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Formulation of Refined, bleached and deodorised Palm Stearin with Zinc dialkyl-dithiophosphate Additive and Its Tribological Performance

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Abstract

Vegetable oils have recently received worldwide attention for their use as a lubricant base stock that has numerous advantages, including their environmental friendliness. In this study, a refined, bleached and deodorised palm stearin was selected as the base lubricant, and its friction and wear performance were investigated with a pin-on-disk tribotester. The effect of zinc dialkyl-dithiophosphate (ZDDP) additive in concentrations of 1wt%, 3wt% and 5wt% on friction and wear performance were evaluated. Commercial semi-synthetic oil SAE 15W50 was used for comparison purposes. The experiments were conducted at a sliding speed of 1.5 m/s under a normal force of 9.81 N for 60 min. Results show that an increase in ZDDP concentrations improved both friction reduction and wear performance of the lubricant. The coefficient of friction (COF) of RBD palm stearin was reduced approximately at 71% when 5wt% of ZDDP was added and it shows that the friction reduction performance of PS+5wt% (COF=0.039) was comparable to SAE 15W50 (COF=0.035). While, wear coefficient of RBD palm stearin was reduced significantly from 2.08×10^{-3} to 8.89×10^{-5} when 5wt% ZDDP additive was added and it shows that the wear performance of PS+5wt% was better than that of SAE 15W50, 1.94×10^{-4}. Further analysis of the wear worn surface with a high-resolution optical microscope was also conducted with a surface profilometer to examine the metallurgy of the pin surface and the roughness of the pin.

Keywords: RBD palm stearin, ZDDP, coefficient of friction, wear coefficient

1.0 INTRODUCTION

In 2004, approximately 37.4 million tonnes of lubricants were consumed worldwide in automotive applications (53%), industrial lubricants (32%), process oils (10%) and marine oils (5%) [1]. Many countries are heavily dependent on petroleum- or mineral oil-based lubricants as a source for many machinery applications. The world is currently facing the depletion of crude oil reserves, increases in oil prices and an increase in environmental problems [2 - 3]. Thus, the only possible solution to these problems is finding an alternative lubricant that can fulfil the demand for lubricants and serve as a renewable and biodegradable source. These concerns have stimulated an increased interest in renewable and biodegradable lubricants to replace mineral-oil-based lubricants.

Vegetable oils have attracted special attention from many researchers because of their advantages in terms of renewability, biodegradability, non-toxicity and environmental friendliness compared with mineral oil [4 - 5]. Some vegetable oils, such as soybean oil, castor oil, rapeseed oil, palm oil, coconut oil, canola oil and Jatropha oil, are commonly studied by researchers because of their wide availability. Among these vegetable oils, palm oil has the world's largest production at 38.5 million tonnes, with Malaysia producing more than 40% of it [6]. Previous researchers demonstrated that palm oil can be used as a lubricant in various applications, including engine oil [7], biodiesel [8], industrial-cutting lubricants [9], metal-forming process [10], hydraulic fluids [11] and as a source of lubrication in the biomedical industry [12]. Researchers suggested that palm oil has potential use as an automotive and industrial lubricant in the near future.

Palm oil is a versatile vegetable oil that can be used for both food and non-food products. Different types of oils are produced, such as palm fatty acid; refined, bleached and deodorised (RBD) palm olein; palm stearin (PS) and RBD palm kernel. RBD palm olein is used extensively for cooking oil production, but the other oils are not widely commercialised. The excess supply of palm oil has been reported [6], and discovering alternative applications for palm oil has been suggested. This study focuses on RBD PS, which will not disturb food proportion. Very limited references have reported on the use of RBD PS as the base lubricant and blended with an additive to improve its lubrication performance.

Although vegetable oils have excellent lubrication properties, they have drawbacks in terms of their oxidative, thermal and hydrolytic stabilities [13 - 14]. The reason for the oxidative instability of vegetable oil is the rapid reactions occurring at the 'double bond' of carbon in molecule [15]. Putting additives in vegetable oils is required to reduce friction and wear to a minimum. The zinc dialkyl-dithiophosphate (ZDDP) additive is commonly used as a lubricant additive; it is known for its ability to significantly enhance resistance to wear and its behaviour as an antioxidant [16]. Some recent studies have shown the effectiveness of a ZDDP additive in vegetable oil-based lubricants [17 - 20].

The objective of this study, therefore, is to investigate the friction and wear performance of various concentrations of ZDDP additives in RBD PS with the use of a pin-on-disk tribotester. Commercial semi-synthetic oil SAE 15W50 was used for comparison purposes. RBD PS was selected as the base lubricant because palm oil is widely grown in Malaysia.

2.0 EXPERIMENTAL METHODOLOGY

2.1 Pin-on-Disk Tribotester

The friction and wear properties of the tested lubricants were evaluated with a pin-on-disk tribotester, in which the stationary pin is made of pure aluminium A1100 that forms a point contact with a rotating SKD11 tool steel disk. Normal force was applied with a dead weight that has been suspended on one end of the lever. The friction force between the stationary pin and the rotating disk was measured with a load cell, whereas wear was measured with a linear voltage differential transformer sensor. The disk was designed to have a groove to ensure that the tested lubricants do not flow out during the rotation of the disk. Acetone is used to clean the surface of the disk because no debris should be found on the surfaces. Each test was repeated twice under the same conditions to ensure a good repeatability of the results and for a precise evaluation of tribological properties.

2.2 Materials and Lubricants

The pin used in this research is made up of pure aluminium A1100, and the disk is from tool steel SKD11. The density of A1100 was 2.71 g/cm^3, and that of SKD11 was 7.85 g/cm^3. The dimensions of the pin were 6 mm in diameter with a hemispherical end and 30 mm in length, whereas the geometry of the disk was 160 mm × 10 mm (see Figure 1).

Refined, bleached and deodorized (RBD) PS was used in this study, with and without a ZDDP additive. The ZDDP concentrations added into the RBD PS were 1%, 3% and 5% in weightage. For comparison purposes, commercial semi-synthetic oil SAE 15W50 was chosen. Table 1 shows some physical properties of the tested lubricants. The contact point of the pin and rotating disk was lubricated under a limited amount of lubricant (2.5 mL). A mixture of RBD PS and ZDDP additive was prepared in volumes of 100 g. The two substances were mixed with a mixer at a high speed for about 1 h and heated at 40 °C–50 °C to form a homogeneous mixture.

2.3 Experimental Procedure

The friction reduction and anti-wear properties of ZDDP in RBD PS were evaluated with a pin-on-disk tribotester. The stationary pin was in contact with the disk at a constant vertical force, whereas the disk was rotated at a specified speed and created a sliding contact. All tests were conducted at 1.5 m/s sliding speed for 60 min under 9.8 N load at room temperature, which is around 25 °C (±2° C). The pins were cleaned with acetone before and after each test.

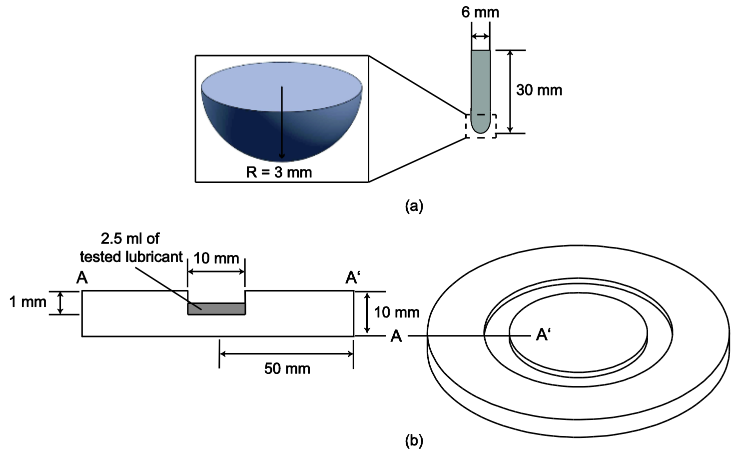

Figure 1 Geometry of the (a) pin and (b) disk

Table 1 Some physical properties of the RBD palm stearin blended with various concentration of ZDDP additive

Lubricant	SO	PS	PS+1%	PS+3%	PS+5%
Specific density (g/cm³)	0.87	0.88	0.90	0.90	0.90
Kinematic viscosity at 40℃ (mm²/s)	112.90	38.01	34.90	37.37	35.73
Dynamic viscosity at 40℃ (mPa s)	98.22	33.45	31.41	33.63	32.16
Kinematic viscosity at 100℃ (mm²/s)	20.90	8.55	9.42	10.74	12.05
Dynamic viscosity at 100℃ (mPa s)	18.18	7.52	8.48	9.67	10.85
Viscosity index (VI)	211.89	212.56	270.94	294.90	351.60

2.4 Friction and Wear Analysis

Frictional force was measured with a load cell connected to the pin, and the values were taken directly from the software with an installed image acquisition system. The coefficient of friction was then calculated by division of the normal force pressing the pin against the disk. Then, the effectiveness of the ZDDP additive in wear reduction was identified by measurement of the wear scar diameter on the pins. The wear scar diameter on the pins was measured with an optical microscope to calculate the wear volume (V), as in Equation (1) [21].

$$V = \frac{\pi r^4}{4R} \qquad (1)$$

where r is the radius of the pin wear scar (in unit mm), and R is the original pin radius (in unit mm).

Then, the wear volume is calculated with Archard's law to characterise the tribological response of the pin and disk contacts, as shown as Equation (2).

$$K = \frac{VH}{SF} \qquad (2)$$

where K is the dimensionless wear coefficient, V is the volume of material removed by wear, H is the hardness of the specimen, S is the sliding distance and F is the applied force [22]. In this study, the hardness of the pin is 30 HV.

2.5 Surface Analysis

The surface roughness of the pins was measured at the end of the experiment with a surface profiler. Surface roughness parameter Ra represents the arithmetic mean of the profile calculated from the absolute values of the profile amplitudes and the arithmetic mean of the measured profile [23]. Surface roughness parameter Ra was used to describe the surface features of the wear components and analyse the influence of the lubricants used. The surface roughness parameter of the pin surfaces was measured perpendicular to the direction of sliding.

The worn surface of the pins was analysed after each test, and it was observed with an optical microscope. The surface analysis of the worn pins was important to prove that the ZDDP additive can improve the anti-wear performance of the RBD PS. To ensure that no excess oil can be found on the surface of the pin, the pins were cleaned carefully after each test.

3.0 RESULTS AND DISCUSSION

3.1 Friction-Reducing Performance

The experiments were conducted with a pin-on-disk tribotester in accordance with ASTM G99. The pin-on-disk tribotester was run at 1.5 m/s sliding speed under a normal load of 9.8 N at room temperature (25 °C ± 2 °C) for an hour. For comparison purposes, the test was repeated with a commercial semi-synthetic oil SAE 15W50 (SO). A ZDDP additive was added at three different concentrations, which were 1wt%, 3wt% and 5wt%, to improve the friction-reducing performance of RBD PS. The coefficient of friction (COF) was calculated by division of the frictional force obtained directly from the data acquisition system with the normal load applied; this is plotted in Figure 2. Without a ZDDP additive, RBD PS possesses a high COF compared with SO. The figure shows that an increase in additive concentration improves the friction-reducing performance of RBD PS. A large reduction in the COF, approximately 39%, was observed only when 1wt% of the ZDDP additive was added, and then the friction continues to be reduced until 0.039 when the ZDDP additive is 5wt%. PS+5wt% has a friction-reducing performance compared with SO, which has a COF of 0.035.

The high content of unsaturated fatty acid in RBD PS may be considered to contribute to the high COF. A high content of unsaturated fatty acid in vegetable oil is highly known to decrease its resistance to oxidative degradation. According to Joseph and Sharma, vegetable oil oxidises like hydrocarbon mineral oil following the same free radical oxidation mechanism but at a faster rate [24]. The COF seemed to decrease with an increase in the concentration of ZDDP. This observation means that ZDDP has the ability to enhance the friction-reducing performance of sliding surfaces. ZDDP forms a thin film on the surface, called the ZDDP tribofilm, to prevent the contact between surfaces and thus reduce friction and wear.

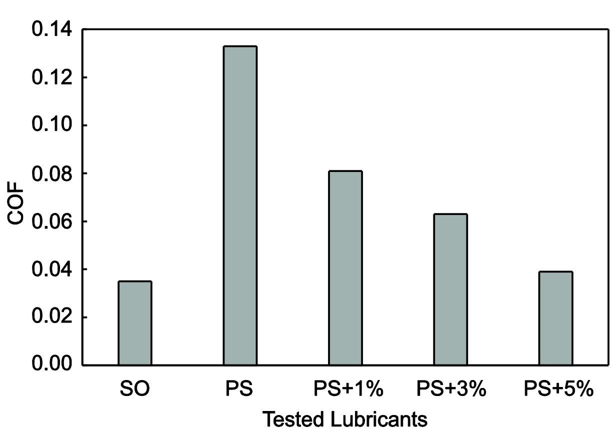

Figure 2 Coefficient of friction values at sliding speed 1.5 m/s and 9.8 N normal load

3.2 Wear Performance

The wear scar diameter of the pin surfaces was measured with an optical microscope, and the values were used to calculate the pin volume loss to obtain the wear coefficient. Then, the wear coefficient of the pin specimen was plotted in Figure 3. The wear coefficient of RBD PS, which is 2.08 x 10^{-3}, is significantly larger than that of SO, which is 1.94 x 10^{-4}. The addition of 1wt% ZDDP additive in RBD PS significantly reduces the wear coefficient of RBD PS from 2.08 × 10^{-3} to 3.62 x 10^{-4}. Further addition of the ZDDP additive improves the wear performance of RBD PS, where PS+3wt% has the same anti-wear performance as SO, and PS+5wt% shows the best anti-wear performance. These results proved that the ZDDP additive can effectively control wear in RBD PS.

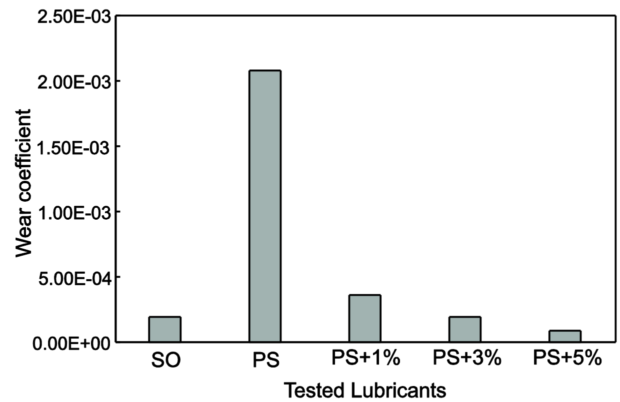

Figure 3 Wear coefficient of the pin specimen

RBD PS without additives added has a large wear scar diameter because of the chemical reaction on the surface by the fatty acids in the oil. The effective lubricant layer on the metal surfaces formed earlier will rub away and produce non-reactive detergents, which in turn increase wear [25]. The presence of the ZDDP additive in RBD PS improves wear properties. The ZDDP additive reduces friction and wear by forming a protective film (tribofilm) between the sliding surfaces to prevent direct metal-to-metal contact. Lin and So stated that the anti-wear performance of ZDDP results from a physisorbed film that prevents contact between interfaces at low temperatures [26].

In addition, the concentration of the ZDDP additive affects the rates of tribofilm formation on the surface; an increment in ZDDP concentration improves the wear properties of metal surfaces. This phenomenon was supported by Asadauskas *et al.*, who mentioned that the rates of tribofilm formation depends on the concentration of the ZDDP additive on the metal surface [18]. Choi *et al.*, however, claimed that the anti-wear capability of antiwear (AW) additives depended on the shear strength of the protective film formed [27]. Tribofilm provides good wear protection because of both its sufficiently high shear strength, which enhances its integrity, and its sufficiently low shear strength, which ensures that shear deformation occurs primarily in the protective tribofilms [28].

3.3 Surface Analysis

Figure 4 shows the arithmetic mean deviation of the surface roughness (Ra) of the pin specimen. The measurement was taken at a constant line length of 0.40 mm with a surface profiler. The wear debris generated during the wear acts as an abrasive material that gradually transforms the two-body abrasive mechanism into a three-body abrasive mechanism and leads to more material loss. This material loss affects the value of the Ra because the presence of the abrasive groove represents the material loss. The plots show that PS has a rougher surface than SO, in which a rougher surface roughness represents a deeper groove. RBD PS has a highly unsaturated fatty acid composition, so it easily undergoes oxidation and thus causes the removal of the soap film during sliding. The destruction of this soap film causes great metal-to-metal contact and generates deep scratches on the pin surface. The addition of 1wt% surprisingly increases the surface roughness of PS, but the surface roughness of the pin becomes smoother as the ZDDP concentration increases. The figure also shows that PS+5wt% has a smooth surface compared with that of SO, although the SO has a lower COF. The presence of ZDDP in the RBD PS contributed to the prevention of rapid oxidation, which minimised the rate of removal of the soap film and thus resulted in a smooth surface.

Further confirmation of the wear behaviour of the pin surfaces lubricated with SO and RBD PS with and without additive was made by analysis of the wear worn surface. The wear worn surface of the pins was examined with a high-resolution microscope in a 200µ measurement. Figure 5 shows the physical appearance of the worn pin surfaces lubricated by a commercial semi-synthetic oil SAE 15W50 (SO), an RBD PS, a PS + 1wt% ZDDP, a PS + 3wt% ZDDP and a PS + 5wt% ZDDP. Generally, the figure shows that abrasive wear was the dominant wear mechanism represented by the parallel groove found on the surface. From this figure, a deep and abrasive groove was observed in PS+1wt%, and some dark regions can also be seen on the wear surfaces of the pin. However, the scratches are fewer with an increment in the concentrations of the ZDDP additive. For the specimens tested with RBD PS with a 5wt% ZDDP additive, smooth worn surfaces were observed. This result means that at this concentration, the surface was fully protected by the ZDDP additive.

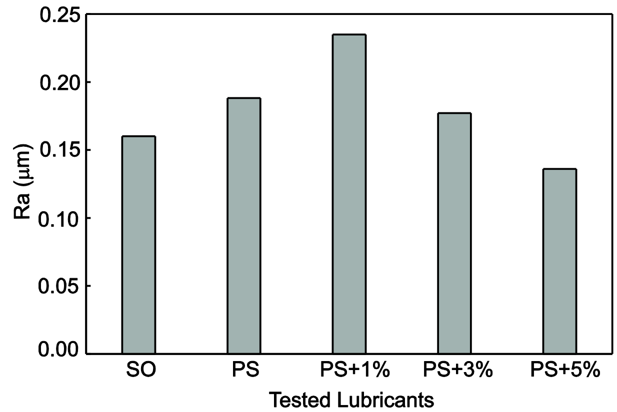

Figure 4 Arithmetic mean deviation of the surface roughness (Ra) of the pin specimen

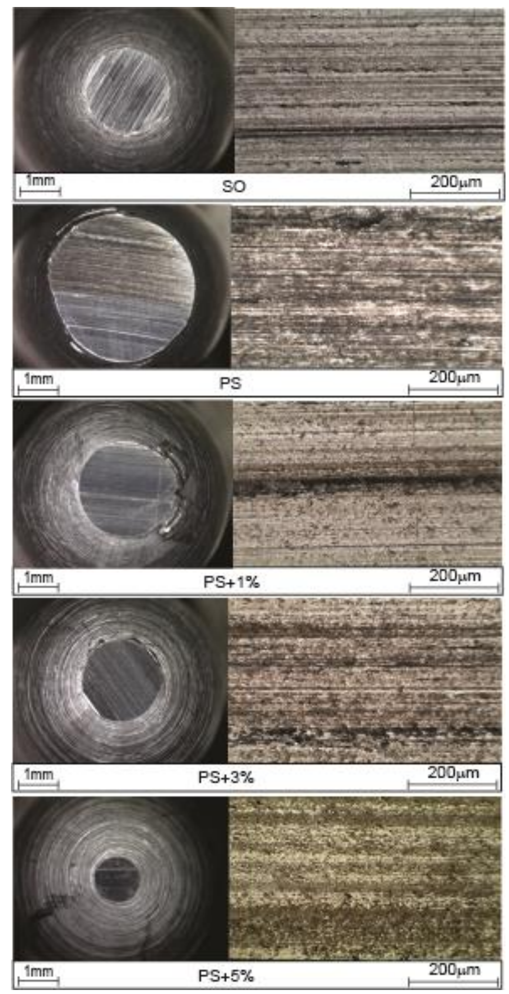

Figure 5 Physical appearance of the pin's worn surface

4.0 CONCLUSION

The tribological properties of a ZDDP additive in RBD PS have been evaluated with a pin-on-disk tribotester. Commercial semi-synthetic oil was used for comparison purposes. The findings can be summarised as follows:

1. Unformulated RBD PS generates a higher coefficient of friction (73%) and wear coefficient (90%) than commercial semi-synthetic oil SAE 15W50 (SO).
2. The formulation of RBD PS with a ZDDP additive improves both the friction-reducing and anti-wear properties of the lubricant. The optimum ZDDP additive concentration in this study is 5wt%.
3. PS+5wt% ZDDP exhibits excellent anti-wear properties, and SO exhibits excellent friction-reducing performance.
4. Worn surface analysis with an optical microscope shows abrasive wear as the dominant wear mechanism for both with and without ZDDP additive in RBD PS and a commercial semi-synthetic oil.

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Nomenclature

V	wear volume
r	radius of the pin wear scar
R	original pin radius
K	dimensionless wear coefficient
H	hardness of the pin specimen
S	sliding distance
F	applied force
Ra	arithmetic mean surface roughness

References

[1] Nagendramma, P., and S. Kaul. 2012. Development of Ecofriendly/Biodegradable Lubricants: An Overview. *Renewable and Sustainable Energy Reviews.* 16(1): 764-774.

[2] Syahrullail, S., C. S. N. Azwadi, and T. C. Ing. 2011. The Metal Flow Evaluation of Billet Extruded with RBD Palm Stearin. *International Review of Mechanical Engineering.* 5(1): 21-27.

[3] Arumugam, S. and G. Sriram. 2012. Effect of Bio-Lubricant and Biodiesel-Contaminated Lubricant on Tribological Behavior of Cylinder Liner–Piston Ring Combination. *Tribology Transactions.* 55(4): 438-445.

[4] Quinchia,L. A., M. A. Delgado, T. Reddyhoff, C. Gallegos, and H. A. Spikes. 2014. Tribological Studies of Potential Vegetable Oil-Based Lubricants Containing Environmentally Friendly Viscosity Modifiers. *Tribology International.* 69: 110-117.

[5] Sapawe, N., S. Syahrullail, and M. I. Izhan. 2014. Evaluation on the Tribological Properties of Palm Olein In Different Loads Applied using Pin-on-Disk Tribotester. *Jurnal Tribologi.* 3: 11-29.

[6] Lam, M. K., K. T. Tan, K. T. Lee, and A. R. Mohamed. 2009. Malaysian Palm Oil: Surviving the Food versus Fuel Dispute for a Sustainable Future. *Renewable and Sustainable Energy Reviews*. 13(6-7): 1456-1464.

[7] Zulkifli, N. W. M., M. A. Kalam, H. H. Masjuki, M. Shahabuddin, and R. Yunus. 2013. Wear Prevention Characteristics of a Palm Oil-Based TMP (trimethylolpropane) Ester as an Engine Lubricant. *Energy*. 54: 167-173.

[8] Haseeb, A. S. M. A., S. Y. Sia, M. A. Fazal and H. H. Masjuki. 2010. Effect of Temperature on Tribological Properties of Palm Biodiesel. *Energy*. 35(3): 1460-1464.

[9] Rahim, E. A. and H. Sasahara. 2011. Investigation of Tool Wear and Surface Integrity on MQL Machining of Ti-6AL-4V using Biodegradable Oil. *Proceedings of the Institution of Mechanical Engineers Part B: Journal of Engineering Manufacturing*. 225(9): 1505-1511.

[10] Hafis, S. M., M. J. M. Ridzuan, R. N. Farahana, A. Ayob, and S. Syahrullail. 2013. Paraffinic Mineral Oil Lubrication for Cold Forward Extrusion: Effect of Lubricant Quantity and Friction. *Tribology International.* 60: 111-115.

[11] Nik, W. B. W., F. Zulkifli, S. S. Lam, M. M. Rahman, A. A. Yusof, and M. M. Rahman. 2014. Experimental Studies on the Rheological and Hydraulic Performance of Palm Based Hydraulic Fluid. *Jurnal Teknologi.* 66(3): 7-13.

[12] Razak, D. M., S. Syahrullail, N. Sapawe, Y. Azli, and N. Nuraliza. 2015. A New Approach Using Palm Olein, Palm Kernel Oil, and Palm Fatty Acid Distillate As Alternative Biolubricants: Improving Tribology in Metal-on-Metal Contact. *Tribology Transactions*. 58(3): 511-517.

[13] Wagner, H., R. Luther, and T. Mang. 2001. Lubricant Base Fluids Based on Renewable Raw Materials Their Catalytic Manufacture and Modification. *Applied Catalysis A: General.* 221: 429-442.

[14] Zulkifli, N. W. M., H. H. Masjuki, M. A. Kalam, R. Yunus, and S. S. N. Azman. 2014. Lubricity of Bio-Based Lubricant Derived From Chemically Modified Jatropha Methyl Ester. *Jurnal Tribologi.* 1: 18-39.

[15] Arumugam S. and G. Sriram. 2012. Synthesis and Characterisation of Rapeseed Oil Bio-Lubricant - Its Effect on Wear and Frictional Behaviour of Piston Ring-Cylinder Liner Combination. *Proceedings of the Institution of Mechanical Engineers Part J: Journal of Engineering Tribology*. 227(1): 3-15.

[16] Barnes, A. M., K. D. Bartle, and V. R. A. Thibon. 2001. A Review of Zinc Dialkyldithiophosphates (ZDDPS): Characterisation and Role in the Lubricating Oil. *Tribology International.* 34: 389-395.

[17] Jayadas, N. H., K. Prabhakaran Nair, and G. Ajithkumar. 2007. Tribological Evaluation of Coconut Oil as an Environment-Friendly Lubricant. *Tribology International.* 40(2): 350-354.

[18] Asadauskas, S. J., G. Biresaw, and T. G. Mcclure. 2010. Effects of Chlorinated Paraffin and ZDDP Concentrations on Boundary Lubrication Properties of Mineral and Soybean Oils. *Tribology Letters.* 37: 111-121.

[19] Mahipal, D., P. Krishnanunni, M. R. P, and N. H. Jayadas. 2014. Analysis of Lubrication Properties of Zinc-Dialkyl-Dithio-Phosphate (ZDDP) Additive on Karanja Oil (Pongamia pinnatta) as a Green Lubricant. *International Journal of Engineering Research*. 3(8): 494-496.

[20] Azhari, M. A. and F. Tamar. 2015. Physical Property Modification of Vegetable Oil as Biolubricant using ZDDP. *ARPN Journal of Engineering and Applied Sciences.* 10(15): 6525-6528.

[21] Oğuz, H., H. Düzcükoğlu and Ş. Ekinci. 2011. The Investigation of Lubrication Properties Performance of Euro-Diesel and Biodiesel. *Tribology Transactions.* 54(3): 449-456.

[22] Waara, P., J. Hannu, T. Norrby, and Å. Byheden. 2001.

Additive Influence on Wear and Friction Performance of Environmentally Adapted Lubricants. *Tribology International.* 34(8): 547-556.

[23] Parthasarathi, N. L., U. Borah, and S. K. Albert. 2013. Correlation between Coefficient of Friction and Surface Roughness in Dry Sliding Wear of AISI 316 L (N) Stainless Steel At Elevated Temperatures. *Computer Modelling and New Technologies*. 17(1): 51-63.

[24] Joseph, P. V. and D. K. Sharma. 2010. Improvement of Thermooxidative Stability of Non-Edible Vegetable Oils of Indian Origin for Biodegradable Lubricant Application. *Lubrication Science*. 22: 149-161.

[25] Ing, T. C., A. K. M. Rafiq, Y. Azli, and S. Syahrullail. 2012. Tribological Behaviour of Refined Bleached and Deodorized Palm Olein In Different Loads using a Four-Ball Tribotester. *Scientia Iranica.* 19(6): 1487-1492.

[26] Lin, Y. C. and H. So, 2004. Limitations on Use of ZDDP as an Antiwear Additive in Boundary Lubrication. *Triboogy. International.* 37: 25-33.

[27] Choi, U., B. Ahn, O. Kwon, and Y. Chun. 1997. Tribological Behavior of Some Antiwear Additives In Vegetable Oils. *Tribology International.* 30(9): 677-683.

[28] Komvopoulos, K., V. Do, E. S. Yamaguchi, and P. R. Ryason. 2004. Nanomechanical and Nanotribological Properties of an Antiwear Tribofilm Produced from Phosphorus-Containing Additives on Boundary-Lubricated Steel. *Journal of Tribology*. 126: 775-780.