Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant

N.W.M. Zulkifli a,*, M.A. Kalam a, H.H. Masjuki a, M. Shahabuddin a, R. Yunus b

a Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
b Institute of Advanced Technology, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia

A R T I C L E   I N F O

Article history:
Received 2 September 2012
Received in revised form 9 January 2013
Accepted 14 January 2013
Available online 17 February 2013

Keywords:
Sliding wear
Bio-lubricant
Coefficient of friction
Lubrication

A B S T R A C T

This paper presents the experimental results carried out to evaluate wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester using a four-ball machine for different regime of lubrication. The TMP ester is produced from palm oil, which is biodegradable and has high lubricity properties such as a higher flash point temperature and VI (viscosity index). Three different regimes of lubrications are investigated, which hydrodynamic, elasto hydrodynamic and boundary lubrications. Under these test conditions, the wear and friction characteristics of different TMP samples are measured and compared. For boundary lubrication, it is found that up to 3% addition of Palm oil-based TMP ester in OL (ordinary lubricant) decreases the maximum amount of WSD (wear scar diameter) and reduces (COF coefficient of friction) up to 30%. Highest amount of load (220 kg) carrying capacity was also found from the contamination of 3% TMP. For hydrodynamic lubrication, addition of 7% of TMP reduces the friction up to 50%. It is well known that mechanical efficiency of machinery component increases with decreasing COF. The results of this investigation will be used to develop new and efficient lubricant to substitute the petroleum-based lubricant partially for automotive engine application.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

There has been enormous interest in the use of oils from renewable sources such as animal fats, vegetable oils and bio-lubricants [1–3]. The uncertainty of the crude oil supply, pollutants emissions and its higher price give biodegradable biolubricants more advantages over mineral base oils. However, vegetable oil in its natural form has limited usage due to its poor oxidation stability [4] and inferior low temperature properties [5]. The first biodegradable lubricants were developed for two-stroke outboard engines in the early 1980s, using neopentylpolyl esters of branched-chain fatty acids as based fluids [6]. Eychenne and Mouloungui [7] have reviewed the developments in environmentally friendly lubricating oils based on neopentylpolys such as neopentyl glycol, pentaerythritol and trimethylolpropane. Other researches [8,9] have worked on engine oil prepared from a mixture of trimethylolpropane esters having both sufficiently high viscosity and low pour point. Jayadas et al. [10] found that coconut oil could be a good boundary lubricant as far as the coefficient of friction is concerned. But the wear rate is higher than ordinary lubricants, which may not be recommended as an engine oil in the unmodified form. The major function of engine oil is to decrease the frictional force, by forming a thin film between the moving parts in the engine such as piston and cylinder. Consequently, wear of the moving parts is reduced and diminished the power loss. Besides, engine oil also used to cool the engine by carrying away the heat, inhibits corrosion, cleans and improves sealing. One of the most important properties of engine oil is viscosity, which should be high enough to maintain the lubricating film thickness, and low enough to make sure the oil can flow through all the engine parts. The TMP (trimethylolpropane) ester is produced from a palm oil methyl ester through transesterification. Transesterification eliminates the hydrogen molecule on the beta carbon position of the palm oil substrate, thus improving the oxidative and thermal stability of the TMP ester; an important lubricity property in vegetable oils [11]. In addition, TMP esters have good friction-reducing properties and acceptable anti-wear properties [12]. However, in contrast, Waara et al. [13] found that pure synthetic ester (TMP-Oleate and TMP-C8-C10) in a sliding contact resulted in high wear rates and a lot of abrasive marks on the surface. To understand the lubricity performance, the Strieber diagram can be seen in Fig. 1. This diagram shows the coefficient of friction in a rotating bearing, plotted
against Stribeck variable (known as the dimensionless Sommerfeld number). The Stribeck variable is shown in equation below.

\[ \text{Stribeck variable} = \frac{\mu N}{P} \]

\( \mu \) = viscosity, 
\( N \) = rotational speed, 
\( P \) = unit load

Lubrication under low values of Stribeck region is known as boundary lubrication. Low values of Stribeck variable correspond to low viscosity, low speeds, and high loads. In this case, the surfaces asperities are actually in contact to each other [14]. Therefore, extreme pressure and anti wear additives played an important role to form a boundary lubricating film [14–16] to protect the surface. In addition, surface characteristic also plays an important role contacting two surfaces. There are many locations in the modern diesel engine where boundary lubrication occurs such as in piston rings at the top and bottom dead centers, and the fuel-injection system. Lubricity is the fluid property that characterizes friction and wear phenomenon in boundary lubrication. The lubrication in the large values of the Stribeck is called hydrodynamic region. Large values of the Stribeck variable correspond to high viscosity fluids, high rotational speeds, and light loads. Under these conditions, an oil film supports the load/carry the load at low friction. In this condition, fluid properties are of greatest significance for wear and friction, and the surface characteristics such as surface asperities of the bearing are not important since the surfaces are not in contact [17,18]. In an engine, hydrodynamic lubrication occurs in journal bearing, crankshaft bearing and when the piston rings are moving [19,20]. It can be highlighted that frictional forces consume about 15–20% of fuel in an internal combustion engine. Only the development of low coefficient of friction lubricant and surface development is the solution to reduce this energy consumption. Hence, in order to have a better understanding of reduction of frictional forces through the tribological study, a new type of lubricant substitute TMP is introduced. The effect of TMP ester on different lubrication regime using four-ball machine and HFRR (high frequency reciprocating machine) wear tests have been investigated. The output of these experimental results would give a correlation of actual frictional behavior in internal combustion engine. The objectives of this study are to investigate the tribological properties under boundary and hydrodynamic lubrication when added palm-oil based TMP ester in OL (ordinary lubricant).

2. Experimental method

2.1. Lubricant sample preparation

Palm oil-based TMP ester was synthesized by the transesterification of methyl esters as shown in Fig. 2 [21]. The preparation process of palm oil-based TMP ester is shown in Fig. 3. The trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propane-diol] was chosen due to its lower melting point compared to other polyols. A 200 g volume of palm oil methyl ester and a known amount of TMP were 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 POME (palm oil methyl esters). The mixture was then heated to the reaction temperature in the presence of catalyst. A vacuum was gradually applied to the system until the desired pressure was reached. This pressure was maintained until completion of the reaction. The peaks appeared were identified and labeled based on the number of alkyl carbon groups that attached to TMP backbone. The esters formed are identified by making comparisons by standard or by using the standard of TG (triglycerides), DG (diglycerides) and monoglyceride (MG) [22]. Fatty acid composition is shown in Table 1.

Both palm oil-based TMP esters were blended with OL using a stirrer at 110 rpm and heated to 100 °C. Detail properties of OL are shown in Table 2. The blended lubricants consisted of 5%, 10%, 15%, 20% and 100% palm oil TMP esters (volume basis) with OL. Compositions of the lubricant samples are shown in Table 3.
2.2. Lubricant properties test

**Density:** Density was measured using a DMA 35 portable density meter. The samples were tested at 15 °C. Only 2 ml of each sample was used per test.

**Viscosity index (VI):** The viscosity index (VI) was calculated using ASTM D2270. This method uses the kinematic viscosities at 40 °C and 100 °C to determine the VI. The experiments were carried out using an ISL automatic Houillon viscometer.

### 2.3. Wear and friction test

#### 2.3.1. Four-ball machine

The four-ball wear test is used to investigate the effect of Palm oil-based TMP ester under wear preventive test (hydrodynamic test). The four-ball wear tester is the predominant wear tester used by the oil industry to study lubricant chemistry. The four-ball wear tester consists of three balls held stationary in a ball pot plus a fourth ball held in a rotating spindle as shown in Fig. 4. The balls used in this study were steel balls, AISI 52-100, 12.7 mm in diameter, with 64–66 Rc hardness. These balls were thoroughly cleaned with toluene before each experiment. The sample volume required for each test was 10 ml. The test method used to investigate wear preventive characteristic was ASTM D4172 [23]. The test conditions were 40 kg load, operating temperature of 75 °C ± 2 °C, rotational speed of 1200 rpm and operation time of 60 min. For the extreme pressure test, ASTM 2783 [24] where the load is increased by 20 kg at 64–66 Rc hardness. These balls were thoroughly cleaned with toluene before each experiment. The sample volume required for each test was 10 ml. The test method used to investigate wear preventive characteristic was ASTM D4172 [23]. The test conditions were 40 kg load, operating temperature of 75 °C ± 2 °C, rotational speed of 1200 rpm and operation time of 60 min. For the extreme pressure test, ASTM 2783 [24] where the load is increased by 20 kg for every 10 s until the ball is welded. The wear produced on the oil-based TMP ester under wear preventive test (hydrodynamic test).

#### 2.3.2. HFRR (High frequency reciprocating rig) configuration

The HFRR wear test was used to investigate the effect of Palm oil-based TMP ester under fluid film lubrication as shown in Fig. 5. The HFRR test (ASTM D6079) used in this study involves a weighted cast iron pin cylinder (6 mm length) and a stationary cast iron plat (15 mm × 15 mm), which is completely submerged in a 10 ml of sample. The ball and disk is tested at room temperature and brought into contact with each other and the entire apparatus is vibrated at 10 Hz for 60 min with the load 10 N. The sliding stroke is maintained at 2 mm. Several blends of Palm oil-based TMP ester including 1%, 3%, 5%, 7% and 10% are tested and analyzed. Each test was carried out three times repeatedly to observe any errors need to be analyzed.

### 3. Results and discussion

#### 3.1. Physicochemical properties of palm oil-based TMP ester in OL (ordinary lubricant)

The data were used to evaluate the differences between OL and to serve as a basis for comparing the blended fuels with palm oil-based TMP esters. The percentage of palm oil-based TMP esters and OL in each sample is shown in Table 2. All of the lubricant properties are listed in Table 4.

The VI (viscosity index) of oil is a number that indicates the effect of temperature changes on its viscosity. A low VI signifies a relatively large change in viscosity with changes in temperature. In other words, the oil becomes extremely thin at high temperatures and extremely thick at low temperatures. A high VI signifies relatively little change in viscosity over a wide range of temperatures. The ideal oil for most purposes is one that maintains a constant viscosity throughout different temperature changes. Considering automotive lubricants can easily show the importance of the VI. The oil having a high VI resists excessive thickening when the engine is cold and, consequently, promotes rapid starting and prompt circulation. It also resists excessive thinning when the engines sliding components are hot and thus provides full lubrication and prevents excessive oil consumption. The VI of oil is determined based on known viscosities at any two temperatures (here 40 °C and 100 °C). It can be seen from Table 3, TMP 1 has the highest viscosity as 108.75 cSt.

The density of a lubricant fluid can provide indications of its composition and nature. The density of lubricants, mainly hydrocarbons, varies between 0.860 and 0.980 g m⁻³. The densities of OL and TMP100 were 0.850 and 0.9012, respectively.

#### 3.2. Effect of palm oil-based TMP ester under wear preventive test (hydrodynamic test)

The WSD results for the different percentages of palm oil-based TMP ester in OL are shown in Fig. 6. The significance improvement in WSD was found for TMP3, which is 30% as compared to OL. This can be explained that an increase in the number of ester groups leads to greater binding of the molecules, which provide a greater

### Table 1

<table>
<thead>
<tr>
<th>Fatty acid composition (%)</th>
<th>Oils (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoester 5</td>
<td>OL 0</td>
</tr>
<tr>
<td>Diester 5</td>
<td>TMP5 5</td>
</tr>
<tr>
<td>Triester 90%</td>
<td>TMP10 10</td>
</tr>
<tr>
<td></td>
<td>TMP15 15</td>
</tr>
<tr>
<td></td>
<td>TMP20 20</td>
</tr>
<tr>
<td></td>
<td>TMP100 100</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Property</th>
<th>Ordinary lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15 °C (g/cm³)</td>
<td>0.877</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-36</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>228</td>
</tr>
<tr>
<td>TBN (mg KOH/g)</td>
<td>8.6</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Palm oil-based TMP ester (%)</th>
<th>OL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>TMP5</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>TMP10</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>TMP15</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>TMP20</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>TMP100</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 4. A schematic of the four-ball test machine.
resistance to shear forces. However, increasing TMP ester more than 3% does not show any improvement on WSD. This can be attributed to the fact that, more than 3% of Palm oil-based TMP ester could not form the stronger lubricant film formation. This finding is similar to the findings reported by Yunus et al. [25], who found the lower wear scar diameter using palm oil-based TMP ester with compared to ordinary hydraulic fluid (not the engine lubricant). In addition, Masjuki et al. [26] also found that palm-based lubricating oil had a better wear performance compared to mineral oil. Fernandez et al. [27] reported that the addition of a synthetic TMP ester to a low viscosity polyalphaolefin acted as a wear reducer. According to Havet et al. [28] the length of the fatty acid chains tends to increase the adsorbed film thickness, therefore increasing the surface area protected.

The values of COF (coefficient of friction) for the various lubricant samples are shown in Fig. 6. It has similar trend like WSD. In general it can be stated that the COF reduces with the addition of Palm oil-based TMP ester except for TMP100. Based on the value of COF and WSD it is found that TMP 3 has the best lubricity performance. At TMP 100, WSD is maximum of around 0.78 mm. Based on Fig. 7, it can be seen that after the operation time of 20 min, the thin film layer has started breaking down. This is because of low viscosity in TMP 100, the lubricant film formed is not able to support the load throughout the operation time.

The continuous rotation of the top ball causes the rupture of the micro-joints and creates pits and grooves. Surface morphology shows that adhesive is very minimal for OL as we can see there is transferred material. For lubricant added Palm oil-based TMP ester, the appearance of the worn surfaces seems to present corrosive product of black color at higher temperature. The higher percentage of palm oil-based TMP esters added, the black color is darker. This may be explained from the fact that at higher temperature, lubricant can be oxidized and thereby produces different types of corrosive acids that enhance corrosive wear [29,30]. In addition, it is found that this boundary lubricating films acts as a sacrificial layer. The reaction products of tribochemistry provide a layer; so instead of the surface being worn, this layer is removed [31]. It can be seen that, from Fig. 8(TMP 10), the black color areas have a severe wear compared to non-black area. Further it can be explained that the existence of oxygen might accelerate the generation of inorganic oxides like Fe₃O₄, Fe₂O₃, which plays an important role in the formation of lubrication film on the rubbing surface [32]. For TMP 100, it seems like the fluid film of lubricant is completely breakdown. The direct interaction between two solids that remove material from, while at the same time producing polished surface on [33]. Based from Fig. 8(TMP100), material removal in this case occurs as the very small slabs of surface steel ball being lifted out the surface, probably

<table>
<thead>
<tr>
<th>Sample</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity (cSt)</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
</tr>
<tr>
<td>OL</td>
<td>101.86 ± 1.53</td>
</tr>
<tr>
<td>TMP 1</td>
<td>108.75 ± 1.22</td>
</tr>
<tr>
<td>TMP 3</td>
<td>107.21 ± 1.41</td>
</tr>
<tr>
<td>TMP 5</td>
<td>101.42 ± 1.30</td>
</tr>
<tr>
<td>TMP 7</td>
<td>102.15 ± 1.17</td>
</tr>
<tr>
<td>TMP 10</td>
<td>97.637 ± 1.21</td>
</tr>
<tr>
<td>TMP100</td>
<td>40.03 ± 1.32</td>
</tr>
</tbody>
</table>

Fig. 6. Wear scar diameters (WSD) and coefficient of friction (COF) for different percentages of the palm oil-based TMP esters in OL. Maximum error WSD: ±0.05 μm, maximum error COF: ±0.005.
by some form of delamination. The polished wear mechanism occurs here as a result of severe abrasive wear. It can be seen also from Fig. 8 (TMP100) that, the light reflected from real surfaces.

This phenomenon was confirmed with the results of surface roughness measurement, as shown in Fig. 9. The surface roughness test was conducted in order to understand the wear scar texture on the bottom three balls. A stylus profilometry test was performed to evaluate the surface texture of the worn halo on the rotating ball and the wear scars on the stationary balls. The profilometry trace was fed into a microprocessor and the resulting signal was displayed on a chart recorder providing surface roughness graphs. The profilometer traces were taken perpendicular to the direction of sliding. Sample TMP 7 showed a comparatively smooth wear pattern compared to the other samples. No significant difference is observed among the tested lubricant samples except TMP 100, which shows the maximum surface roughness of 0.07.

3.3. EP (Extreme pressure) characterization

Under extreme pressure, the wear rate from the rubbing surface can be minimized by reducing the bearing stress or enhancing the strength. At extreme pressure the flash temperature is elevated and the extreme pressure additives decompose to form a chemical reaction film which tends to increase the bearing area and consequently reduce the contact pressure. The performances of the EP additives are dependent on three factors, which are: strength of the tribo-film, reaction rate between the additives and the rubbing surface, and finally the compatibility between the base oil and the additives [34]. To evaluate the friction and wear characteristics of different biolubricants the extreme pressure characteristics were investigated for a load range of 20 kg up until the balls specimens weld with each other, which is defined as the FSL (final seizure load). The rotational speed applied was 1200 rpm, the temperature was 27 ± 7 °C and an operation period of 10 s was employed for each sample.

Fig. 10 shows the variation in the coefficient of friction under different loads for different TMP ester added lubricant. The magnitude of the coefficient of friction indicates that the lubrication regime occurring in the rubbing zone were both elasto-hydrodynamic and boundary lubrications. Most of the TMP ester presented a lower coefficient of friction (COF) compared to the OL. It seems quite clear that the COF for TMP 1, TMP 3, TMP 5 and TMP 7 were lower as compared to petroleum-based ordinary lubricant while TMP 10 and TMP 100 showed the higher COF throughout the load range. The OL, TMP 1 and TMP 3 were found to be more stable in terms of a FSL (final seizure load) which is defined as the load at which lubricants film totally break down and testing ball materials become welded. It can also be noted that TMP 1 imparted lowest
COF up to initial seizure load (ISL) of the load at which a considerable amount of wear is occurred however, after FSL the lowest COF was found to be using TMP 3. The results of Fig. 10 imply that the TMP 1 and TMP 3 have the greatest ability to retain its properties up to the load of 220 kg without the lubricating film breaking down. This can be attributed to the fact that at higher loads the lubricating film thickness becomes thinner than some of the asperities present in the boundary lubrication regime. However, these asperities are covered by the long chain fatty acid and the esters of the biolubricants, which are known as surface active materials. TMP 1 and TMP 3 showed the best performance in terms of reducing the COF, which can be interpreted as the fatty acid present in the TMP esters acting as an active surface material which is adequate for these two lubricants, and above that the fatty acid does not take part because the rubbing contact surface is fully covered by them. Another important fact is that above 3% addition the TMP adversely affects the quality of the lubricant.

3.4. Effect of palm oil-based TMP ester under fluid film lubrication

According to results presented in Fig. 11, TMP 7 has shown the lowest friction torque around 0.02 Nm. The OL shows the highest friction torque because the viscosity is too high and created a thick film, which will cause more friction. Addition of Palm oil-based TMP ester in the OL reduced the viscosity of the lubricant, hence provides a better thin film at the surface and thus reduced the friction. Based on the experimental results, it can be stated that, the addition of Palm oil-based TMP ester in the base lubricant leads to improve the frictional torque characteristics of the lubricants. In contrast with boundary lubrication, at low load, TMP 100 still can maintain the film lubrication. The weight loss of the cast iron flat plate is very small. It can be assumed almost no wear occur in this regime lubrication.

4. Conclusion

The experimental results show that Palm oil-based TMP ester based lubricant improves the wear preventive lubrication properties in terms of COF and WSD. The TMP 3 shows the lowest WSD and COF with compared to others lubricants analyzed in this study. In addition, under extreme pressure condition maximum load bearing capacity of 220 kg was found to be using TMP 3 by retaining its quality without breakdown. Under the fluid film lubrication using reciprocating test the TMP 7 shows the best lubricity property with the lowest friction torque. In order to utilize Palm oil-based TMP ester as an engine oil, many other properties including oxidative, thermal and hydrolytic stabilities need to be examined. Palm oil-based TMP ester is environmentally desired to mineral oil-based lubricants, research to investigate the properties of palm oil-based TMP ester to make it technologically competitive as automobile lubricant, and should be encouraged.

Acknowledgments

The authors would like to thank the University of Malaya, which made this study possible through the research grant FRGS FP020/2011A, PV070/2011B and high impact research grant no UM.C/HIR/MOHE/ENG/07.

References