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Rheological review on potential of bio-lubricants

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Abstract
The rapid industrialization and population boom (especially in developing countries) has put the non-renewable resources of the world under tremendous pressure. Every country now-a-days are trying to reduce the exchequer on import oil bills. Alternate fuels like biodiesel, bioethanol and biomass are being continuously researched so that their application can be broadened to other fields like lubricants. Since the bio based lubricants are being produced from raw vegetable oils, they possess lower hydrolytic stability, low viscous properties and also low thermos oxidation stability. However, these shortcomings can be addressed by incorporating additives into lubricant world can be greatly increased. This review provides a detailed treatment on bio-lubricants their physicochemical properties, the various additives used to improve the properties of bio-lubricants. This paper provides a detailed insight to researchers and practioners in the field of tribology

Keywords: Industrialization, vegetable oil, lubricants, biodiesel

Introduction

Fossil fuels have played a very important role in th industrialization. The ever increase consumption of these nonrenewable resources has started to impact our lives [1]. According to Owen *et al*. [2]. The demand for resources will be more than supply by 2015. Critical needs has araised over a period of time to explore alternate sources of energy.

The use of vegetable oils for fuel and lubrication purpose has been in practice from many decades now. Bio-based lubricants have been synthesized and commercialized by many companies [3]. Bio-based lubricants are derived from edible and non-edible vegetable oils and possess better thermos-tribological properties. While some shortcomings are there which are addressed by incorporation of special chemical additives for specific usage environment. Recent reviews have shed great light on physiochemical properties and additives and there interrelationship with tribological properties of oils [4-8].

This paper gives a detailed description about various vegetable oils used produced bio-lubricants and there physicochemical properties, while giving special emphasis on the properties of bio lubricants in comparison to conventional oil based products. This review also deals with the additives added to bio lubricants to enhance their properties and performance.

Types of vegetable oil used for production of Bio-lubricants

Bio based lubricants should be made from waste crops [9] because it can create demand supply problems as far as edible oils are concerned but considering the constraint of fertile land available for cultivation is limited therefore some land should be earmarked for bio oil production by the government and farmers should be given free seeds and subsidies for its production.

Some vegetable oils produced for bio lubricants are as

1. **Sunflower oil:** This oil is extracted from sun flower seed which is primarily used for cooking. This oil is much cheaper as compared to olive oil [11]. Sunflower varieties vary in there fatty acid content [12]. High oleic sunflower oil has many qualities that render it suitable for lubricants such as good oxidation stability and lubricity [13, 14]. High oleic sunflower oil is used as substitute for mineral oil in textile and tannery applications without technical problem or modification. Sunflower is excellent alternate to lubricant used for chain saw.
2. **Rapeseed oil:** It contains free fatty acids, phosphatides (gum), enzymes (myrosinase) and glucosinolate [15]. Due to its bitter taste due to presence of glucosinolates [16]. This can be used as a potential oil for bio based lubricants with incorporation of appropriate additives.

3. **Soya bean oil:** It is widely cultivated edible oil, it is widely gaining application for di electric liquid for transformers [17, 18]. Soya bean oil was used in hydraulic lift for statue of liberty in new York [19]
4. **Palm oil:** One hectare of oil palm is sufficient to produce 10 times as much oil compared to other vegetable oil [20] due to high production per hectare it becomes a potential candidate for large scale production. extensive experiments have been carried out in engine for palm oil being used as lubricant [21,22] it has been also tested for production process like cold forward extrusion [23] and minimum quality lubrication (MQL) [24].
5. **Coconut oil:** Coconut oil has high quality of saturated fatty acids (91%) and hence doesn't oxidize easily. Coconut oil is widely being used a traditional lubricant for rickshaw and some two wheelers in some parts of coastal India. It is also used as fuel owing to its less smoke emission property [25].
6. **Jatropha oil:** It has high fatty acid content (61-63%) [28]. commonly used for biodiesel [26, 27] but less research has been revived in literature for its usage as lubricant. Hence posing to future research in the times to come.
7. **Castor oil:** Castor oil has better low temperature viscosity and high temperature stability compared to other oils owing to these it can be used bearing lubrication at high temperature and speed. Only limitation of this oil is its limited solubility in aliphatic petroleum solvent.

Chemical modification of vegetable oil

To improve the low temperature properties and oxidation stability of vegetable oils following chemical processes are undertaken

1. **Transesterification:** It is a reaction whereby triglycerides molecules react with three moles of methanol in presence of an acid or base catalyst [123, 124] resulting in glycerol and mixture of fatty acid methyl esters. It was found by padmaya *et al.* [136] that PE have grater thermal stability followed by TMP and NPG esterrstransesterification of trimetylopropane and methyl esters from vegetable source [29-33].

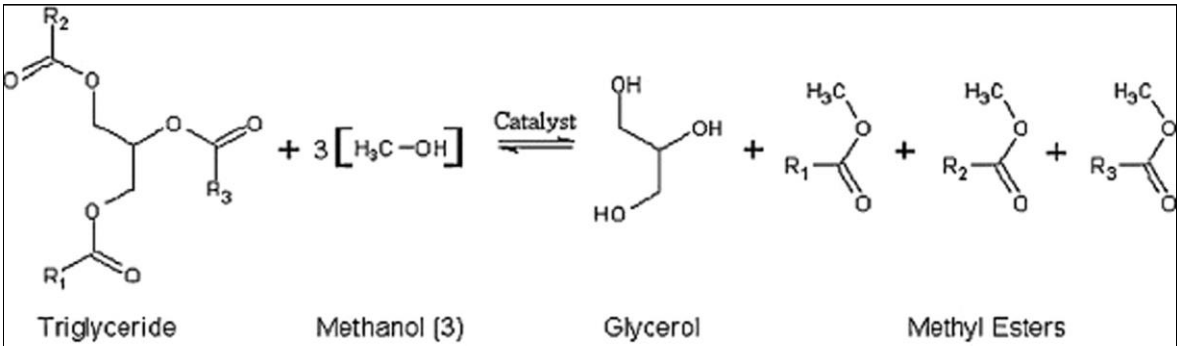

Fig 1: Chemical reaction of the transesterification process [5]

2. **Hydrogenation:** it is a process in which hydrogen is added to c=c bond in triglycerides o an oil molecule [34]. The hydrogenation process of vegetable oil involves three simultaneous chemical reaction 1. Saturation of double bond 2. Geometric cis Trans isomerization. 3. Positional isomerization.
   The unsaturated fatty acids were transferred into a single unsaturated fatty acid without increasing the saturated component of substance. Several studies have been carried out to determine the increase in percentage of hydrogenation of multiple unsaturated fatty acids through heterogeneous and homogenous catalytic system [35-39].
3. **Epoxidation:** Epoxidases vegetable oils are produced by reaction of double bonds by proxy acids [40] and removal of c=c bond. Alkene is reacted with proxy acid in order to synthesize epoxide group o oxirane rings, [wu *et al.*, 45], epoxisised rapeseed oil using conventional expoxidation method, whereby carboxylic acid is reacted with hydrogen peroxide. The epoxidised rape seed oil has better friction reducing characteristic and extreme pressure capability compared to rape seed oil.

Additives used in bio-based lubricants to improve their properties: limitations of vegetable oil such as poor thermos oxidative stability and cold flow behavior may be enhanced by use of additives. Additives are up to 5% (by weight) for some oils. The presence of additives help improve the properties of lubricants and bio based lubricants in terms of corrosion inhibition as well as friction and wear characteristics. In general, esters with bio degradable additives are more superior to pure oils [42]

Table 1: showing properties of various oils

Vegetable Oil	Viscosity at 40 °C (mm^2/s)	Density (×10 kg/m^3)	Flash Point (°C)	Pour Point (°C)	Viscosity index
Sunflower oil	31.3	0.920	315	−12.0	-
Rapeseed oil	34.8	0.917	323	-15.0	218
Palm oil	39.6	0.918	267	-	-
Jatropha oil	35.4	0.918	186	-	-
Soybean oil	29.0	0.913	328	−10.0	246
Coconut oil	28.1	0.920	-	-	-

Nano particle additives

Nano particle additives are better as compared to conventional extreme pressure and anti-wear additives due to their environmental properties [43].

The effect of Ti O_2 [92], Cu O [186-188] and ZnO [43] Nano particles on properties of bio based lubricants have been investigated.

The zinc borate ultra-fine powder (2 ZnO. $3B_2$ O_3. 3.5 H_2 O) show outstanding friction reduction and anti-wear properties when used as additives with sunflower oil. However, both Zn O and Cu O do not show good anti-wear properties when used with epoxidase sunflower oil and soya bean oil [43].

Corrosion inhibitor additives

Corrosion inhibitors are additives that help protect metal from oxygen, water, acid, base and salt attack.

Borated and non-borated carboxylates are good corrosion inhibitors, particularly in presence of borate. N- Acyl-N-hydrocarbon oxy alkyl aspartic acid ester is found to be suitable for both mineral and non-mineral oils (including vegetable oil). Hence it is suitable for lubricant additive.

Pour point depressant additives

PPD are developed to overcome the formation of large crystals during solidification and ensure oil flow at low temperature. Pouring point of lubricant decreases with increase in chain length of ester branching. It has been seen that ester branching group with a chain length of at least six carbon are the most affective to impose the desired molecular spacing, resulting in most desirable pour point properties.

Extreme wear and extreme pressure additives

Friction and wear can be reduced by addition of anti-wear and extreme pressure additives into lubricant. EP and EW additives contain chlorine, phosphorous and Sulphur [44]. These protect the metal surface with layers of sulphides, chlorine or phosphide. Environment concern limit there usage. Di butyl phosphite is also used as EP and EW additive.

Discussion

The usage of bio-lubricants is determined by their physiochemical composition and hence the literature review provides adequate information regarding their usage and limitations at different operating conditions. Chemical additives are being further investigated.

Conclusion

This review provides a detailed over view of various vegetable oils, chemical additives tribological properties needed for wide scale usage as bio lubricants. The properties of bio lubricants can be further improved by addition of anti-oxidants, Nano particles, corrosion inhibitors, extreme pressure and extreme wear additives. Significant improvement has been obtained to bio lubricants making them promising alternates to conventional petroleum lubricants. One should expect that the bio- lubricants are available on a commercial scale within next few years.it will certainly ease off the heavy burden on fossil fuels, additives added should be environment friendly and there disposal shall be thoroughly investigated for carcinogenic and other harmful effects on biotic life. This would also help in forcing governments to convert waste lands into cultivable ones so that they could produce oils to help in national growth and also reducing carbon foot prints of economies to a great level. In brief bio lubricants can help from economics to environment, hence special attention should be given to their development and commercialization.

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