



Recent development on biodegradable nanolubricant: A review



Sathuramalingam Pillay Darminesh^a, Nor Azwadi Che Sidik^{a,b,*}, G. Najafi^c, Rizalman Mamat^d,
Tan Lit Ken^b, Yutaka Asako^b

^a Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81300, Johor, Malaysia

^b Malaysia – Japan International Institute of Technology (MJIT), University Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra (Jalan Semarak), 54100 Kuala Lumpur, Malaysia

^c Tarbiat Modares University, Tehran, Iran

^d Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Malaysia

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ABSTRACT

Naturally, biodegradable oil has better viscosity index, pour point, flash point, good tribology properties and its environmental friendly. Even though biodegradable lubricant is one of the best choice for lubrication purposes, however the properties are slightly lesser than mineral oil. A common solution for this problem is to provide effective additives into the base stock of biodegradable oil which leads to significant improvement to the lubricant by enhancing thermal properties, tribological properties and anti-oxidation capability. Nanoparticles are a type of effective additives which provides promising approach to enhance the biodegradable lubricant's properties. In this article, we reviewed the current progress and recently published data related to biodegradable lubricant, nanoparticles and its improvement on the biodegradable lubricant properties.

1. Introduction

In recent days, environmental health aspects and increase in pollution have become each and every nation issue to provide better sustainable development for the public. In equipment lubrication sector, the main concern is the loss of lubricants into the environment. Soil and water is directly affected by lubricant system failure whereas the air is polluted by volatile lubricants. Due to increase in environmental awareness, it has become driving force for technology improvement on lubrication. Thus, implementation of biodegradable lubricants has extensively used in environmental sensitive areas [1,2]. Many researchers have also stressed the need of biodegradable lubricants to replace the conventional mineral oils lubricants [3–5]. Other than non-toxic characteristic of biodegradable oils, they have very low volatility due to high molecular weight of triglyceride molecule. However, the biggest challenge of development of biodegradable base stock as new generation lubricant is the capability to perform better properties than mineral oils. Among the main disadvantages of bio lubricants are poor oxidative stability, high pour point and high coefficient of friction at elevated temperature [6–8].

In early days, vegetable oils have been used extensively as lubricant in machinery and transportation vehicles until the discovery of petroleum. Since the petroleum exhibits better performance and cheap in cost, it has taken over the lubrication sector. Recently, the legal issue

and fluctuation price of crude petroleum oil has provided better scope for vegetable oil as lubrication. Due to this, it can increase markets for uncommon seeds and its oil which could increase farmer incomes and maximize application of agriculture products [9]. The vegetable oil based lubricants have its own merits and demerits. It has all the qualification as lubricants with its outstanding physical properties but poor thermo-oxidation property which has caused restriction for vegetable oil as lubricant at elevated temperatures [10].

Most of the research for the vegetable oil lubricant has been conducted to improve the thermo-oxidation property to ensure equivalent properties compared to petroleum based lubricant, for example, research on rapeseed oil [11,12], coconut oil [13,14], jojoba oil [15], Pongamia oil [16], soybean oil [17,18] and sunflower oil [19].

In recent decade, there has been attention for the use of nanoparticles in many types of base fluid [20–23]. For example, dispersion of nanoparticles in water could enhance the thermal conductivity and proven as an excellent heat transfer fluid, especially for solar collector application [21,24]. Nanocoolant, dispersion of nanomaterials in traditional coolant (water/ethylene glycol, etc), has been considered in real applications since early 2000s. Peyghambarzadeh et al. [25] used Al₂O₃–water nanofluids in car radiator to determine the tube side heat transfer coefficient. The heat transfer enhancement was found to be 45% higher compared to pure water for turbulent flow condition. In another study, Lee [26] numerically investigated the heat transfer in a

* Corresponding author at: Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81300 Johor, Malaysia.
E-mail address: azwadi@mail.fkm.utm.my (N.A.C. Sidik).

domestic water heat exchanger using water-based nanofluids. Copper (Cu) nanoparticles and alumina (Al_2O_3) nanoparticles were considered at volume fraction ranges 0.5–3.0%. She reported that the efficiency of domestic water heat exchanger system was optimum when 1.5% copper or alumina nanoparticles was added to the base fluid.

The addition of nanoparticles in lubricant is expected to exhibit anti-wear and anti-friction properties on nanolubricant. However, improved properties fully dependent on nanoparticle characteristics such as shape, size and concentration. It also has been stated that major improvement on anti-wear and anti-friction due to appropriate amount of nanoparticles added into the lubrication oil [27].

Though, the main challenge is to formulate stable suspension based nanoparticles because sediments and agglomerates will form due to less stable suspension over long period of lubricant in stationary condition [20,28–31]. Thus, compatibility of nanoparticles and base oil is an important factor which must be considered to ensure that effective suspension or nanolubricant has been produced. Other than that, tendency of nanoparticles deposit in the lubricants during operation are also due to large size particles and with presence of humidity and oxygen, the tribological properties of nanolubricant is relatively poor becomes limiting factor in practical application [32]. Various researches have been conducted on addition of nanoparticles with different sizes in range from 2 to 120 nm which act as friction modifier and effectively reduce the wear and friction. All the researches has been conducted using various nanoparticles such as metal, metal oxide, metal sulphide, metal borate, metal carbonate, carbon compound, and SiO_2 . They all agreed that the tribological performance of the nanolubricant dependent on the degree of crystallinity (defect), shape, size and concentration [33–36].

Based on the above brief review, there are a number of researches on the crop oil based, biodegradable lubricants. However, the review on the progress of biodegradable nanolubricants is scarce. Therefore, the goal of this work is to review the current approaches in nanolubrication technology with much details. To the best of authors' knowledge, there is no comprehensive literature on the subject.

2. Vegetable oil as biodegradable lubricant

The vegetable oil has become alternative lubricant base stock in many industries because of their environmental friendly and non-toxic characteristic (see Table 1). The vegetable oil has become good choice as lubricants due to its triacylglycerol structure with long fatty acid chains and presence of polar groups which makes the oil with amphiphilic character. These triacylglycerol structures in vegetable oil have molecules which arrange themselves making a closed packed monomolecular layer which enhanced the surface film and the high

Table 1
Vegetable oil based lubricants developed for industry application [37].

Vegetable Oil	Application
Canola oil	Hydraulic oil, tractor transmission fluids, metal working fluids, food grade lubes, penetrating oils, chain bar lubes
Castor oil	Gear lubricants, greases
Coconut oil	Gas engine oils
Olive oil	Automotive lubricants
Palm oil	Rolling lubricants, grease
Rapeseed oil	Chain saw bar lubricants, air compressor-farm equipment, grease
Safflower oil	Light colour paints, diesel fuel, resins, enamels
Linseed oil	Coating, paints, lacquers, vanishes, stains
Soybean oil	Lubricants, biodiesel fuel, metal casting/working, printing inks, paints, coatings, soaps, shampoos, detergents, pesticides, disinfectants, plasticizers, hydraulic oil
Jjoba oil	Grease, cosmetic industry, lubricant application
Crambe oil	Grease, intermediate chemicals, surfactants
Sunflower oil	Grease, diesel fuel substitutes
Cuphea oil	Cosmetics and motor oil
Tallow oil	Steam cylinder oils, soaps, cosmetics, lubricants, plastics

molecular weight provides low volatility and better viscosity properties.

However, as stated earlier, the nature form of the vegetable oil is not suitable for the industry application because of its poor thermo-oxidation due to the presence of bis-allylic protons. When oil oxidation occurs, oil viscosity and acid content increase, corroding metal parts, generating sludge and as a consequent, reducing the efficiency. In addition, many researchers admitted that most vegetable oils undergo precipitation, cloudiness, solidification and poor flow under severe condition of temperature, pressure and environment [38–41]. The performance limitation of vegetable based lubricant stem from inherent inferior physicochemical properties to those based on mineral oil. A lot of research and development on vegetable oils is being carried out with an aim to prepare a perfect biodegradable lubricant.

Syahrollail et al. [42] have compared the wear scar diameter on the ball bearings lubricated with the 100% palm oil fatty acid (PFAD), 100% commercial hydraulic oil and mixture of PFAD + Hydraulic oil. Since the palm fatty acid distillate carries oxygen bond, it causes the oxidation on the surface of the ball bearing and made the structure brittle with producing the highest wear scar diameter. In a similar study [43], a comparison among commercial stamping oil with *Jatropha* oil, RBD Palm Olein and PFAD also proved that nature condition of vegetable oil reflect greater wear scar diameter on ball tester bearing under extreme pressure compared with commercial lubricant. They insisted that an additive is required to improve the properties of natural condition of vegetable oils as lubricant.

Erhan and Asadauskas [44] experimentally investigated the oxidative stability of two vegetable oils (soybean and sunflower oils). For this purpose, the micro oxidation test has been used to measure the anti-oxidant depletion rates of the oils. The pour point (the lowest temperature at which the oils become semi solid and loses its flow characteristics) was also determined in their study. They found that the vegetable oils have lower oxidative stability and higher pour point than the mineral oil. These limit vegetable oils application as lubricant at low temperature condition.

Jayadas and Nair [13] investigated the potential coconut oil, sesame oil and sunflower oil as lubricant. Although the coconut oil has the highest pour point, their results proved that the pour point of coconut oil can be brought down using suitable additive or by chemical modification processes.

Due to the drawbacks mentioned above, extensive research has been undergone by many researchers on the vegetable oil to improve its properties. Suitable additives have been one the method to enhance the vegetable oil nature properties such as oxidation stability, anti-friction, anti-wear (AW), anti-corrosion and stability against biological degradation. The major issue on the base stock oil carrying additives is that it should be homogenous at all time during operating condition. On current lubrication manufacturing industry, all the final product will have at least 10% of additives. However, the additives application varies depend on the application as per shown in Table 2 [45].

The use of antioxidants to prevent oxidation of Indian origin vegetable oils has been tried by Joseph and Sharma [46]. With a proper proportion of amine to phenol types of antioxidants, maximum stability of vegetable oil was obtained. In 2002, Ruger et al. [47] measured the potential of few antioxidants to delay the viscosity increase of soybean oil. To simulate as close as real operating condition of a crankcase of gasoline engine, the temperature was set up at 105 °C and 10 mg of colloidal metals (copper and iron) were also added to the test oil. They confirmed the previous finding by Pokorny [48] that the TBHQ (tertiary butylhydroquinone) could significantly stabilized the viscosity of soybean. The optimum concentration of antioxidant was determined at 0.01%, which is similar to an amount added in food application.

In another study, Becker and Knorr [49] claimed that Zinc dimethyl dithiocarbamate (ZDDC) could performed as an excellent antioxidant for rapeseed oil. Years later, Sharma et al. [50] demonstrated that the mixture of ZDDC and antimony dialkyldithiocarbamate (ADDC) additives provide the best oxidation stability of soybean oil. Motivated by

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