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ANTI-WEAR CHARACTERISTICS OF JATROPHA TRIMETHYLOLPROPANE (TMP) ESTER

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A ABSTRACT

This paper presents the experimental results from an evaluation of the wear prevention characteristics of a jatropha oil-based trimethylolpropane (TMP) ester using a four-ball machine (ASTM D4172). The load, speed and lubricant sample temperature were set at 40 kgf (393 N), 1200 rpm and 75 °C, respectively. Under these test conditions, the wear and friction characteristics of different TMP samples were measured and compared. The TMP ester was produced from jatropha; it is biodegradable and has high lubricity properties such as a higher flash point temperature and viscosity index (VI). It has an affinity to surface at asperity, hence reduces wear between sliding contacts. The results presented in this investigation include the viscosity index (VI), density, total acid number (TAN), total base number (TBN), wear scar diameter (WSD), coefficient of friction (COF), a wear micrograph using scanning electron microscopy (SEM) and the surface roughness of ball wear. It was found that at certain blends of TMP in the lubricant decreased WSD and COF. Sample TMP10 (10% TMP and 90% original lubricant) showed the lowest wear and COF, as confirmed by SEM results. The results of this investigation will be used to develop new and efficient lubricants for automotive engines.

Keywords: Automotive engines, sliding wear, liquid impact erosion, rolling friction, TMP.

1. INTRODUCTION

There has been enormous interest in the use of oils from renewable sources such as animal fats and vegetable oils (Rhee,1996; Waara et al.,2001; Sharma et al.,2009). In addition to a continuous supply, the biodegradability of bio lubricants, the uncertainty of the crude oil supply and its price give bio lubricants more advantages over mineral base oils. However, vegetable oil in its natural form has limited usage due to its poor oxidation stability (Erhan et al.,2006) and behaviour at low temperatures (Adhvaryu et al.,2002). Therefore, many investigations have been undertaken in order to improve the working range and applicability of biodegradable lubricants (Yunus et al., 2003; Quinchia et al., 2009; Shah et al., 2010).

The trimethylolpropane (TMP) ester is produced from a jatropha methyl ester through transesterification. Transesterification eliminates the hydrogen molecule on the beta carbon position of the jatropha substrate, thus improving the oxidative and thermal stability of the new TMP ester; a property seldom found in vegetable oils (Gunstone et al.,1994). In addition to this, TMP esters have good friction-reducing properties and acceptable anti-wear properties (Randles, 1999). However, in contrast, (Rieglert and Kassfeldt, 1997) found that a “conventional” mineral oil offered 3 to6 times fewer wear than a rapeseed oil/synthetic blend or a pure synthetic ester under boundary lubrication conditions.

Wear studies under lubricated conditions can be understood following the three important aspects: (i) the friction surfaces are in contact at surface micro asperities, (ii) the hydrodynamic effects of lubricating oil or the rheological characteristics of bulk do not significantly influence surface wear, and (iii) interactions in the contact between friction surfaces and between friction surfaces and the lubricant (including additives) dominate tribological characteristics (Hsu et al., 2002).

This paper describes wear and friction mechanisms under hydrodynamic lubrication conditions, also known as wear prevention test characteristics, when TMP was used as an alternative lubricant.

2. METHODOLOGY

2.1 Lubricant sample preparation

For this investigation, jatropha TMP esters were supplied by Universiti Putra Malaysia and mixed with SAE 40 engine oil manufactured by a known company. These TMP esters were synthesized by the transesterification of methyl esters prepared from palm oils and TMP. The TMP was selected due to its lower melting point compared to other polyols. A 200 g volume of jatropha methyl ester and a known amount of TMP was placed into a 500 ml three-neck reactor and constantly agitated by a magnetic stirrer. The weight of TMP was determined based on the required molar ratio and the calculated mean molecular weight of the jatropha methyl esters (JOME). The mixture was then heated to reaction temperature, and the catalyst was added. A vacuum was gradually applied to the system until the desired pressure was reached. This pressure was maintained until the reaction reached completion.

Both jatropha oil-based TMP esters were blended with SAE 40 using a stirrer at 110 rpm and heated to 100 °C. The blended lubricants consisted of 5%, 10%, 15%, 20% and 100% jatropha TMP esters (volume basis) with SAE 40 (shown in detail in Table 1). The standard that used to measure these properties are listed in Table 2 along with their accuracy levels of the equipment.

Table 1: Percentages of the jatropha oil-based TMP ester and SAE 40 in each sample

Sample	TMP ester (%)	SAE 40 (%)
TMP0	0	100
TMP10	10	90
TMP20	20	80

Table 2: List of the pieces of test equipment used and their accuracy levels

Test parameters	ASTM standard	Accuracy level (Equipment)
Density (g/cc)	ASTM D2270	± 0.001
Viscosity index and viscosity (cSt)	ASTM D445	± 0.01
TAN/TBN (mg KOH/g)	ASTM D664/D2896	± 0.01
Flash point (°C)	ATM D93	± 1
Pour point (°C)	ATM D97	± 1
Briness hardness tester	-	± 0.5
Four-ball machine	Hydrodynamic test	-

2.2 Wear and friction testing machine

The four-ball wear tester is the predominant wear tester used by the oil industry to study lubricant chemistry. It has been widely used to study the lubricating properties of oils and the chemical interactions at wear contacts (Hsu and Klaus, 1978).

The four-ball wear tester consists of three balls held stationary in a ball pot plus a fourth ball held in a rotating spindle. The balls are 1.27 cm (0.5 in) in diameter. Loads are applied by way of a spinning ball, which presses into the centre of the triangular formation of the three stationary balls. The load may be selected within the range of 1 to 180 kgf, while the rotation speed may be chosen from 60 to 3000 r/min. The temperature of the sample chamber can be controlled by means of a heater attached to the ball pot. With the balls in place, the ball pot has sufficient capacity for 10 ml of lubricant. The primary measurement made with a four-ball machine is wear. The wear produced on the three stationary balls is measured under a calibrated optical microscope and reported as the scar (WSD) or calculated volume. The wear volumes are usually calculated on the assumption that the wear occurs only on the stationary balls. The missing metal is assumed to come from spherical segment of the stationary balls that correspond to the net volume occupied by the rotating spherical ball that fits into scar wear (I-Ming,1962). Studies have shown that the measured wear volume and the calculated wear volume can differ greatly depending on the location of wear (Willermet et al., 1983).

2.3 Friction materials

The four-ball machine described by Weller and Perez, 2001 and Masjuki and Maleque, 1997 was used to determine the friction and wear characteristics of the test fluids. The balls used in this study were steel balls, AISI 52-100, 12.7 mm in diameter, with 64-66Rc hardness. These balls were thoroughly cleaned with toluene before each experiment. The sample volume required for each test was approximately 10 ml. The test conditions were 60 min with an operating temperature of 75 °C ± 2 °C, and 1200 rpm.

2.4 Wear prevention test

A wear prevention test (hydrodynamic lubrication) was performed using the four-ball test machine. The test method used was ASTM D4172/D2266, which describes three hard steel balls in a locked position. A fourth ball was rotated against the three stationary balls, producing a wear scar on each of the three balls, from which an average wear scar diameter was obtained. This test was run under light to medium loads. Normally, seizure or welding does not occur. Hydrodynamic lubrication normally exists in engine bearings and piston rings. In hydrodynamic lubrication, the fluid completely isolates the friction surfaces [h>>R], and the internal fluid friction (dynamic viscosity) alone determines the tribological characteristics such as wear and friction.

3. RESULT AND DISCUSSION

All of the tests and data analyses for the different lubricants were performed in the tribology laboratory, Department of Mechanical Engineering, University of Malaya. The data were used to evaluate the differences between these lubricants and to serve as a basis for comparing the blended fuels with jatropha oil-based TMP esters. The percentage of palm TMP ester and SAE 40 in each sample is shown in Table 1. All of the lubricant properties are listed in Table 3.

Table 3: Properties of the different percentages of the TMP ester in SAE 40

Properties \ Sample	TMP0	TMP10	TMP20
Kinematic viscosity at 100 °C (cSt)	15.53	12.476	11.389
Kinematic Viscosity at 40 °C (cSt)	107.41	82.544	68.708
Viscosity index	154	148	160
Density at 15 °C (g/cm^3)	0.871	0.8759	0.8794
TAN(mg KOH/g)	1.02	0.78	0.58
TBN (mg KOH/g)	8.23	6.81	5.51
Flash point (°C)	220	235	251
Pour point (°C)	-35	-33	-28

The study of wear properties was based on the average wear scar diameter (WSD) formed on the stationary balls. The scars were measured using an optical microscope. The coefficient of friction (COF) was calculated from the equation described by Weller and Perez, 2001 and Masjuki and Maleque, 1997. The wear properties of test samples were schematically compared with the commercial SAE 40 lubricant.

The wear scar diameter results for the different percentages of jatropha oil-based TMP ester in SAE 40 are shown in Figure 1. It was found that the maximum improvement in WSD was found for TMP10, around 43% TMP compared to commercial SAE 40. This finding was similar to the findings reported by Yunus et al., 2004, who found a jatropha oil-based TMP ester to have a better WSD compared to commercial hydraulic fluid. In addition, Masjuki et al., 1999 also found that palm-based lubricating oil had a better wear performance compared to mineral oil. However at TMP 20 and TMP 100, WSD increased with increasing TMP ester. Fernández Rico et al., 2002 reported that the addition of a synthetic ester (TMP) to a low viscosity polyalphaolefin acted as a wear reducer. This was because the decreased kinematic viscosity and increased flash point with increasing amounts of TMP in SAE 40 improved the WSD. According to Havet et al., 2001 the length of the fatty acid chains tends to increase the adsorbed film thickness, therefore increasing the surface area protected. In addition to this, an increase in the number of ester groups leads to greater binding of the molecules and therefore a greater resistance to shear forces.

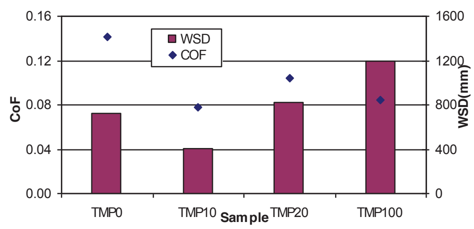
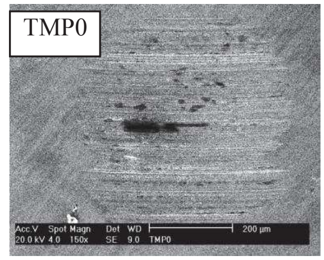


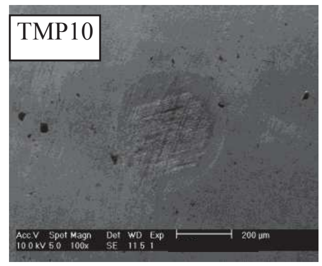
Figure 1: Wear scar diameters (WSD) and CoF for different percentages of the jatropha oil-based TMP esters in SAE 40

The values of COF for the various lubricant samples are shown in Figure 1; TMP10 and showed the lowest levels of COF. This was mainly due to a reduced kinematic viscosity compared to the SAE 40 lubricant. The low kinematic viscosity reduced the intermolecular shear forces that are helpful in effective load transfer. For TMP 100, even the WSD is larger, COF is lower. It is believe due to the continuous removal of metallic soap film that is formed as a result of the reaction of the oil with the metallic surface during sliding (Bowden and Tabor, 2001). The metallic film is continuously reformed by further chemical reaction. Since the metallic soaps are of low shear strength, the coefficients of friction will be low.

The optical photomicrographs of the area around the wear scar and the worn surfaces of the ball specimens for the different percentages of the TMP esters are shown in Figure 2. It can be seen that different wear mechanisms occurred in samples SAE 40, TMP 0 and TMP15, and TMP 20 such as adhesive, erosive and corrosives wear. This means that the lubricant film frequently broke down because the proper film strength was not established. However, the TMP 5 and TMP 10 samples showed better surfaces where surface wear only occurred due to friction between the sliding components (Liu et al.,1992)



(a)



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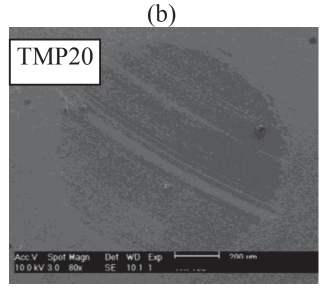

(c)

Figure 2 Micrographs of different percentages of the jatropha oil-based TMP ester in SAE 40. (a) TMP0, (b)TMP10, (c) TMP20

4. CONCLUSION

For the tests performed on a four-ball wear machine using different percentages of a TMP ester in SAE 40, the following conclusions were drawn:

Wear and friction were influenced by the intermolecular behaviour of different TMP percentages in the original lubricant SAE 40. From the SEM test results (Figure 2), it was found that erosive/corrosive wear happened due to lubricant film breakdown in some of the samples such as TMP0 and TMP20. This was because erosive/corrosive matter is related to intermolecular lubricant film formations. This effect was not found in sample TMP10. The wear in sample TMP10 was due to the sliding friction between lubricant-ball surfaces, meaning that it had a better film formation compared to the other samples. From physical observations of the worn surfaces of the specimens, it can be suggested that TMP10 acted as an excellent anti-wear lubricant. In addition, a study of the micrographs showed that the wear scar surfaces in TMP10 appeared to be much smoother, thus resulting in less material transfer.

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REFERENCES

Adhvaryu, A., S. Z. Erhan and J. M. Perez,2002. "Wax appearance temperatures of vegetable oils determined by differential scanning calorimetry: effect of triacylglycerol structure and its modification." Thermochimica Acta 395(1-2): 191-200.

Bowden, F. and D. Tabor,2001. The friction and lubrication of solids, Oxford University Press.

Erhan, S. Z., B. K. Sharma and J. M. Perez,2006. "Oxidation and low temperature stability of vegetable oil-based lubricants." Industrial Crops and Products 24(3): 292-299.

Fernández Rico, J. E., A. Hernández Battez and D. García Cuervo,2002. "Wear prevention characteristics of binary oil mixtures." Wear 253(7-8): 827-831.

Gunstone, F. D., J. L. Harwood and F. B. Padley,1994. The Lipid Handbook.

Havet, L., J. Blouet, F. Robbe Valloire, E. Brasseur and D. Slomka,2001. "Tribological characteristics of some environmentally friendly lubricants." Wear 248(1-2): 140-146.

Hsu, S., R. Munro and M. Shen,2002. "Wear in boundary lubrication." Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 216(6): 427-441.

Hsu, S. M. and E. E. Klaus,1978. "Estimation of the Molecular Junction Temperatures in Four-Ball Contacts by Chemical Reaction Rate Studies." ASLE Transactions 21(3): 201 - 210.

I-Ming, F.,1962. "A new approach in interpreting the four-ball wear results." Wear 5(4): 275-288.

Liu, J.-J., Y. Chen and Y.-Q. Cheng,1992. "The generation of wear debris of different morphology in the running-in process of iron and steels." Wear 154(2): 259-267.

Masjuki, H. H. and M. A. Maleque,1997. "Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test." Wear 206(1-2): 179-186.

Masjuki, H. H., M. A. Maleque, A. Kubo and T. Nonaka,1999. "Palm oil and mineral oil based lubricants - their tribological and emission performance." Tribology International 32(6): 305-314.

Quinchia, L. A., M. A. Delgado, C. Valencia, J. M. Franco and C. Gallegos,2009. "Viscosity modification of high-oleic sunflower oil with polymeric additives for the design of new biolubricant formulations." Environmental Science and Technology 43(6): 2060-2065.

Randles, S. J.,1999. Esters. Synthetic lubricants and high-performance functional fluids. New York, Marcel Dekker 63-101.

Rhee, I.,1996. "Evaluation of Environmentally Acceptable Hydraulic Fluids." NLGI Spokesman 60(5): 28-35.

Rieglert, J. and E. Kassfeldt,1997. "Performance of environmentally adapted hydraulic fluids at boundary lubrication." Tribology Series 32: 467-473.

Shah, S. N., B. R. Moser and B. K. Sharma,2010. "Glycerol tri-ester derivatives as diluent to improve low temperature properties of vegetable oils." Journal of ASTM International 7(3).

Sharma, B. K., A. Adhvaryu and S. Z. Erhan,2009. "Friction and wear behavior of thioether hydroxy vegetable oil." Tribology International 42(2): 353-358.

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.

Weller, D. E., Jr. and J. M. Perez,2001. "A study of the effect of chemical structure on friction and wear: Part 2- Vegetable oils and esters." Lubrication Engineering 57(5): 20-26.

Willermet, P. A., S. K. Kandah, W. O. Siegl and R. E. Chase,1983. "The Influence of Molecular Oxygen on Wear Protection by Surface-Active Compounds." ASLE Transactions 26(4): 523 - 531.

Yunus, R., A. Fakhru'l-Razi, T. L. Ooi, S. E. Iyuke and J. M. Perez,2004. "Lubrication properties of trimethylolpropane esters based on palm oil and palm kernel oils." European Journal of Lipid Science and Technology 106(1): 52-60.

Yunus, R., A. Fakhru'l-Razi, T. L. Ooi, R. Omar and A. Idris,2003. "Preparation and Characterization of Trimethylolpropane Esters from Palm Kernel Oil Methyl Esters " Journal of Oil Palm Research 15(2): 42-49.