Bio-based Lubricants from Modification of RBD Palm Kernel Oil by Trans-Esterification

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ABSTRACT

Bio-based products nowadays has been used as a substitution of non-renewable resources such as for petroleum oil to fulfil the increase in demand and solving environmental issue. Petroleum crude oil has been long utilize for producing lubricants and among several studies made to replace the sources are from palm oil products. Palm oil products are been process to various type of oil such as palm olein, palm fatty acid distillate (PFAD), refined bleached and deodorized (RBD) palm stearin (PS) and RBD palm kernel oil (PKO) where the potential of this products has been tested and proven as a good lubricant resources. However, some of this palm oil products existed in the solid form and need to be modified into liquid form. Commonly, biodiesel used in the combustion engine is engineered from trans-esterification process of used oil, animal fats and vegetables oil. In this study, trans-esterification used to modify the RBD palm kernel oil from solid

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into liquid state with the presence of basic catalyst and alcohol in various parameters such as reaction time, reaction temperature, catalyst percentage and molar ratio between alcohol and RBD PKO. The successful liquefy ester product then proceed to the fourball tribotester machine to test for its lubricity and coefficient of friction (COF). Results shows that by implementing various reaction time of 3, 4.5 and 6 hours, the objectives is achievable with the new liquid modified RBD palm kernel oil can maintain its liquidity form at 0°C temperature. It was also concluded that ester products yield form trans-esterification process shows a good performance in coefficient of friction and wear compare to semi-synthetic oil.

Keywords: *Bio-based lubricants; Trans-Esterification; Catalyst; Wear; Coefficient of friction*

Introduction

Oil has a definition of a hydrocarbon liquid that is greasy to the touch and are not soluble to the water. Most of common commercialised lubricant oil used today are made from the crude petroleum oil resources which demand are increasing globally and subjected to the depletion. Besides, environmental issue of the crude oil are a serious topics discussed among researchers. The conventional lubricant had caused an ecological pollution from its toxicity and high flammability properties [1]. It was observed that 12 million ton of lubricants waste dispose to the environment as stated by Delgado et al. (2010). Following the issue arise, an effort to search for a substitute or alternative of petroleum resources has widely been made through the studies by using vegetables oils such palm oil. The studies and researches conducted are mainly on reducing the wear and friction [3]-[4]. Palm oil has a huge potential as substitute and alternative option to the petroleum oil with the properties of renewable, non-toxic and biodegradable.

Palm oil are been process into many products which widely used in food industry such as cooking oil. Among those palm oil products, there is several products such as palm kernel oil, palm stearin and palm fatty acid distillate which exist in the semi and solid form. This products lately been tested for its potential as a lubricants in many experiments such as pin-on-disk [5], plane extrusion [6]-[8] and fourball tribotester machine [9]-[12]. It was also proven that the level of biodegradability of palm oil products are better compared to petroleum-based lubricants [13]. However, PKO, PS and PFAD tested in their original form of solid lubricants without any modification made with the oil need to be heated till the melting points before undergo any test.

Trans-esterification process usually used to convert animal fat, vegetables oil and fat into biodiesel by adding alcohol with the present of catalyst where researchers aiming to maximize the free fatty acid (FFA) conversion of oil into biodiesel by analysing different parameters of molar ratio, catalyst percentage, reaction time and reaction temperature. This process generally is to convert FFA with alcohol into fatty acid ester and glycerol as shown in the following chemical reaction:

$$R\text{-}COOH + R'\text{-}OH \rightarrow R\text{-}COO\text{-}R' + \text{glycerol}$$

Palm Oil Research Institute of Malaysia had produced the palm oil methyl ester from crude palm oil by transesterification method [14]. In this paper, RBD PKO will undergo trans-esterification process by adding methanol with the presence of Calcium Oxide (CaO) catalyst to liquefy the oil from solid to liquid. With initial slip melting point of 27.5°C for RBD PKO, the trans-esterification process was able to reduce the melting point to 0°C by removing the free fatty acid from oil content and breaks the crystalline structure. The oil that succeeded transferred from solid to liquid form are been analyse for its lubricity and friction force performance using fourball tribotester machine and compared to the commercial engine oil.

Methodology

RBD Palm Kernel Oil used was produced from Keck Seng (M) which existed in a semi solid state at room temperature. The trans-esterification process done was to convert the semi-solid state of RBD Palm Kernel Oil into a well-known lubricant state which is in liquid. Trans-esterification process theoretically been used to removes FFA content in oil as this method widely used in biodiesel production. Free fatty acid content is believed the reason of crystalline structure of RBD Palm Kernel Oil at low temperature.

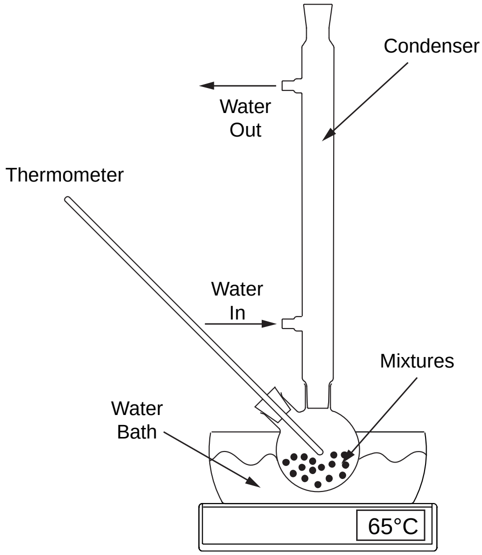

Figure 1: Trans-esterification schematic diagram

In this study, RBD Palm Kernel oil was mixed with methanol in the presence of Calcium Oxide, CaO catalyst for a varied reaction time of 3 hour, 4.5 hour and 6 hour with constant reaction temperature at 65°C. The trans-esterification test setup was illustrated as in Figure 1. After the trans-esterification reaction, the final products are filtered to separate the catalyst from methyl ester and been kept cool in the refrigerators at 0°C to monitor the ester liquid structure sustainability of the modified oil before proceed to Four-ball tribotester machine. CaO catalyst was been calcine in the oven with temperature of 70°C overnight then further process in the furnace for 3 hours at 900°C and kept cool at room temperature. This process was to removes any moistures and impurities in the catalyst. FFA conversion after the trans-esterification process was calculated as in Equation (1).

$$\text{FFA Conversion} = (AV_1 - AV_2) / AV_1 \text{ X } 100\% \qquad (1)$$

Where AV_1 is initial acid value and AV_2 is after trans-esterification acid value.

Four-ball tribotester machine was used in this study to evaluate Anti-Wear (AW) test. Figure 2 shows the schematic diagram of four-ball tribotester main components such as oil cup assembly, collet and ball bearings. The test was conducted using a ball bearing with a diameter of 12.7 mm composed of chrome alloy steel, made from AISI E-52100 with grade 25 extra polished and have a Rockwell C hardness of 64 to 66. One ball bearing is moving rotationally at certain speed is in contact with three stationary ball bearings which immersed in the tested lubricant under a certain load. The experiment was done according to ASTM D 4172. The top bearing rotates against three stationary ball bearings at 40kg of load, speed of 1200 rpm and temperature of 75°C for duration of 60 minutes for each test.

The coefficient of friction value was determined to evaluate the performance of lubricant. This data was generated automatically by four-ball tribotester based on coefficient of friction Equation (2). The coefficient of friction was measured based on the average of frictional force. The coefficient of friction indicates the transmission efficiency of the moving components. Higher in efficiency means less resistance to the moving parts, hence in terms of lubricity, less friction is desirable.

$$\text{Coefficient of friction, COF} = \frac{T\,(\sqrt{6})}{3Wr} \qquad (2)$$

Where T is the coefficient torque in kg/mm, W is the force applied in kg and r is the length between the centres of the contact surface on the lower balls to the rotation axis (3.67 mm).

The lubricant performance was also determined from the mean wear scar diameter. Wear scar diameter was measured from the three pieces fixed balls using charge couple device (CCD) microscope to capture the photomicrograph. Generally, the bigger the wear scar diameter means the more severe the wear.

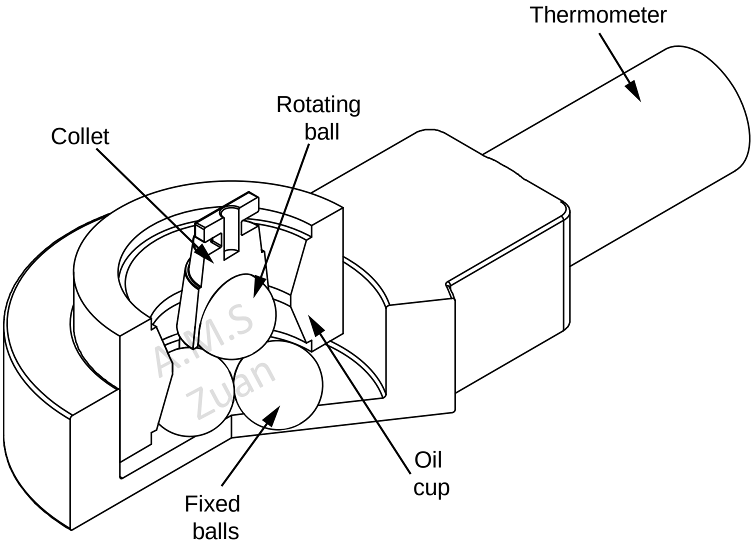

Figure 2: Main parts of the four-ball tester

All modified bio-based oil from trans-esterification which succeed in liquefy are proceed to the fourball tribotester machine to test for its lubricity and COF performance. This test compared the modified bio-based oil with semi-synthetic oil to observe the performance where 10mL of oil are used for each 60 minutes test according to ASTM standards. Three static balls are immersed in the tested lubricant while one balls are rotating at constant speed of 1200rpm with normal load of 40kg been applied upward as shown in Figure 3. The test are repeated three times and data for COF and wear are taken as average value from all static balls.

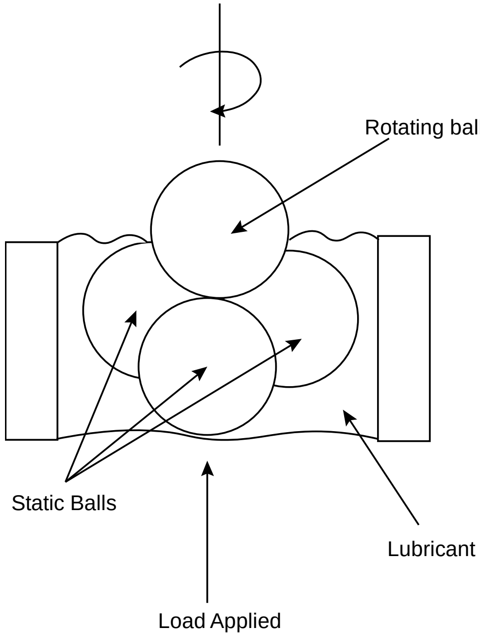

Figure 3: Fourball mechanism

Results and discussion

Trans-esterification Parameters

Several parameters had been study in the trans-esterification process in searching of a combination to liquefy the RBD PKO from solid to liquid state. The parameters studied was molar ratio, percentage of catalyst used, reaction time and reaction temperature as shown in Table 1.

Table 1: Variables of Trans-esterification process parameters

Parameters	Ranges
Molar ratio (methanol:oil)	3 to 12
Catalyst Percentage (wt %)	1 to 6
Reaction Time, (hours)	3 to 6
Reaction Temperature (°C)	40 to 70

From Table 1, molar ratio of oil to methanol used was 3:1, 6:1 and 12:1 with the others parameters remain constant at 4.5 hours, 1.5 wt% of catalyst and 65°C reaction temperature. All molar ratio combination was successfully liquefy the RBD PKO with minimum temperature of 15°C. When molar ratio increases from 3:1 to 12:1, the quantity of final products increases with whitish colour. Yaakob and Bhatia, 2004 study the reaction rate and conversion of palmitic acid to methyl palmitate found that by increasing the excess or methanol to oil ratio will increase both reaction rate and equilibrium conversion. Practical molar ratio to perform methanolysis is by the ranges of 3.3:1 to 5.25:1 and greater molar ratio will not increase the productivity [15]-[16]. However, when catalyst variation done with constant molar ratio of methanol to oil 6:1, reaction time of 4.5 hours and 65°C reaction temperature, it is observed that higher percentage of catalyst lead to solidification of RBD PKO at room temperature. For temperature variation, lower reaction temperature at 40°C do not success to liquefy the oil but higher reaction temperature at 70°C reduce the final products quantity even though successfully convert the oil into liquid. The findings was contradicted with Narvaez et al. 2007 where they found that by increasing temperature can increase the conversion as well as productivity of palm oil to methyl ester. This happen might due to the test reaction time differences where this study conducted at 4.5 hours of reaction time compared to Narvaez et al. 2007 which study conducted at 1 hours and 20 minutes where the oil has longer time to evaporate. With variation of reaction time of 3, 4.5 and 6 hours, RBD PKO was successfully converted into liquid lubricant. These oil able to maintain its liquidity form after been put in the refrigerator for one day at 0°C. Table 2 shows the FFA conversion for the reaction time variables.

Table 2: Properties of RBD PKO for reaction time variation

Variables	Acid Value, AV (mgKOH/g)	Fatty Acid, FA (%) (as Palmitic)	FFA Conversion (%)
RBD PKO	0.78	0.28	-
3 hour	0.59	0.21	24
4.5 hour	0.40	0.14	49
6 hour	0.02	0.01	97

As reaction time increases, AV and FA content observed a decreasing value. At 6 hours reaction time, AV recorded highest conversion of FFA with 97% value while lowest FFA conversion recorded at reaction time of 3 hours while 4.5 hours reaction time recorded FFA conversion of 49%. FA % as palmitic recorded decreasing value when reaction time increases were 3, 4.5 and 6 hours reaction time recorded 0.21, 0.14 and 0.01 of FA.

Lubricity and Wear Analysis

All successful conversion of RBD PKO form solid form into liquid was been tested for its lubricity performance by fourball tribotester machine. In the fourball machine, each tested lubricants undergo 1 hours of testing procedure at 75°C, molar ratio variables methanol to oil of 12:1 only tested for 10 minutes before the oil run out due to evaporation and cannot be completed. This due to the higher methanol content in the oil that's contribute to the higher evaporation rate at high temperature.

During trans-esterification process, reaction time variables of 3, 4.5h and 6h are successfully liquefy with melting point reduced from 27.5°C to 0°C and final products yield efficient quantity of lubricants to be tested for coefficient of friction and wear in fourball tribotester machine. Figure 4 shows the result for coefficient of friction at 40kg load test with constant speed of 1200 rpm, temperature of 75°C in 60 minutes testing method.

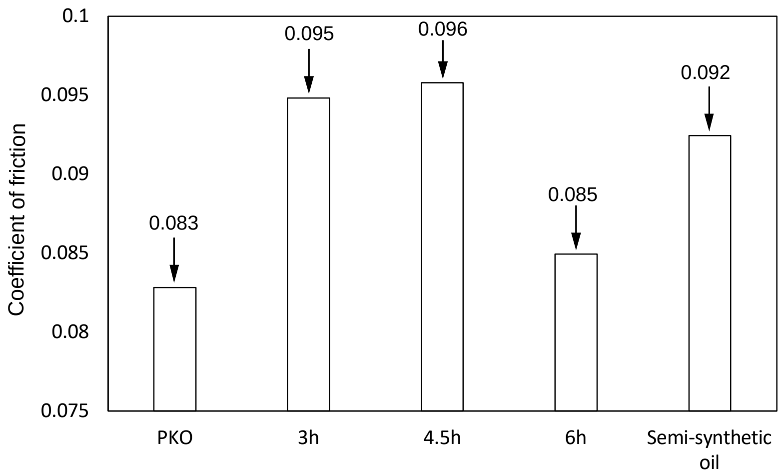

Figure 4: Coefficient of friction of tested lubricants

PKO recorded lower COF value compare to semi synthetic oil at, however after modification by trans-esterification with time variables parameters, the COF value increases in which 3h, 4.5h and 6h recorded 0.095, 0.096 and 0.085 as shown in Figure 4. Lowest COF recorded by RBD PKO at 0.083 and highest COF recorded by 4.5h reaction time at 0.096 while semi synthetic oil at 0.092. Long fatty acid chain in PKO helps to maintain the thin film and helps reducing COF [18] and by chemically modified the molecule structure by trans-esterification to liquefy the PKO has disrupt and affecting the hydrocarbon chain structure [19] those increasing the COF value.

When wear scar diameter been plotted as in Figure 5, semi synthetic oil recorded lowest wear scar diameter at 462µm while RBD PKO recorded highest wear scar diameter at 575µm. The results shows a contradicted pattern with COF where when PKO are chemically modified, it improves the wear scar diameter. According to Havet et al. 2001, the existence of ester group helps to strengthen the molecules bindings and increase the resistance to the shear force. Trans-esterification process can create an ester from palm-based oil with improved oxidation stability that contribute to a lower wear scar diameter.

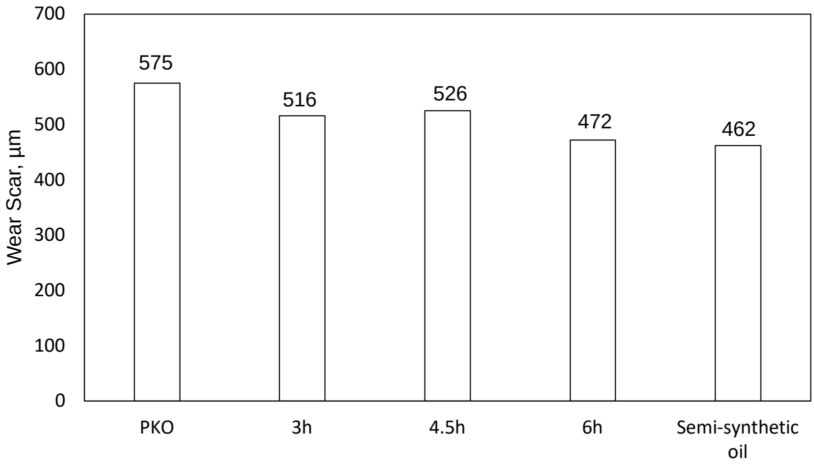

Figure 5: Wear scar diameter of tested lubricants

Image shown in Figure 6 are taken from CCD camera for 4.5h, semi-synthetic oil and RBD PKO to see the surface area where friction occurs in the fourball tribotester machine test. The figure shows three different wear scar occurring for 4.5h modified oil, semi synthetic oil and RBD PKO. Modified PKO by trans-esterification at 4.5h has almost round shape with consistent mild grooves wear. This shows that the oil able to maintain the film thickness between two moving parts during the test. RBD PKO has a largest wear scar diameter with lowest COF, the surface of the ball shows several pits created which helps as an oil reservoir to reduce the COF value. Semi synthetic oil are formulated with an additives to improves both COF and wear scar [21], only abrasive wear observed on the surface.

Figure 6: Wear picture taken from CCD camera of tested lubricants

Conclusion

This paper was to investigate the potential of RBD PKO as an alternative lubricant source with chemically modified by trans-esterification to change the semi solid form into liquid at 0°C. Results shows that trans-esterification process with the presence of catalyst was able to convert the solid form of RBD PKO into liquid from melting point of 27.5°C to 0°C. Coefficient of friction analysis done by fourball machine shows modified RBD PKO by reaction time of 3h, 4.5h and 6h has almost similar performance when compared with semi synthetic oil in COF and wear scar diameter. It is concluded that modified RBD PKO by trans-esterification was able to perform competitively with semi synthetic oil, however there is a room to improve the performance of modified RBD PKO by adding additives such as anti-wear, anti-friction and viscosity modifier. Therefore it is said that a renewable resources from modified RBD PKO has a potential as a substitute for petroleum base oil for lubricant.

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