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Friction and wear study of passenger car piston top ring sliding on cast iron material lubricated with palm fatty acid distillate (PFAD)

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KEYWORDS

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Friction and wear
Bio-based engine oil
Palm fatty acid distillate (PFAD)

ABSTRACT

Piston top ring - cylinder liner situation was simulated using a passenger car engine top ring sliding on a cast iron disk. The simulation was done on a pin-on-disk tribo-tester. Friction and wear control performance of neat palm fatty acid distillate (PFAD), its ZDDP and dithiocarbamates formulates were evaluated under a severe load (200N) serving condition possible with today/future cars' internal combustion engines. 0.5%(wt) molybdenum dialkyldithiocarbamates (MoDTC), doped PFAD produced lower friction and wear, while 0.1%(wt) ZDDP in the same PFAD offered lower coefficient of friction but slightly higher wear when compared to a commercial premium engine oil tested for benchmarking. PFAD can be a "cost-competitive green base oil" in Malaysia, and a contributor to the growing global bio-lubricants market.

1.0 INTRODUCTION

Environment sustainability and energy independence, are factors in adopting vegetable oils as basestocks for engine oils. Vegetable oils possess extremely low toxicity, high biodegradability, attractive tribological characteristics and solubilising power, superior to petroleum-derived and synthetic oils (Bongfa, 2015). The last two characteristics grant that with the aids of additives, vegetable oils can meet the tribological demands in modern days and future generation vehicle engines.

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In the automotive engine, a major representative motion mechanism whose tribological characteristics largely impact the engine's fuel and oil consumptions, power loss and emission of harmful exhaust is the piston rings - cylinder bore mechanism (Kapsiz, 2011). The tribological influence of the said mechanism accounts for a proportionately large energy loses to friction, estimated to be around 40 to 50%, and resultant severe wear of the tribo-contact (Ali et al., 2016; Mabuchi, 2013; Obara , 2016). The culprits of this severe wear are the contact-surfaces of the piston rings and the cylinder bore. Among the tribo-pair mechanisms in the internal combustion engines, the tribological interaction of the piston ring-cylinder bore mechanism is the most complicated to analyse. This is because during one single stroke of the piston assembly, the cylinder wall-piston ring interface may practically encounter boundary, mixed, and hydrodynamic lubrication; caused by large fluctuation of parameters, majorly temperature, speed, load, and lubricating oil availability (Kapsiz et al., 2011). Among these lubrication regimes, the boundary lubrication condition is the most critical. It occurrence is at the top dead centre (TDC) and the bottom dead centre (BDC), and more severe at TDC where temperature and load are very high, while the speed is low. However, these sliding counter-faces are supposed to generate very low friction, and experience low loss of materials under proper boundary lubricated conditions (Banerji, 2016; Meng-Burany, 2011).

In light of these, a potential lubricating base oil for this tribo-contact should have strong attaching polar heads, and excellent shear-stable tails which can survive high load and temperatures. The base oil should be an excellent carrier of surface-active additive(s) that will provide the adequate friction and wear mitigation.

Recent global rise in demands of passenger cars in emerging economies have stimulated growth of lubricants market, especially bio-based (for environmental reasons). Malaysia, like the developed and other developing economy, is concern over the effects of waste oil on the environment as she has reasonable share in the rise in demand of passenger cars and other vehicles, implying rise in demand for automotive engine oil. Freedonia Group predicted in a recent report that the growth in demand for automotive engine oil in Malaysian lubricant market is at a compound annual rate of 2.9 percent from a total demand of 175,000 tons in 2016 to 202,000 tons in 2021 (Kellenberger, 2018). This demand is supported by the popular trend that Malaysian consumers do follow religiously the guidelines on oil drain interval from original equipment manufacturing (Kellenberger, 2018). Moreover, the speculated reinstitution of the Malaysia's End of Life vehicle policy aims at bolstering the car manufacturing industry among other reasons will require the retirement of older vehicles which in turn will increase fleet of newer light-duty vehicles and engine oil drain intervals (Kellenberger, 2018). This will no doubt increase this demand.

This huge lubricant demand can be complimented from successful research into bio-based lubricating oils. Different plant seed oils are being studied to meet these lubricant demands. In Malaysia, palm fruit oils are the most studied, among which is PFAD. PFAD can be a "cost-competitive green base oil" in Malaysia, as it is produced in large quantity in the country (average of 0.678 million metric tons in 2015) (Zero & Rainforest Foundation Norway, 2015). Its use in formulating bio-based engine oil will reduce environmental impact from engine lubricating oils, improve vehicle engines efficiencies, and extend the market for the product.

Studies on the tribological properties of vegetable oils such as coconut, sunflower, soya bean oils (Shankar, Mohanraj, & Ponappa, 2017) as cutting fluids, neem seed and jatropha curcas seed oils as wire drawing fluids (Muhammad, Dauda, & Bongfa, 2016), palm- and soybean-based vegetable oils as engine oils (Aiman & Syahrullail, 2017) have been reported. Ruggiero et al, studied the tribological properties of hydrotreated vegetable oil and fatty acid methyl ester from raw jatropha curcas L. oil and raw rapeseed oil using a AISI E52100 steel ball reciprocating on a flat X210Cr12 steel on a tribometer under different loads and frequencies (Ruggiero, D'Amato, Merola, Valašek, Muller, 2017). The mechanism approximates closely the piston ring – cylinder liner operation, except for the rolling ball.

The tribological properties of PFAD have been extensively studied for lubricant applications. For example, Salleh and co-researchers (Salleh, 2017) studied the tribological behaviour of PFAD as alternative transmission fluid for wet clutch to replace the conventional petroleum-based automatic transmission fluid, Golshokouh et al (Golshokouh, 2013) investigated the tribological properties of PFAD for hydraulic fluid application. However, no study has adequately mimic the real contact, and severe conditions which lubricants are exposed to at the interface of the piston ring-cylinder bore of the internal combustion engine.

The objectives of this study are two. To evaluate the performance of PFAD as lubricant base stock for the serving conditions possible with today and future cars internal combustion engines, and to study the effect of customary additives ZDDP, molybdenum dialkyldithiocarbamates, and mythelene bis(dibutyldithiocarbamate) on the tribological performance of PFAD as engine lubricating oil. The additives are chosen based on reports of their previous performances in friction and wear control of tribo-systems, and contributions to oxidation stability of lubricants (Bongfa, 2016). ZDDP and MoDTC are particularly good for modern engine lubricants formulation because they have been discovered as lubricant components which suppress low speed pre-ignition (LSPI) – a challenging phenomenon which came with downsized, direct injection, turbocharged, fuel saving engine technologies, manifesting in "uncontrolled combustion when air-fuel mixture get ignited by yet-to-be-known initiator(s) before the spark plug actually sparks – leading to knocks (Beercheck, 2016). Good performance of ZDDP and MoDTC in PFAD will, in particular, be welcomed in Asia and Africa lubricant markets as these "new (LSPI prone), turbocharged, down-sized gasoline direct injection engines are rapidly being introduced in Asia" (Beercheck, 2016) as well as Africa.

2.0 MATERIAL AND METHODS

Acceptable friction and wear evaluation should simulate nearly exact and actual operating conditions of the mechanism. In the current work, the test methodology is employed under laboratory conditions to simulate the engine (cylinder bore-piston ring) operating environment including the use of sliding-contact materials, a cast iron disk having very near composition and surface profile to cylinder bore, and a compression piston ring piece of a passenger car engine. The ring was cut to 30mm chord length (to fit properly into the pin holder unit for clamping and used as the pin. To prevent excessive, redial deflection of the ring (pin) under load due to its curvature, a small stud is used to support it radially. The schematic arrangement of the top piston ring piece and cast-iron disk on the pin-on-disk Tribo-tester is shown in Figure.1. This arrangement was run on the machine under applied normal load of 200N for a sliding distance of 1500m at ambient temperature (25°C) and rotating speed of 100 rpm. New pins (top piston ring piece) as well as new disks surfaces were used for each test.

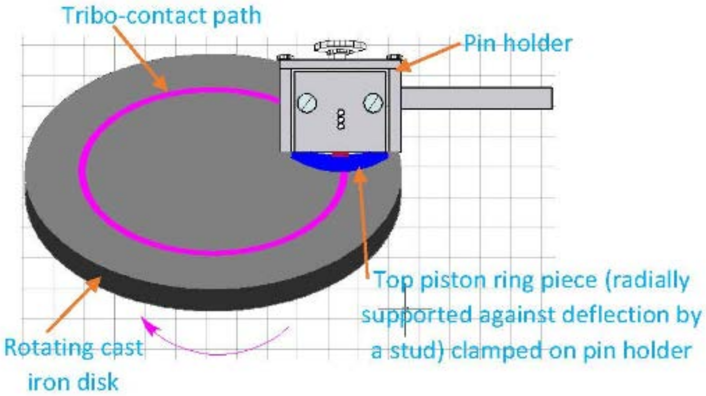

Figure 1: Schematic arrangement of top piston ring piece and cast-iron disk.

The 200N load was selected based on established concept from the work of Obert et al. (Obert, 2016). The authors (Obert et al., 2016) observed and concluded, after series of tests with various loads, that meaningful evaluation of wear in engine liners is only possible at load up to 200N (Obert et al., 2016). The same normal contact load of 200N, is said to simulate the nominal radial pressure applied after combustion at 50% of maximum engine load (Morina et al., 2016; Ali et al., 2016).

In this test, manipulating of some of a key parameter - lubricating oil composition on a pin-on-disk Tribotester was carried out to determine the best composition that offer good wear protection and lower friction. Lubricating oil composition is well recognized by researchers (Kapsiz et al., 2011) to influence significantly friction coefficient and wear at the cylinder bore-piston rings interface. We first examined the friction and wear behaviour of the arrangement under the lubrication of 3ml of neat PFAD and later under PFAD separately additivated with ZDDP, molybdenum dialkyldithiocarbamates (MoDTC), mythelene bis(dibutyldithiocarbamate) (MyDTC), ZDDP + MoDTC, and MoDTC + MyDTC. A premium commercial engine oil (CEO) was also used as a lubricant under the same test conditions for comparison. In each test, 3ml of the oil sample was supplied at the rubbing interface to simulate the oil starvation lubrication characteristics of the compression ring-cylinder liner arrangement.

3.0 RESULTS AND DISCUSSION

3.1 Friction

Friction effects in this test was quantified from the coefficient of friction versus time for each test and the average coefficient of friction reported by the interfacing software of the machine installed on a PC.

Figure 2 shows six representative experiments out of a series of several tests. The Figure details the coefficient of friction versus time signals for neat PFAD, formulated PFAD, and the benchmark commercial premium engine oil. First, we observed that the fluctuation or unsteady state of coefficient of friction over time is very pronounced with neat PFAD than with its formulates and also the commercial engine oil. This might be due to higher experience of fracture of tribo-film layers on the wear surface, giving rise to loss of energy and, resultant increase in instantaneous friction between the tribo-interfaces.

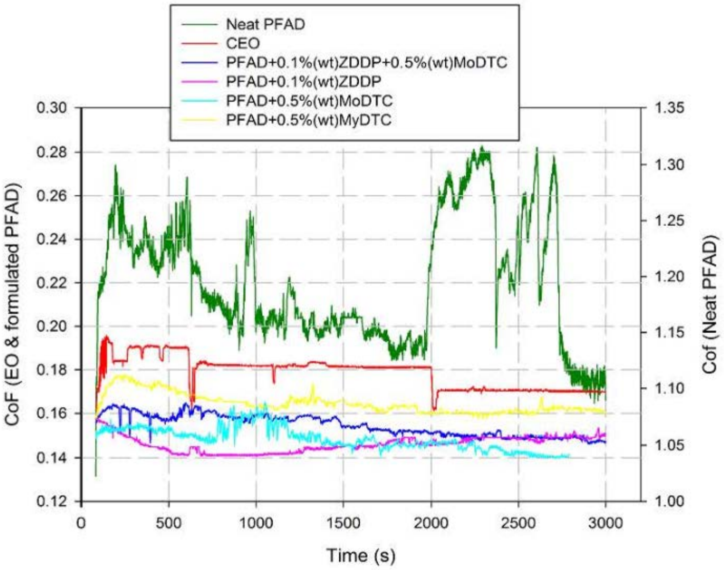

Figure 2: Coefficient of friction (CoF) versus time.

Relative steady state friction was attained earlier in the tests with PFAD + 0.1%(wt) ZDDP and PFAD + 0.5%(wt) MyDTC as lubricants than the test with the rest of the lubricants presented in the Figure. This means that PFAD + 0.1%(wt) ZDDP and PFAD + 0.5%(wt) MyDTC formulations have quick tribofilm distribution, and stable film layers could better resist fracture and retain energy than PFAD, PFAD + 0.1%(wt) ZDDP + 0.5%(wt) MoDTC, PFAD + 0.5%(wt) MoDTC, and even the benchmark oil (CEO).

The influence of additives appears much more significant on the friction control of PFAD, both in reduction and the steadiness over time of the values of the coefficient of friction. The general trend with all the lubricated contacts is that there is slide reduction of the coefficient of friction as time increases. This implies improve afinity between the lubricant, especially the additive components, and the substrates as time goes, resulting in more active tribo-film in each case. Although in the case of PFAD + 0.1%(wt) ZDDP there is steady slide increase later after 1000 seconds. The reason to this is unclear as this test is even at low temperature, constant speed and load. It might be that the friction mitigating surface chemistry started reducing gradually after the stated time and/or Zn radicals from the additive commenced a catalytic oxidation process which affected the lubricity of the formulation.

Figure. 3 presents the average coefficient of friction (CoF) of the tribo-arrangement (piston ring-disk contact) lubricated with each of the various tested oil samples. The Figure shows that boundary lubrication condition exists in the case of neat PFAD lubrication test, while either boundary or mixed lubrication conditions could be the case with the additives treated oils. This is due to high values (greater than 0.1) of CoF recorded.

There is excessively high value of CoF under neat PFAD lubrication test. This implies that as general characteristics of unformulated vegetable oils, PFAD could not retained its position in between the tribo-pair, undoubtedly, due to the high loading condition. There are no sufficient oil molecules and also poor sustenance of reaction products film from the oil chemistry under the severe loading. The results imply direct surface contact such that the load is majorly supported by the substrates' asperities. Very minimal formation of reaction products or chemical films from oil chemistry at the contact zone of the substrates may be available to reduce friction. The deficient performance of neat PFAD attested to the common reports by researchers: that vegetable oil in untreated form cannot provide sufficient lubricity and wear protection under severe loading condition (Bongfa et al., 2016).

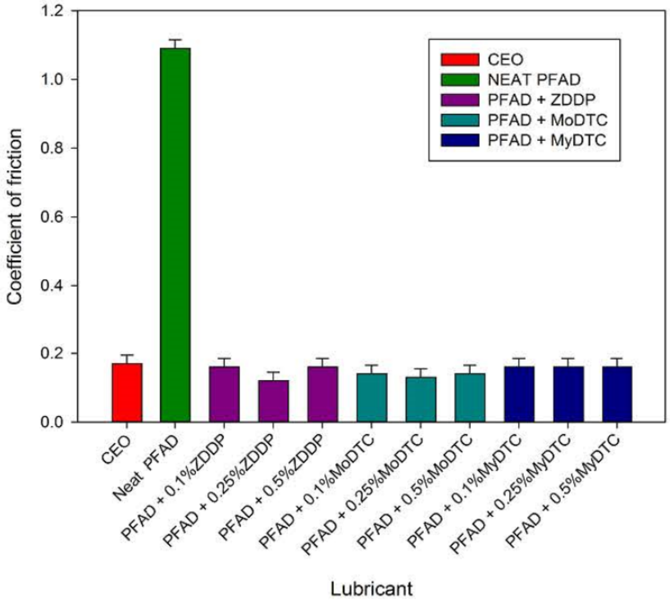

Figure 3: Coefficient of friction versus additives concentration.

Blend of PFAD with each of the additives presented significant reduction in CoF, comparable to that of the commercial engine oil (CEO). This should be due to the high solubilizing power of PFAD, being vegetable oil, which enable it in the company of the additives to form high shear-stable tribofilm matrices at the interface of the piston ring-disc arrangement.

From the friction control point of view, 0.25%(wt) ZDDP led in the performance, followed by MoDTC at 0.25%(wt), then 0.1%(wt) and 0.5%(wt). MyDTC maintained virtually a constant level of CoF at all administered concentrations. The physisorption and chemisorption of these compounds result in reduced friction and wear. It is worthy of note that low concentration of ZDDP offered the best CoF as in previous study (Morina, 2006). ZDDP might have achieved this by formation of tribofilm comprises Zn, S, and P species, being its active chemistry in wear and friction control. The performance of ZDDP at 0.1%(wt) and 0.5%(wt) concentrations, in terms of friction reduction, shows that the concentration which offered the optimal tribo-film in this test is 0.25%(wt). MoDTC controls friction by forming MoS2 at the tribo-contact zone of the substrates. A product from decomposition of MoDTC acting as a soft base react with iron (from substrates) as soft acid to form iron sulphide (FeSx) which in collaboration with nitrogen-based compounds (from the decomposed MoDTC) and polar heads from high free fatty acids of PFAD, become the tribo-film composition. Like ZDDP, 0.25% (wt) offered the optimal deposit of friction control species from MoDTC.

MyDTC controls friction by deposition of low shear strength layers of S and N complex compounds on surfaces of substrates after itself undergoes thermal decomposition reaction. The almost-equal performance by the various concentration of MyDTC implies that it might require higher dose to produce sufficient surface-active matrix to affect any further reduction in friction, or higher test temperature than the ambient used here, to decompose the additives to form active tribological radicals for formation of sufficient surface-active matrix.

3.2 Wear

Figure 4 details the wear versus time signals of the sampled six representative tests whose coefficient of friction versus time are represented in Figure.2. Unlike the result of coefficient of friction versus time (Figure.2) of these tests, we observed that neat PFAD and its formulates demonstrated relative steady wear over the time duration of the test. This implies steady wear surface protection chemistry. Moreover, neat PFAD and its formulated compounds exhibited steady increase in wear overtime. Howbeit, 0.1%(wt) ZDDP doped PFAD offered constant wear rate as time increases. This actually mean that there was a long-time retention of hard surface chemistry which offered relatively consistent resistance against wear, but detrimental to friction reduction (observed in Figure.2). The reduction trend in wear rate overtime offered by CEO (Figure.4) should be due to the oil treatment.

From Figure. 5, We noted from the wear results that PFAD produced quite higher wear than the benchmark oil, CEO. One will deduce that the lubricant film in the test with PFAD got squeezed out from the contact zone, leaving only the asperities and the reacted chemo-shorb to carry the load, confirming starved and boundary lubrication condition. PFAD could not retained tough surface films or reaction chemistry to protect the piston ring surface from wear.

We observed (Figure.5) that 0.1%(wt) and 0.25% (wt) of either ZDDP or MoDTC in PFAD contributed significantly to the lowering of wear of the piston ring. While increased %(wt) of ZDDP increased wear, increased of MoDTC to 0.5%(wt) reduced the wear rate to the lowest value in this test, implying that MoDTC has significant anti-wear properties as observed in previous studies (Morina et al., 2006; De Barros'Bouchet, 2005). There is higher provision of surface protective chemistry by MoDTC at 0.5%(wt) than at lower concentrations. Dithiocarbamate ligands possess strong ability to donate electron, and metals surfaces have strong electron-accepting tendency such that at tribo-contact zone of this arrangement there may be sufficient physi-sorption as well as chemisorption of the dithiocarbamate groups on cast iron disk and the piston ring surfaces giving rise to enhanced wear protection.

It can be seen that degradation of ZDDP in PFAD, as relative contact sliding took place resulted in the formation of tribo-layer containing the wear preventive chemistry of ZDDP at lower concentrations but at high concentration of 0.5%(wt), the tribo-film chemistry favored friction control but excessively increase wear, more than double the value of untreated PFAD. By implication, high dose of ZDDP in PFAD will not only place the formulation at environmental disadvantage but also increased wear.

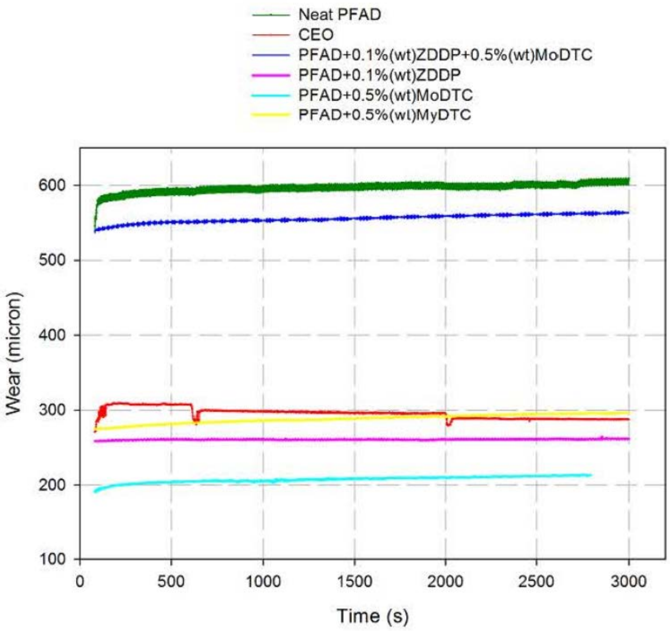

Figure 4: Wear versus time.

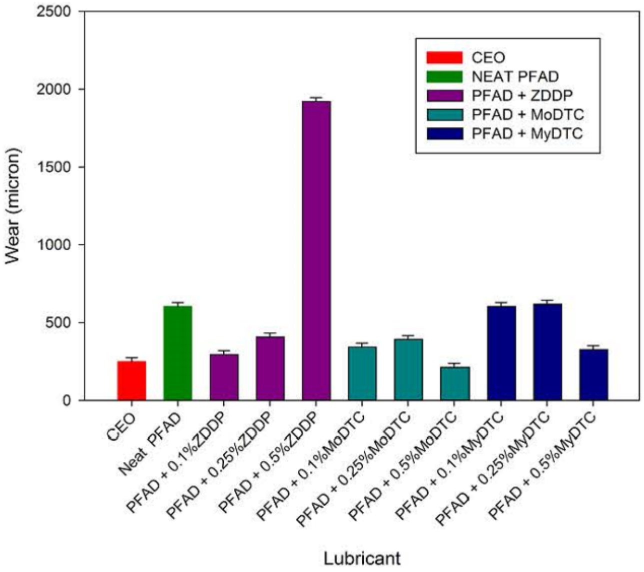

Figure 5: Wear versus additive concentration.

Lower values of %(wt) of MyDTC in PFAD showed no influence on the wear control (Figure.5). This is likely due to poor degradation during sliding contact, such that the ion exchange reaction between the additive and the substrates formed tribo-layer that have only low shear strength to reduce friction but not hard enough to reduce wear, until its composition reached 0.5%(wt). This shows that dithiocarbamates, at reasonable dose, would generally perform well in wear mitigation. The molybdenum compounds (such as MoS2) from decomposed MoDTC may be responsible for the superior performance of MoDTC over MyDTC in this work.

3.3 Friction and Wear Under Effect of Combined Additives

MoDTC at 0.5%(wt) offered the most attractive wear reduction (Figure. 5) and reasonable friction control (Figure. 3), hence it is selected as the parent additive at this concentration. This said additive concentration (0.5%(wt) MoDTC) is blended in PFAD in company of 0.1%(wt) ZDDP and 0.5%(wt) MyDTC separately and each tested under the same conditions. Note: the choice of 0.1%(wt) ZDDP and 0.5%(wt) MyDTC for this respective combination are based on their superior wear reduction characteristics among the initially tested doses of the respective additives. The two blends were separately tested under the same conditions and the results extracted and analyzed.

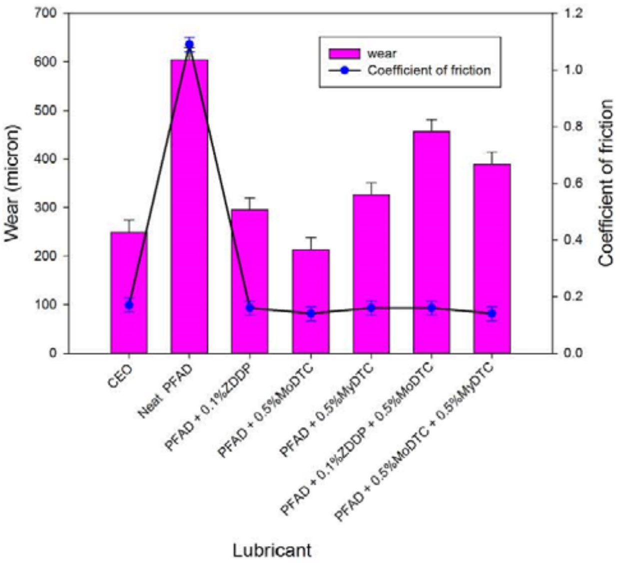

Figure 6: Effect of additives combination on wear and coefficient of friction.

The wear and friction reduction characteristics of the two separately combined additives blends are plotted in Figure. 6. The results of CEO, neat PFAD, PFAD + 0.1%(wt) ZDDP, PFAD + 0.5%(wt) MoDTC, and PFAD + 0.5%(wt) MyDTC were plotted along for ease of comparison or reference. It can be seen from the Figureure (Figure. 6) that instead of the expected synergistic ligand exchange reaction between ZDDP and MoDTC in the tribo-system (De Barros'Bouchet et al., 2005), there was higher wear, and insignificant impact on coefficient of friction as reported elsewhere (Morina et al., 2006). This may be due to non-conformity to equi-molar concentration of the additives as reported in previous study (De Barros'Bouchet et al., 2005) and/or differed decomposition mechanisms of the additives in PFAD. The third reason for this undesirable performance of the combined two additives can be due to antagonistic interactions of their tribo-film species in PFAD.

The combination of 0.5%(wt) MoDTC and 0.5%(wt) MyDTC in PFAD resulted in interestingly lower coefficient of friction compared to their individual performances. Unfortunately, this same combination step-up wear. The reason behind this increase in wear is yet to be understood.

3.4 Average Values of Tribo-Film Temperature of Selected Tests

The average values of tribo-film temperature extracted from the recorded data in selected tests were reported in Figure. 7. It is evident from the Figure that friction do increase temperature of the tribo-zone as all the reported average temperatures of the tribo-film during each test is higher than the ambient value. The average values of tribo-film temperature reported by neat PFAD and it additive-treated forms are lower compared to the commercial engine oil (CEO). This should be due to the fact that vegetable oils in neat and formulated forms normally exhibit better thermal conductivity than petroleum-derived lubricants. This characteristic will place the formulated PFAD lubricant at an advantage against thermo-oxidative breakdown.

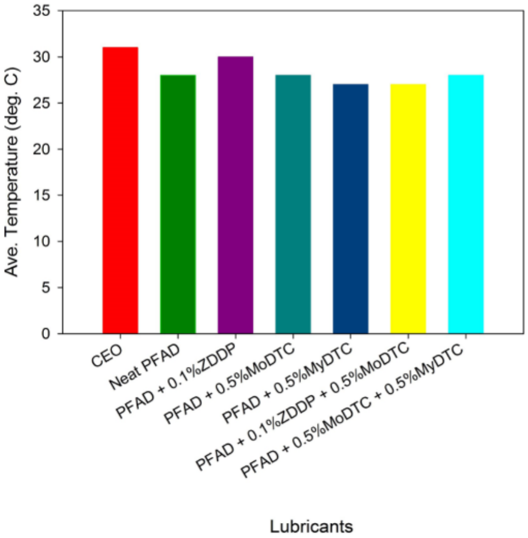

Figure 7: Ave. tribo-film temperature of selected tests.

3.5 Worn Surface Analysis

From a stand point of convenience, microscopic images of the worn surfaces of the piston rings tested under lubrication of commercial engine oil (CEO), neat PFAD, PFAD +0.5%(wt) MoDTC, and PFAD + 0.1%(wt) ZDDP + 0.5%(wt) MoDTC each are presented in Figure.8. The wear images (Figure. 8) are elliptical approving true contact mechanism of the simulated engine parts as reported in the literature (Kapsiz et al., 2011). Although the worn surfaces are dark in colour compared to the non-contact surfaces of the rings, those lubricated with PFAD-based lubricants are brighter than that of the CEO, with PFAD + 0.1% (wt) ZDDP+0.5% (wt) MoDTC being the brightest. This might be due to oxidation reaction of the vegetable oil and/or molybdenum reactive radicals with the ring surfaces. The surfaces also show some faint scratches along the sliding direction (laying vertically in the Figure arrangement). These might be indications of abrasive wear, implying the presence of fine debris as constituents of the tribo-film.

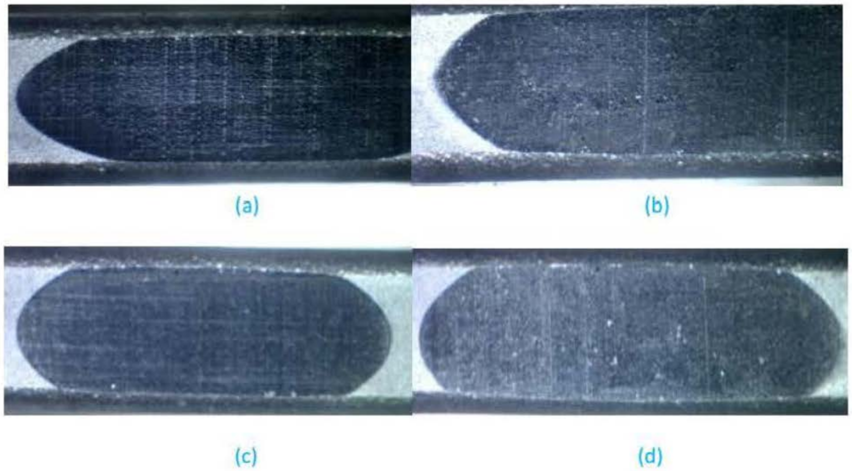

Figure 8: Microscopic images of the worn tested rings surfaces (500X). (a) CEO, (b) Neat PFAD, (c) PFAD + 0.5% (wt) MoDTC, (d) PFAD + 0.1% (wt) ZDDP+0.5% (wt) MoDTC.

4. CONCLUSIONS

Piston top ring-liner situation was simulated using a passenger car engine top ring, sliding on a cast iron disk on a pin-on-disk tribo-tester. The influence of neat PFAD and its ZDDP, MoDTC and MyDTC formulates, as lubricants, on the wear and friction control at the rubbing zone of the arrangement were studied under the same load of 200N, for a distance of 1500m at room temperature (27°C). 0.5%(wt) MoDTC, followed by 0.1%(wt) ZDDP separately doped PFAD resulted in preferable friction and wear control, and tribo-film temperatures compared to a commercial premium engine oil (CEO) tested under the same conditions for benchmarking. 0.5%(wt) MoDTC or 0.1%(wt) ZDDP in PFAD may offer acceptable wear and friction moderation at start-up or ambient temperature condition of the engine, and will perform satisfactorily in tribo-film temperature regulation.

A combination of the two additives doses in the base oil showed antagonism, the reason to this was not experimentally studied in this work.

The worn surface morphology is elliptical in shape, approving the true contact mechanism of the simulated engine top piston ring – cylinder liner situation.

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