessed that over 90% of all lubricants could be replaced by bio lubricants [3]. The current major areas of applications where biodegradable lubricants have been put to real use are as follows

Table 2: Current major areas of applications of biodegradable oils [4]

Applied area	Potential candidate	Region
Boating two stroke lubricants	Rice bran oil and karanja oil	Western Europe and US
Forestry and chain saw lubricants	Rapseed and sunflower oils	Europe, US, Canada and Australia
Concrete mould release fluids	Synthetic oil	Germany
Hydraulic system oils	Sunflower oil	European union, US and Japan
Manufacturing industries	Synthetic oil	Germany

Bio lubricants can be mainly classified into two on the basis of the base fluid selected for lubricant preparation, they are

1. Vegetable oil based bio lubricant

2.Synthetic oil based bio lubricant(polyalphaolefins,polyglycols,synthetic esters)

Even though synthetic oils are much effective, their cost is prohibitively higher. They are six times costlier than vegetable oils. Also vegetable oils are renewable and non toxic resources. It is in this context vegetable oil gains importance as bio lubricant [5]. Research work on the field of vegetable oil based lubricants has been going on over the past two decades. Significantly, more work has been done in hydraulic and tractor transmission fluids as well as total loss lubricants, that is, lubricants that are consumed through their use. Although some work has been done with engine oils to date, the Chemical Manufacturers Association (CMA) or International Lubricant Standardization and Approval Committee (ILSAC) has certified no vegetable-based engine oil [2]. It is mainly because engine oils work at extremely high operating temperatures that are not suitable for raw vegetable oils. So to use them as engine oil as

well as under other extreme conditions certain modifications are necessary for vegetable oils [2]. Some of them are additive addition, chemical modification and genetic modification of oil plants. Among these the most successful till now is chemical modification [4,16]. But the costs are very high as lubricants are prepared from commercially available fatty acids which are very costly [5].

Additive addition promises to be a better alternative. Additives had provided a major contribution in extending the useful life of mineral oil lubricants. It is the discovery of Zinc dialkyldithiophosphate (ZDDP) as a multifunctional additive (anti oxidant, anti wear, anti corrosion) that revolutionized the petroleum lubricant industry. The present day petrochemical lubricants are outcomes after six decades of extensive research.

Early generation vegetable based lubricant formulators utilized performance chemistry similar to those used in petroleum-based fluids creating lubricant products that did not meet industrial performance requirements. This approach was not effective as the characteristics of vegetable oils are vastly different than those of petroleum oils. The table below shows typical characteristics of vegetable oils as compared with petroleum and synthetic oils [2]

Table 3: Characteristics of various base oils [2]

Characteristics	Petroleum oil	Vegetable oil	Saturated ester	PAO
Lubricity	Low	High	high	low
Oxidative stability RPVOT	300	50	180	300
Viscosity index	100	200	165	150
Hydrolytic stability	High	High	low	High
polarity	Low polar	Highly polar	polar	Low
saturation	Saturated	Unsaturated	saturated	Saturated
Flash point	200	450	400	350
Pour point	-35	-15	-40	-50

To make high-performance fluids from vegetable oils, a clean sheet approach must be utilized, and the fluid must be designed with the specific characteristics of the base fluids and the specific requirements of the end products [2].

The challenge before us is to improve the characteristics of vegetable oil without compromising its excellent tribological and environmentally relevant properties. Properties to be controlled are

1. Oxidational Stability
2. Wear and Frictional properties
3. Poor cold flow properties
4. Poor thermal stability
5. Hydrolytic Stability
6. Compatibility with materials and seals
7. Viscosity range limitations
8. Corrosive properties

## 2. VEGETABLE OIL

Vegetable oils are semisolid or liquid plant products. The triglyceride structure shown in figure 1 forms the backbone of most vegetable oils and these are associated with different fatty acid chains.

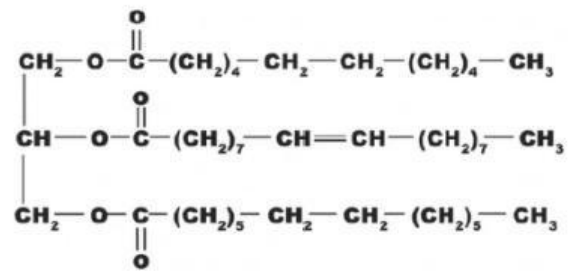


Figure 1: schematic representation of triglyceride structure

Triglycerols composed of three fatty acid chains joined by glycerol center. Fatty acids in vegetable oil triglycerides contain 12-22 carbon atoms and have varying levels of unsaturation. It is therefore a complex association of different fatty acid molecules attached to a single glycerol structure that constitutes vegetable oil matrix. The alcohol component (Glycerol) is the same in all vegetable oils. The fatty acid components are plant specific and therefore the chemical nature of vegetable oils is variable. The variability in the fatty acid proportion depends upon the type of plant, the region, and the climate. Hence it is mainly the fatty acid constitution of the triglyceride structure that determines the properties of vegetable oil. The properties that are desirable and undesirable due to triglyceride structure of vegetable oil are listed in the table below [4]

Table 4: Properties of vegetable oil

Desirable properties	Undesirable properties
1.High lubricity 2.Lower volatility 3.Higher viscosity index 4.Lower toxicity 5.Higher detergent action 6.Rapid biodegradation 7.Good boundary friction lubricity 8.General wear protection	1.Reduced oxidation stability due to unsaturation 2.Susceptability to hydrolysis 3.Poor low temperature properties 4.Narrow range of viscosities are available

## 2.1 Tribological Properties

It is known that lubricity of vegetable oil is attributed to their ability to adsorb onto the metallic surfaces and to form a firm monolayer, with polar head adsorbing to the metallic surfaces and carbon chains orienting itself in perpendicular directions to the surface. Mineral oil with same viscosity of vegetable oil is not so effective as later since it does not possess the lubricity nature of vegetable oils [5]. The antiwear characteristics of vegetable oils depend on three phenomena namely physical adsorption, chemical adsorption and chemical reactions on substrate [6].

The adsorption mechanisms and surface chemical reactions result from the interaction of the polar group (-COOH) of the constituent fatty acids of the respective vegetable oils with the metallic surface resulting in a surface film believed to inhibit metal to metal contact. Strength of adsorption of lubricants on metallic surfaces depend on the nature of adsorption viz. physical adsorption and chemical adsorption which in turn depend on the electrostatic attraction of the polar head of the vegetable oil molecules and the metal atoms and the electron sharing between vegetable oil molecules and metal atoms [7].

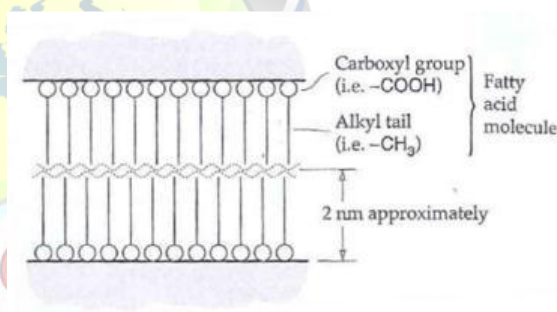


Figure 1: Adsorbed polar molecules on metallic surfaces [2]

The first possible adsorption mechanism is physisorption. Physisorption occurs when binding interactions are less than 40 kJ/mol. No specific chemical function are needed for physisorption. So all the lubricants have some potential to form such boundary films. Physical adsorption involves intermolecular forces like vander Waals or hydrogen bonds [1].

The second possible adsorption mechanism is chemisorption. With chemisorption, the binding energy is much higher than for physisorption as the binding interactions are more than 40 kJ/mol. Chemical adsorption involves that valence electrons are shared by both the molecule and the substrate. The chemisorption can be symmetric (through the two oxygens) or asymmetric (through one oxygen)



when the hydrogen is not dissociated from the hydroxyl group [1].

The most effective is the one that can combine a chemical reaction with the surface and cohesive interactions between the alkyl chains to maintain the monolayer. In the case of multilayers films, the first film is chemisorbed and then other films are physisorbed. Physisorbed layers are less durable than chemisorbed layers. Once film is formed the van der Waals forces cause molecules to align themselves parallel to each other. Repulsion between contacting alkyl groups ensures that the shear strength of the layer formed will be low [7]. Also at high temperatures formation of iron soaps of fatty acids due to surface chemical reactions occurs. It influences the tribological behavior of vegetable oils. These metallic soaps are having low shear strength offering low resistance to shear and hence account for the observed low Coefficient Of Friction [8,9,10]. The main problem while dealing with vegetable oil is their instability in performance under high temperature environments. There is a critical temperature for fatty acids after which desorption of fatty acids occurs. Also iron soaps are formed at soaps are formed at high temperatures. Their continuous formation and removal due to sliding action result in high wear rate at high temperatures [1].

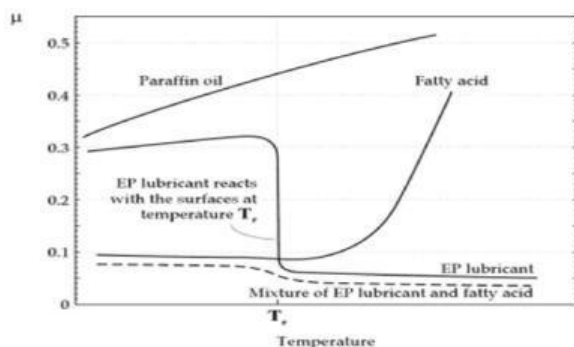


Figure 2: Effect of temperature on the friction coefficient of different lubricant: extreme pressure lubricant, fatty acid, mixture of ep lubricant and fatty acid, paraffin oil [1]

### 2.1.2 Effect of Unsaturation, Chain length on Tribological properties

Wear test results shows a decreasing trend in coefficient of friction and wear scar diameter with increasing carbon chain length [7]. Lateral cohesive

force increases as the chain length increases. It results in close molecular packing [6]

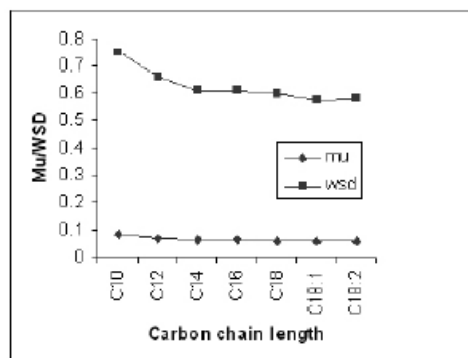


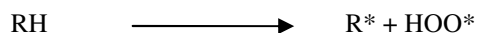
Figure 3: Coefficient of friction and wear scar diameter vs. carbon chain length of fatty acids [7]

Since saturated fatty acids have no double bonds, they can align in a straight chain, which is closely packed on the surface providing a strong protective layer. However unsaturated fatty acids, which have at least one double bond, prevent rotation around that point, making them no longer able to form a straight chain. This results in a weaker protective layer which causes higher wear in unsaturated oils [8,9].

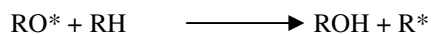
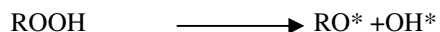
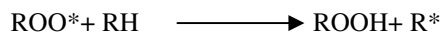
### 2.2 Thermal & Oxidational stability

Vegetable oils are sensitive to temperature and will undergo oxidation rapidly. Lipid oxidation is a slow process at room temperature, but the rate of reaction increases exponentially with absolute temperature [9]. Majority of vegetable oils breakdown rapidly at temperature range 120–150°C. It causes significant effect on shelf life and product quality [8]. Oxidative degradation starts at lower temperature than thermal degradation [11]. It is limited by unsaturated bonds. They are active sites for many reactions. As the number of unsaturated bonds increases, the susceptibility to oxidation increases. It is found that vegetable oils containing increased % of monounsaturated fatty acids autooxidise at increased temperature, whereas polyunsaturated fatty acids autooxidise at room temperature itself [10]. Degradation of triglyceride fatty acids also causes increased level of wear [8,9]. The auto-oxidation mechanism essentially a free radical chain reaction consists of the following distinct reaction steps [10]

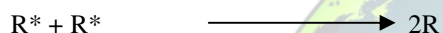
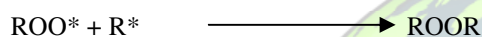
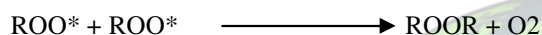
### Initiation



### Branching and Propagation



### Termination



Oxidation process is initiated by the formation of free radicals which react with oxygen to form a peroxy radical as an intermediate product. This peroxy radical then attacks another lipid molecule to form a hydroperoxide and another free radical, thus propagating the oxidation process. Hydroperoxides continue to build up in the oil which decompose into secondary compounds like epoxides and polymeric compounds. Oxidation products of vegetable oils can be classified as

#### 1. Primary

Important compounds formed are hydroperoxides. Increased amount of hydroperoxide causes increased level of wear. All secondary oxidation products are derived from hydroperoxide decomposition

#### 2. Secondary

It can be classified into two

##### A. Volatiles

Compounds responsible for rancid flavours and odours of oxidized vegetable oil. Mainly it consists of short chained hydrocarbons and alcohols. Due to the low polarity and short chain nature these causes little impact on lubrication

##### B. Non Volatiles

Vast range of non volatiles are there in oxidized vegetable oils. Due to their short life time it is

impossible to determine the impact of all non volatile compounds on lubrication. While the long lived epoxide affects lubrication. Epoxidized vegetable oil possess

1. High viscosity
2. Increased oxidation stability
3. Decreased deposit forming tendencies
4. High molecular weight components

It is produced during the final stage of oxidation process. It occurs at increased temperature and pressure, considering lubrication it is an undesirable aspect as the properties of a standard lubricant should not change with time. It does not necessarily lead to failure of lubricant mechanism

### C. Free fatty acids

Free fatty acids improve boundary lubrication properties. Studies shows that fatty acids are effective in improving boundary lubrication properties of vegetable oils. In mineral oil based lubricants fatty acids are used as boundary lubrication improvers. But it decreases oxidation stability. Amount of free fatty acids formed was higher for highly unsaturated oil. As temperature increases, free fatty acids percentage also increases shows the effect of temperature on oxidation [10].

#### 2.3 Cold flow properties

Petroleum based fluids functions satisfactorily even at  $-25^{\circ}\text{C}$ . But studies reveal that vegetable oils shows

1. Cloudiness
2. Precipitation
3. Poor flow ability
4. Poor pump ability
5. Solidification

at temperatures much higher than that required for standard lubricants [12]. For example coconut oil possess pour point of about  $20^{\circ}\text{C}$  only [14].

Low temperature behavior of triglycerol's relates first of all to their crystallization kinetics. Lack of fundamental knowledge on crystallization of mixed acid triglycerol's does not permit more accurate prediction of the pour point [12]. From studies it has been found that increased molecular weight and full

saturation of fatty acids causes increase in pour point. Unsaturated vegetable oils do not allow individual molecules to come close for easy stacking due to break in symmetry of molecules. This results in the formation of microcrystalline structures rather than macro crystalline structures. At lower temperatures these microcrystalline structures can easily tumble over one another resulting in better fluidity whereas in saturated oils the easy close packing of molecules results in macrostructures which reduces the fluidity at low temperatures [13].

Pour point of saturated vegetable oil can be brought down by introducing branched chain or aromatic hydrocarbon molecules to prevent close packing of molecules during cooling. Low temperature properties of oil can be modified by attaching long chain molecules at the double bond sites by suitably designed chemical processes [11].

## 2.4 Hydrolytic Stability

Vegetable oils are highly susceptible to hydrolysis in the presence of water to produce corrosive acidic breakdown products as compared to mineral-based oils. The carboxylic acids formed by hydrolysis may corrode metal bearings, affect seals and shorten life. Major factor that causes inferior hydrolytic stability is the unsaturation sites in vegetable oils. Reactions at double bonds decrease hydrolytic stability [4].

## 2.5 Viscosity Index

Viscosity index of vegetable oils are much higher than that of mineral oils. High linearity of the oils permits the triglycerides to maintain stronger intermolecular interactions with increasing temperature than branched hydrocarbons or esters. This ensures the high viscosity index of vegetable oils.

Vegetable oils have narrow range of viscosity. The similarity in structure makes most of the vegetable oils exist in only a narrow range of viscosities limiting their applications as lubricants [14].

## 2.6 Other Properties at a glance

### a. Low volatility

Lubricant should possess low volatility under operating conditions. Viscosity gives an indication about volatility. Lower the viscosity higher is the volatility. The high molecular weight of the triglycerol molecule and the narrow range of viscosity change with temperature ensures the low volatile nature of vegetable oils.

### b. Low emission of CO and Hydrocarbons:

Vegetable oil-based lubricants are more effective in reducing the emission level of carbon monoxide and hydrocarbons [22].

### c. Better fire resistance:

The higher flash and fire points of vegetable oils than mineral-based oils indicate their better fire resistance.

### d. Biodegradability:

Vegetable oils are readily and completely biodegradable into carbon dioxide and water molecules [17,18,19].

### e. Toxicity:

Vegetable oils composed of fatty acids are generally non toxic to aquatic and terrestrial environments [17,18,19].

### f. Renewability:

The sources of vegetable oil are crops and they promote self-reliance as ample production capacity exists but the source of mineral oil is a finite mineral deposit. The use of renewable resources not only enables efficient carbon cycling but also reduces CO<sub>2</sub> emissions [22].

## CONCLUSION

From the above review, it is clear about the characteristics of fatty acids that determine the various properties of vegetable oil as an effective lubricant. The unsaturated and branched structure of fatty acids are superior from cold flow point of view. But this diversified structure limits close packing which affects the wear preventing characteristics as well as thermal and oxidative stability. So with vegetable oils alone we could not develop lubricants required for modern day applications. So effective discussions need to be carried out on the modifications required and how it could be accomplished keeping the costs limited. This points to the need of extensive research which must be conducive to develop additives that are compatible with vegetable oils as well as non toxic in nature. If such additives like ZDDP, which revolutionized the petrochemical industry are developed for vegetable oil; then it is sure that they are the potential candidates for future lubrication requirements.



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