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Lubricity of bio-based lubricant derived from different chemically modified fatty acid methyl ester

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ABSTRACT

In this research, polyol ester was used as the source of a biolubricant. The trimethylolpropane (TMP) and pentaerythritol ester (PE) were produced from palm oil methyl ester; they are biodegradable and have high lubricity properties. Two different conditions of lubrication were investigated. Under these test conditions, the wear and friction characteristics of different ester samples were measured and compared. The esters derived from PE and TMP had comparable characteristics to the fully formulated lubricant (FFL) in terms of the coefficient of friction (CoF). In terms of the mixed lubrication condition, the PE ester has the lowest CoF.

1. Introduction

In an engine, engine oil plays an important role as a lubricant by lubricating moving parts such as the piston ring and cylinder liner. It also cleans, inhibits corrosion, improves sealing, and acts as a coolant by carrying heat away. Mineral, synthetic, and semi-synthetic engine oils are not directly involved in the ecological cycle with air and soil. However, leakage, human error, and blown pipes may occur, and disposal of engine oil may damage the ecosystem due to its toxicity. Knowledge of and concern over the usage of petroleum-based products have created the opportunity to produce environmentally friendly lubricants form biodegradable feedstock [1].

Natural oils present an attractive substitute to conventional lubricants, especially in environmentally sensitive areas like agriculture, forestry, and mining since they have low toxicity, high biodegradability [2–5], low friction and wear characteristics [6–8], and improve the surface finish [9]. However, natural triglycerides have some drawbacks, including a low flash point, [10–12] and poor thermal stability [10,13]. In general, it has been widely understood that the hydrogen atoms on the β-carbon atom of the alcohol fragment in ester molecule leads to poor oxidative and thermal stability [14]. The presence of hydrogen atoms will cause a corrosion mechanism that produces acid and alkenes and hence increases viscosity and acidity. These problems only can be solved partially by additives [5,12,15,16]. Consequently, vegetable oil has to be chemically modified by transesterification [17,18] or epoxidation of the vegetable oil [5,12] to eliminate vulnerable sites for oxidation and to interrupt the formation of crystals at low temperatures.

It is thought that natural triglycerides may enhance lubricity as they can provide an effective boundary layer due to the presence of a polar structure, which disperses non-polar molecules or the base lubricant and can act as an anti-wear additive and friction modifier for commercial mineral-based lubricating oil [19,20]. Erhan and Sharma [21] found that the addition of 5% chemically-modified soybean oil (CMSO) products caused a ~50% reduction in wear using a hexadecane-based oil. The coefficient of friction obtained for hexadecane (0.095) was reduced to 0.031 upon the addition of CSMO products under these experimental conditions. In another study, Maleque and Masjuki [22] used viscosity test to show that 5% palm oil methyl esters (POME) can improve the viscosity index (VI) of a mineral-based lubricant up to a load of 500 N. However, corrosive wear and the formation of pits on the damaged surface were the dominant modes of wear at higher temperatures. It is believed that corrosive wear occurs in situations where the POME additive reacts with the metal surface at higher temperatures and the reaction products are worn away from the surface, leading to greater wear and friction. In addition, Goodrum and Geller [23] found that castor methyl ester and Lesquerella oil methyl ester also enhanced lubricity to acceptable levels at concentrations below 1%. It is believed that the high concentration of the unique fatty acid methyl ester methyl ricinolate could be responsible for the lubricity-enhancing properties of castor oil methyl ester.

Several studies have found that oxidation stability and thermal stability could be improved by replacing glycerol with an alcohol that does not contain β-hydrogen atoms, such as PE or TMP [24,25].

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Nomenclature

COF	coefficient of friction
EHL	elastrohydrodynamic
EP	extreme pressure
FFL	fully formulated lubricant
ISL	initial seizure load
PE	pentaerythritol esters
POME	palm oil methyl esters
SDL	seizure delay load
TAN	total acid number
TMP	trimethylolpropane
VI	viscosity index
WL	weld load
WSD	wear scar diameter

However, our understanding of the mechanism and tribological properties of TMP and PE ester is still vague. Therefore, this research was conducted in order to improve the understanding of the tribological properties of TMP and PE ester and to develop both TMP and PE ester as a biolubricant. This research will investigate the effects of different sources of esters in different lubrication regimes.

2. Experimental methods

2.1. Lubricant sample preparation

In this investigation, TMP ester and PE ester were compared to paraffin oil and fully formulated lubricant (FFL). Table 1 presents some of their physical properties. The TMP ester and PE ester were synthesized by the transesterification of methyl esters prepared from palm oils (POME) with TMP and PE respectively, as shown in Fig. 1 [25] and Fig. 2 [26]. A 200 g volume of POME and a known amount of TMP and PE was placed in a 500 ml three-neck reactor and constantly agitated using a magnetic stirrer. The weight of TMP and PE was determined based on the required molar ratio and the calculated mean molecular weight of POME. The mixture was then heated to the reaction temperature and the catalyst was added. A vacuum was gradually applied to the system until the desired pressure was reached. This pressure was maintained until the reaction reached completion. Table 2 shows the fatty acid content in the TMP ester.

2.2. Four-ball wear test

A four-ball machine was used to investigate the effect of esters under boundary and extreme pressure conditions. The four-ball wear tester is the predominant wear tester used by the oil industry to study lubricant chemistry. The device consists of three balls held stationary in a ball pot plus a fourth ball held in a rotating spindle, as shown in Fig. 3. The balls used in this study were steel balls, AISI 52-100, 12.7 mm in diameter, with a hardness of 64–66 *R*c. The balls were thoroughly cleaned with toluene before each experiment. The sample volume required for each test was approximately 10 ml.

To determine the anti-wear characteristics, the test conditions were a 392 N load, operation at room temperature, a rotational speed of 1200 rpm, and an operation time of 60 min. The wear produced on the three stationary balls was measured using a calibrated microscope and reported as the wear scar diameter (WSD) or calculated volume.

For the extreme pressure conditions, the test standard was ASTM 2783. In the machine, a vertical driving spindle rotated a chuck with a speed of 1770 rpm. The load was increased by 196 N every 10 s until the ball was welded. Seizure was indicated by a sharp rise in the coefficient of friction. A number of tribological parameters were determined using the standard procedures prescribed by the manufacturer [27]. For the purpose of illustration, a wear–load curve ABCD is shown diagrammatically in Fig. 4. Each test was carried out three times to determine the experimental error. Error measurements specified in this experiment were based on the maximum deviation between three measurements.

2.2.1. Hertz line

The following equation is used to plot the hertz diameter against load which results in linear proportional line as shown in Fig. 4:

$$d_h = 8.73 \times 10^{-2}(P)^{1/3} \quad (1)$$

The diameter of contact area, d_h also called as hertz scar diameter, is the indentation produced by ball deformation and it is calculated by using equation above [28–31] where *P* is the applied load in Newton. The Hertz line increase linearly due to the linearity of the applied load, causing the hertz diameter to increase linearly.

2.2.2. Initial seizure load

The initial seizure load (ISL) is the load at which the wear–load line deviates from the Hertz line [29] and it is denoted as point C in Fig. 4. It indicates the temporary breakdown of the lubrication film [30] and determined by sudden increase of WSD [28].

2.2.3. Weld load

Weld load (WL) is the load at which the lubricant completely fails and at which so much heat is generated that the fusion of metal occurs between the rubbing surfaces. It is detected by the apparent fusion of the rubbing surfaces of the steel balls [32], indicating the lubricant's EP level had been exceeded [30] and it is identified by point D in Fig. 4.

2.2.4. Mean specific pressure

Mean specific pressure (P_m) is the pressure applied at the contact point [29]. The unit is N/mm^2 and it is expressed as equation below where *P* is the applied load in N and *d* is the diameter of contact area in mm.

$$P_m = 52P/d^2 \times 100 \quad (2)$$

2.3. Lubrication regime determination

During testing, the upper ball was lubricated through contact with the lower three balls by a thin film of lubricant. On the basis

Table 1
Major physical properties of different lubricants.

	Specific gravity at 15.6 °C (g/ml)	Viscosity (cSt)		VI	TAN (mgKOH/g)
		40 °°C	100 °C		
Paraffin oil	0.8283	30.61	5.26	110	–
FFL	0.8549	101.86	14.46	146	1.02
TMP	0.9021	40.03	9.50	194	0.44
PE	0.9300	68.40	12.70	183	0.20