TRIBOLOGICAL ANALYSIS OF BIODIESEL DERIVED WASTE PALM COOKING OIL (WPCO)

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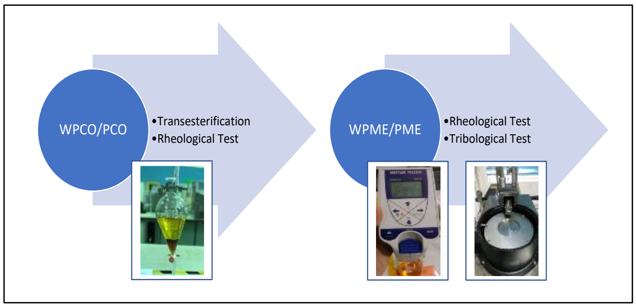
GRAPHICAL ABSTRACT



WPCO is found to have better performance to be used as engine lubricant while WPME has the lowest potential to be a lubricant because of its low viscosity and high coefficient of friction. It can be found that, WPCO that has higher viscosity present a wear scar diameter of 1.888 mm and total average CoF of 0.4296. As for WPME, the wear scar diameter is 2.062 mm with CoF of 0.5483. The surface area of WPCO values were found to be about 9.2% less than WPME. The higher the CoF, the larger the wear scar diameter. Lubricant film of WPME is too thin to provide the total surface separation. Contact between the surface asperities occurs.

ABSTRACT

The demand for sustainable and renewable energy sources is rising globally, which has increased interest in biodiesel manufacturing. The generation of biodiesel derived waste palm cooking oil (WPCO) is the main topic of this study. A versatile and easily accessible feedstock for the synthesis of biodiesel is palm frying oil, which is frequently used in culinary applications. WPCO is transformed into biodiesel using a process called transesterification, in which the oil's triglycerides combine with an alcohol, usually methanol, in the presence of a catalyst. The oils were analysed for their chemical and physical properties such as viscosity and density. The frictional test was carried out using Pin-on-Disc Tribometer for different loads and speed. The findings show that lubricants based on WPCO and WPME have remarkable anti-wear properties and have promise for usage in industrial and automotive applications.

KEYWORDS

Friction, Transesterification, Waste palm cooking oil, Wear.

INTRODUCTION

Biodiesel is produced by transesterification process among vegetable oil or animal fats with an alcohol and in the presence of catalyst (Haseeb et al, 2010). According to Mushtaq et al. (2013) Rudolf Diesel was the first one invented biodiesel in 1900. After Rudolf Diesel exposition in 1990, research using vegetable oils was explained during World War II era. Biodiesel is one of the important contenders of diesel for compression ignition (CI) engines that meets the American Standards of Testing Materials (ASTM) fuel standards among other available choices. Palm-oil is known as the most widely produced vegetable oil globally. Palm oil has been widely used as a cooking oil, ingredient in various food processes and in blends (Moreno-Peñaranda et al., 2015). Inappropriate disposal and possible environmental pollution of waste cooking oil creates significant challenge.

Waste Palm Cooking Oil (WPCO) is vegetable oil that has been used in frying food which is not viable for its intended use (Sirisomboonchai et al., 2015). Thus, by using WCO as a reactant for biodiesel it will not only helps in the disposal but also will minimize the cost of biodiesel production (Mahesh et al., 2015).

Waste cooking oil (WCO) can be easily obtained from any fast food restaurants, homes and school cafeterias. It can also be obtained from rendered animal (feed) fats that have been heated and used for cooking a wide variety of meat, fish or vegetable products (Bart et al., 2010). In Malaysia, people tend to dump their waste cooking oil into the sink. This inappropriate action caused many problems such as clogged pipes, problems to the sewage system, and environmental problems. Therefore, the tackle to this problem is to produce biodiesel from WCO. Besides, this WCO derived biodiesel can also be used as a lubricant in compression ignition (CI) engines (Sudhir & Sharma, 2007).

Repeated frying process for preparation of food makes the vegetable oil no longer capable to use as it contains high free fatty acid (FFA) content. On the other hand, the disposal of waste cooking oil into the environment can cause problems like soil and water pollution and this will cause disturbance to the aquatic ecosystem. In wastewater treatment, animal fat is hard to purify because it contains high acid value and fat-containing floating sludge. If this pollutant is discharged into water systems, it can affect the environment and cause pollution. Waste animal fat is identified to be a good feedstock for biodiesel (Raqeeb, and Bhargavi, 2015). Thus, this type of waste cooking oil can be used to be converted into biodiesel

WCO contain impurities, such as free fatty acid (FFA) and water that are unfavourable to biodiesel yield in alkali-catalysed processes (Apostolakou et al., 2009 and Taylor et al., 2011). According to Bart et al., (2010) WCO usually contain 2-7 wt% FFA. Frying affected the changes in chemical and physical properties of oils and fats. Waste vegetable oil contains more FFAs than virgin oils. FFAs raise the cloud point of the fuel, so biodiesel made from waste cooking oil or animal fat will cloud at higher temperatures than biodiesel made from virgin vegetable oil feedstock (Bart et al., 2010).

WPCO has large molecular mass and chemical structure. Thus, it cannot be used directly in the engine because it can cause oil ring sticking, lubricating problems, poor fuel atomization or even prevention of atomization as a result of plugged orifice, poor cold engine start up, and the creation of the gum and other deposits. According to Jayed et al., (2009); Bhuiya et al., (2015); Attia & Hassaneen, (2015) WPCO contains high viscosity which is higher than the conventional fossil fuels and this will causes a problem to the engine. However, there are some techniques and process that can be used to produce biodiesel as well as reducing the viscosity of vegetable oils. The process that can be used to convert WPCO to biodiesel are micro-emulsification, dilution, and transesterification.

The use of WCO will minimize the cost in biodiesel production since it is cheaper compared to refined oil. Biodiesel source should be obtained easily and reduce the production cost. Instead of using raw cooking oils for the biodiesel production, the use of WCO is an alternative way to reduce the cost (Sudhir & Sharma, 2007; Sirisomboonchai et al., 2015). Recent studies Raqeeb & Bhargavi, (2015); Mahmudul et al., (2017) stated that around 70-95% of the total production cost is related to the cost of the raw material. Several authors Gashaw & Teshita, (2017); Raqeeb & Bhargavi, (2015) conclude that the cost issues can be overcome by using waste cooking oil as the raw material to produce biodiesel.

Lubricity is known as the reduction of friction between solid surfaces in relative motion (Jeyaprakash & Yang, 2020) Internal combustion engine is largely a function of lubrication to reduce the wear and friction. The presence of free fatty acid and diglycerides may also affect the lubricity of biodiesel (Hu et al., 2005). Hydrodynamic lubrication and boundary lubrication are two main mechanism contributed to overall lubricit. In hydrodynamic lubrication, a liquid layer will prevent the contact between opposites boundary while boundary lubricants are compound that adhere to the metallic surfaces, forming a thin, protective anti-wear layer

Good lubricity is important to protect fuel injection systems. In internal combustion engine, piston ring is the most complex tribological component. Power, fuel consumption, hydrocarbon emissions, oil consumption, wear noise, and cooling are affected by the design of the ring-liner interface. Studies of the mechanism of piston ring lubrication and related phenomena have found that piston rings contribute significantly to the total engine mechanical friction losses (Li et al., 2021). Therefore, it is important to select the best lubricant to protect the engine.

The purpose of undergo friction tests are to characterize biodiesel frictional properties under pure sliding motion with respect to three main lubrication regimes which are Boundary Lubrication (BL), Mixed Lubrication (ML) and Elasto-hydrodynamic Lubrication (EHL) (Hamdan et al*.,* 2017). Lubricant properties, applied load, and sliding velocity are the factors that affect the frictional properties of a lubricated contact. Lubricant property is not the only factor that affect the performances of wear and coefficient of friction. Other factor is the sliding conditions of material under lubricant contact condition.

In a car engine, the cylinder liner-piston ring tribosystem has two dead points in which load is combined with zero sliding velocity. At those points, thinner fuel economy engine oils may fail to adequate film thickness unless a suitable lubricant is used. The piston assembly during engine operation reciprocates between bottom dead centre and top dead centre of the cylinder liner. Such piston primary motion induces continuous backward and forward transitions between fluid film lubrication and boundary lubrication regimes along the ring-liner conjunction. Therefore, it is important to analyse the frictional properties of an engine lubricant along its various lubrication regimes.

The tribological performance of lubricants is defined in terms of their friction behaviour. The tribological properties of the lubricants were evaluated by measuring the coefficient of friction (CoF). CoF is defined as the rate of change in friction that correlate with the applied normal load (Chong & Ng, 2016). This friction test was conducted to compare the CoF between WPCO and WPME as engine lubricant at different sliding velocities and when different weight is applied between a stagnant pin and rotating wear disc on pin-on-disc tribometer machine.

Friction characteristic of lubricants diluted with biodiesel with different feedstock need to be measure and compare by frictional analysis test. Therefore, this study intends to differentiate the rheological behaviour and tribological properties of PCO derived PME and WPCO from frying chicken derived WPME. There are a lot of study that has been done on transesterification of vegetable oils but no quantum of work has been done on the properties and fuel analysis of palm oil and waste palm oil derived biodiesel.

METHODOLOGY

Transesterification of Waste Palm Oil Methyl Ester (WPME)

WPCO was first prepared by heated 1 L of the waste oil slowly to 65ºC and the temperature was maintained for 15 minutes. Then it was allowed to settle for 24 hours. After 24 hours, supernatant formed and the supernatant was pipetted from the top. On the other hand, 1 L of PCO was heated at 65°C for 15 minutes before it went through transesterification reaction.

Production of WPME from triglycerides of palm oil can be achieved through transesterification process. With the presence of alkaline catalysts, the process involves a simple global reaction between the triglycerides reactants and short chain alcohol at sufficiently high temperature and mixing. This will result in the production of methyl esters with crude glycerol as the co-product. In this study, potassium hydroxide (KOH) was selected as the catalyst. WPME was heated at 60 °C to 70 °C.

Determination of FAME in WPME by Using Gas Chromatography.

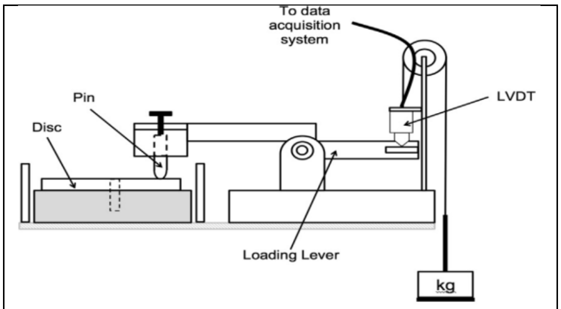
WPME was weighed approximately at 50 mg (about 3 drops) and added into a 2 ml vial. 0.95 ml of n-hexane was pipetted into the vial. The vial was caped and shaken to dissolve the oil in the n-hexane. Then, the cap was removed and 0.05 ml of Potassium Methoxide was pipetted into the vial. Immediately the cap was replaced and vigorously shaken for 5 minutes using a vortex mixer. After 5 minutes, 1 ml of distilled water was added and mixed thoroughly.

It was observed that the mixture changed from clear to turbid as sodium glyceride was precipitated at the bottom of the vial. After 5 minutes, the clear upper layer of methyl ester can be pipetted off for Gas Chromatography (GC) Analysis. 0.1 µl of methyl ester solution was injected into the GC column. The retention times of the constituent fatty acid such as palmitic acid, linoleic acid and stearic acid were measured. The raw data was then printed from the desktop connected with the GC. The same methods were repeated for PME.

Friction test

In this study, the friction tests of WPCO, WPME, PCO and PME lubricated contact are conducted using a pin-on-disk tribometer that is inline to the standard of ASTM G99. Figure 1 illustrates the schematic diagram of the pin-on-disk tribometer setup used for the present study. Speed is set between 20 rpm to 2000 rpm, with a wear track is set at 20 mm giving the sliding velocity of 0.04 ms^{-1} and 4 ms^{-1}. A stationary cast iron pin with a diameter of 10 mm is rotated against a stainless steel wear disc with applied normal load used in this study range from 1kg, 2kg, 3kg and 4 kg.

For every speed and load combination, the friction test is held for three minutes and friction measured is observed to reach steady state as proposed by Kovalchenko et al.(Kovalchenko, Ajayi, Erdemir, Fenske, & Etsion, 2005). This method is used to determine the lubrication regimes transition for lubricated contacts. As suggested by Hamdan et al. (Hamdan, Chong, Ng, Chong, & Rajoo, n.d.), WPME and PME are continuously flow from the pump to the disc/pin conjunction. In order to determine whether the rheological changes is significant of not, the Kinematic viscosity is measured before and after the friction test.



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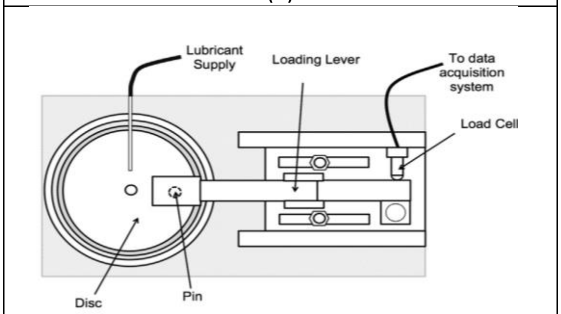


(b)

Figure 1: (a and b) Schematic diagram for a pin-on-disc tribometer (Hamdan, Chong, Ng, Chong, et al., 2017)

Stribeck Curve

The purpose of undergo friction tests are to characterize biodiesel frictional properties under pure sliding motion with respect to three main lubrication regimes which are Boundary Lubrication (BL), Mixed Lubrication (ML) and Elasto-hydrodynamic Lubrication (EHL) (Hamdan et al., 2017). Lubricant properties, applied load, and sliding velocity are the factors that affect the frictional properties of a lubricated contact. Lubricant property is not the only factor that affect the performances of wear and coefficient of friction. Other factor is the sliding conditions of material under lubricant contact condition

Hamdan & Chong, (2018) have stated that the investigations of frictional properties could be done by generating Stribeck curve. Parameters involved in a typical Stribeck curve are the coefficient of friction, lubricant dynamic viscosity, sliding speed, and applied normal load. Stribeck curve is usually performed using tribometer. This allows for the evaluation of the biodiesels in identifying different lubricant regimes which are elastohydrodynamic lubrication (EHL), mixed lubrication (ML), and boundary lubrication (BL) (Kalin et al., 2009). Critical velocity defines the point where transition from EHL to ML occurs (Hamdan & Chong, 2018). Along elastohydrodynamic and mixed lubrication regimes, the lubricant rheology-pressure relation becomes important. This is because contact pressure generated at this regimes is significantly high to affect the lubricant rheology (William et.al, 2019).

RESULTS AND FINDINGS

Chong et al. (2019) mentioned that to predict the tribological performance of engine lubrication systems, physical properties of engine lubricant are extremely important. Thus, rheological information of the lubricant is required. Viscosity is one of the most important rheological properties of biodiesel and should be maintained within pre-determined limits. The rheological properties of all tested lubricants at 40 °C are given in Table 1. The kinematic viscosity was determined at 40 °C because this was the prime parameter required by American Society for Testing and Materials (ASTM) standard.

Kinematic viscosity was calculated by dividing absolute viscosity with density. Kinematic viscosity for WPME and PME was found to be significantly lower than WPCO and PCO. Needless to say, oil that have low viscosity is suitable to be used as fuel but not as lubricant. Lubricant for engine must have sufficiently high kinematic viscosity in order to protect the surface of the engine. When viscosity decrease, there will be a dramatic consequence for the friction losses (Taylor, 2002).

Table 1: Rheological properties of tested lubricants

Type	Density (g/cm^3)	Kinematic Viscosity (mm^2/s)
WPCO	0.8950	33.89
PCO	0.8980	40.09
WPME	0.8623	3.479
PME	0.8620	5.800

It clearly stated that kinematic viscosity for WPCO and PCO are both high. However, the viscosities of PCO shows relatively narrow viscosity range because of their triglycerides structure. Therefore, it is crucial to develop bio-lubricant over a moderate range of viscosity from vegetable oils. Since WPCO has moderate kinematic viscosity, it may be suitable to be used as an engine lubricant.

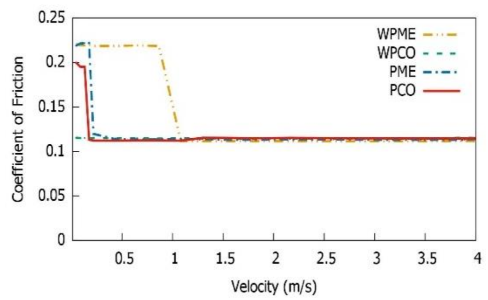
In order to confirm the basic composition of WPME and PME is within the biodiesel range, kinematic viscosity can be determined using American Society for Testing and Materials (ASTM D6751-08) or European standard (EN 14214). According to ASTM D6751-08 and EN 14214, the kinematic viscosity must be in range of 1.96 to 6.0 for ASTM D6751-08 and 3.5 to 5 for EN 14214.The results of kinematic viscosity for produced WPME and PME were found to be 3.4789 and 5.8004 respectively which is in range of ASTM D6751-08 and EN 14214. According to (Aleissa, 2013), lubricant with low viscosity will result in leakage of increased wear due to unsufficient lubrication. However, high viscosity will cause poor atomization, and carbon deposition.

Table 2: Physico-chemical Properties of Standard B100, WPME and PME

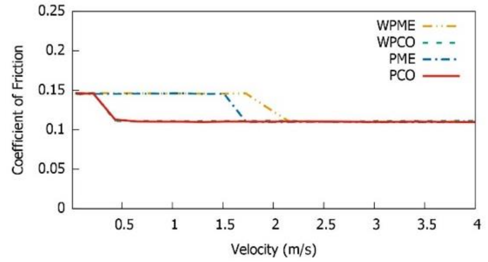
Properties	Standard Biodiesel (ASTM D6751-08)	Standard Biodiesel (EN 14214)	WPME	PME
Density @ 40°C (kg/m^3)	-	860-900	865	867
Kinematic Viscosity @ 40°C (mm^2/s)	1.96-6.0	3.5-5.0	3.479	5.800
Acid Value (mg KOH/g max)	0.5	0.5	0.957	0.776

Despite that density and kinematic viscosity followed the Standard Biodiesel, the acid value of WPME and PME exceed the value for standard biodiesel. The European norm as well as the American standard limits the maximum acid value content for biodiesel should be 0.5 mg KOH/g max. Acid value is a direct measure of free fatty acids content in biodiesel. It can be seen that WPME has higher acid value compared to PME. According to Aleissa (2013), the high acid value of the WPME may be due to excessive use of acid added to break the emulsion formed during frying stage. Ruggiero et al., (2017) reported that high acid numbers will cause corrosion and poor cold flow properties in engine performance. It can also indicate the presence of water in the lubricant.

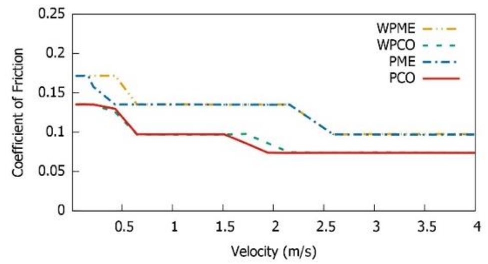
The tribological effect from the friction point of view are shown in Figure 2. the graph for 10N load illustrate steady state condition for all types of oil. Every single tested lubricant shows the same behaviour until it changes from Boundary Lubrication to Dry Contact. Whereas, the graph in Figure 2(b) shows when the number of load increase to 20N, WPCO and PCO still not showing any changes. However, for WPME and PME the transition occurred when it increases from EHL to ML and finally to BL with decrease in velocity.



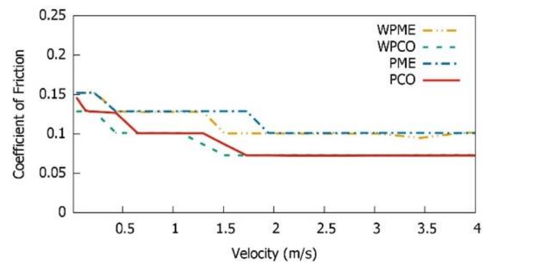
(a) 10N



(b) 20N



(c) 30N



(d) 40N

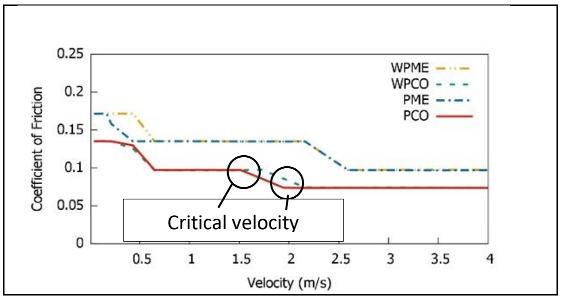
Figure 2: comparison between four different loads using four different materials.

The most significant difference of the changes in the transition of lubrication regimes can be seen on 30N and 40N load. It is also noted that WPCO and PCO produces the lowest CoF values with WPME and PME having the highest CoF values across the investigated sliding velocity range for all four different loads.

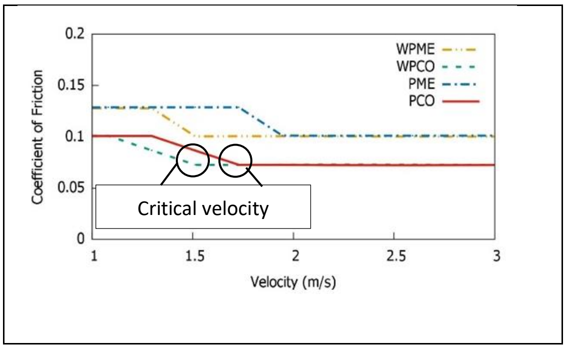
During the transition of lubrication regimes along EHL and ML regimes, lubricant rheology-pressure relation becomes important. The contact-to-contact between pin and disc causes the contact pressure generated at EHL and ML regimes is significantly high to affect the lubricant rheology. However, among the other lubrication regimes, boundary lubrication represents the most critical regime for a sliding contact because of the excessive friction generated as a result of increased surface interactions along opposing rough surfaces (Chong & Ng, 2016). Therefore, the effectiveness of a lubrication system can be determined in the performance of the boundary film during sliding.

Regarding the tribological behaviour of the oil, it emerges that at highest pressure applied, the lowest values of the CoF are found to be the WPCO. This is believed to be due to the fact that at sufficiently high load or low sliding speed, lubricant may be expelled from the friction zone, leaving the rubbing surface unlubricated(Hamdan & Din, 2018). In this case, it will have resulted in severe friction (Yılmaz Özmen, 2016). CoF is basically depends on oil viscosity, sliding velocity and the load. Thus, it can be concluded that WPCO performs a better lubrication compared to the other three types of oil. WPME in fact always presented the highest CoF value. The CoF for PCO and PME are placed in between the other two.

Meanwhile, critical velocity is introduced as the initial point where the lubricants start to shift from EHL to ML. The most striking result to emerge from the graph was shown when 30N and 40N load were applied. Thus, the critical velocity values are extracted from the Stribeck curves measured for 30N and 40N. There is no critical velocity for 10N and 20N since there is no transition of lubrication regimes occurred. Based on Figure 3, when 30N load applied, it can be observed that WPME and WPCO exhibit the highest critical velocity. To compare between WPCO and PCO for 30N, WPCO has higher critical velocity which is 2.161 m/s while PCO has lower critical velocity which is 1.945 m/s.



(a)



(b)

Figure 3: Critical velocity at 40N

From the measured kinematic viscosity, coefficient of friction and the wear scar diameter, the relationship between those three properties can be relate.. The kinematic viscosity, coefficient of friction and wear scar diameter of WPCO and WPME were tabulated in Table 3. It can be found that, WPCO that has higher viscosity present a wear scar diameter of 1.888 mm and total average CoF of 0.4296. As for WPME, the wear scar diameter is 2.062 mm with CoF of 0.5483. The surface area of WPCO values were found to be about 9.2% less than WPME. The higher the CoF, the larger the wear scar diameter. Lubricant film of WPME is too thin to provide the total surface separation. Contact between the surface asperities occurred.

Table 3 : Relationship between kinematic viscosity, wear scar diameter (WSD) and total average coefficient of friction (CoF) for WPCO and WPME

Samples	Kinematic viscosity (mm^2/s)	CoF	WSD(mm)
WPCO	33.89	0.4296	1.888
WPME	3.479	0.5483	2.062

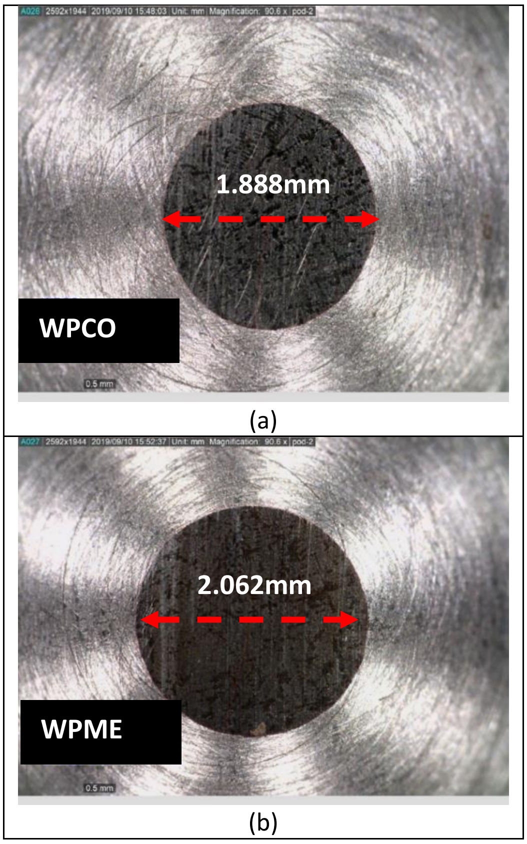


Figure 4: Worn surfaces diameters of the disc after tribotests (a) WPCO, (b)WPME

Figure 4 shows the topography gained information on the wear of the spheres after tribology test will be discuss. The worn surfaces after tribotests are reported using WPCO and WPME as lubricants. Both Figure 4 (a) and (b) show the 3D topographies under several conditions. It is interesting to note that WPME has larger surface area compared to WPCO. It can be seen that WPCO has a smaller surface area of wear scar diameter compared to WPME. This is because WPME is thinner than WPCO. A thin lubricant will cause metal to metal parts rub against each other and thus resulted in wear out or fail prematurely from the lack of proper lubrication.

CONCLUSION

In this study, the analysis revealed that from the rheological and tribological properties, WPCO is the most suitable to be used as lubricant in engine compared to others. With low wear rate at 1.888 mm, smallest critical velocity and low number of COF, WPCO has shown its potential as a substance better than the derived methyl ester itself.

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