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Nano-tribological characterisation of palm oil-based trimethylolpropane ester for application as boundary lubricant

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ABSTRACT

To isolate shearing of boundary film from direct surface-to-surface asperity interactions, the study determines boundary lubrication properties of palm oil-based TMPE (PTMPE) using Lateral Force Microscopy coupled with fluid imaging. PTMPE is produced through a series of 3-step transesterification processes, converting palm oil (PO) into palm methyl ester (PME) and finally into PTMPE. It is shown that PME generates the lowest friction. However, using Eyring thermal activation energy approach, PME is shown to possess less desirable load bearing property, portraying a form of stiction or adhesive nature. Even though friction is higher, PTMPE exhibits better load bearing ability, demonstrating the onset of lubricant laminar flow due to increased hydrodynamic effect, which is not observed for the PO and PME measurements.

1. Introduction

Approximately 35.7% of the total fuel energy supplied to a typical passenger car is used to overcome friction [1]. From these amount of losses, engine friction, mainly generated by piston rings sliding along engine cylinder liner, contributes 45%. If new technological advancements in the field of tribology are being introduced to typical passenger cars, these frictional losses could be reduced by at least 18% [2]. Using a Stribeck curve given in Fig. 1, it is realised that the operating lubrication regime for piston ring lubrication system is typically between mixed and hydrodynamic lubrication regimes. Along hydrodynamic lubrication regime, friction is governed by viscous shearing, where lubricant bulk properties play an important role in affecting lubrication performance. However, the underlying mechanism for friction along mixed lubrication regime is a combination of viscous shearing and surface asperity interaction. Reduction of friction arising from the latter mechanism requires boundary lubrication, where an ultra-thin layer of protective film is typically formed through adsorption of boundary active elements onto opposing surfaces.

In view of the various operating lubrication regimes for piston ring-liner conjunction, it is only imperative that an effective lubricant consists of various additives, blended with base oils to attain specific tribological performance-improving characteristics. These additives include extreme-pressure and anti-wear agents, friction modifiers and viscosity index improvers. They are typically added to engine lubricants up to 30-vol% [3]. If the lubricant is properly formulated and optimized, reduction in frictional losses could be achieved, leading to significant fuel economy improvements [4].

Statistically, the global demand for lubricants are estimated to be around 39 million tonnes in the year 2017, with around 24 million tonnes coming from the automotive sector [5]. This is in-line with the need for the automotive sector in reducing frictional losses, especially for passenger cars. However, 50% of these lubricants are expected to end up in the environment, where 1 L of mineral oil could contaminate up to 1 million litres of water [6]. On top of this, a total of 193 kilo tons of additives, such as anti-wear additive (100 kilo tonnes) and friction modifier (93 kilo tonnes) are added to such an amount of lubricant [7]. Most of these additives are synthetic base. It is brought to light that these additives could also potentially harm the environment if their uses are not properly regulated. A recent study by Pirjola et al. measured particle emissions from modern turbocharged gasoline direct injection passenger car running on different engine lubricants. They found that highest emission factors originated from using lubricants with higher concentrations of additives containing zinc, magnesium, phosphorous and sulphur [8]. An additive example with relation to this observation is zinc dialkyldithiophosphate (ZDDP), which is commonly

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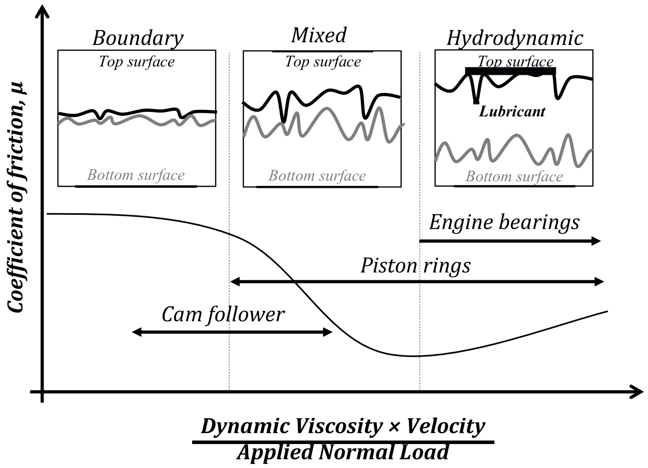

Fig. 1. Lubrication regimes based on Stribeck curve.

known for its effective wear reduction properties. Besides this, ZDDP has also been observed to form ash during combustion, which could poison engine emissions control catalysts [9,10].

An environmentally acceptable lubricant should possess both high biodegradability and low eco-toxicity [11]. Therefore, in order to overcome the environmental impact of existing lubricants, the concept of Green Tribology, which refers to the science and technology of the tribological aspects of ecological balance and of environmental and biological impacts [12], can be adopted. Twelve principles have been formulated for this concept, with one of them focusing on the use of biodegradable lubrication. For this, biolubricants have been shown to demonstrate significantly higher biodegradabilty rates than mineral oil [13]. Hence, Nosonovsky and Bhushan suggested the use of vegetable oil or animal fat based natural lubricant be considered for lubrication in automotive, hydraulic and metal-cutting applications [14]. This suggestion is driven also by the fact that biolubricants have low toxicity, good lubrication properties, high viscosity index, high ignition temperature, increased equipment service life, high load carrying abilities, good anti-wear characteristics, excellent coefficient of friction, natural multi-grade properties, low evaporation rates and low emissions into the atmosphere [15,16].

To date, biolubricants are still not widely being used because of the challenges and difficulties with respect to their performance [16]. On the performance, biolubricants, specifically vegetable oil based lubricants, usually have low thermal oxidative stability, poor temperature performance and limited range of available viscosities [17]. As an example, Honary found that the lack of oxidative stability causes an increase in viscosity for untreated soybean oil, which significantly affect the oil's tribological performance [18]. This performance drawback can be improved by using appropriate chemical modification processes, such as epoxidized vegetable oil [19,20]. Another type of chemical modification process involves the conversion of methyl esters derived from vegetable oils to trimethylolpropane esters (TMPE). Aside from good friction and wear characteristics, Uosukainen et al. observed that rape seed oil-based TMPE lubricant exhibits resistance against oxidation at elevated temperatures as compared to commercially available hydraulic fluids [21]. Yunus et al. [22] and Qiao et al. [23] both also found that the thermal oxidation stability of fatty acid derived TMPE is better than vegetable oil.

Using four-ball tribotester, Yunus et al. observed that friction and wear properties of palm oil-based and palm-kernel based TMPEs are comparable to commercial hydraulic fluids [22]. Ghazi et al. produced TMPE biolubricant from *Jatropha curcas* and found that the tribological properties of this biolubricant is comparable to other types of plant based biolubricant [24]. Interestingly, Zulkifli et al. showed that TMPE derived from palm oil methyl ester actually exhibits better lubrication properties than paraffin oil under extreme pressure loading conditions [25]. This is further supported by recent work by Zahid et al., where they demonstrated that palm oil-based TMPE has more superior load bearing ability and extreme-pressure characteristics than that of polyalphaolefin (PAO) [26].

The literature mentioned thus far focuses on the use of biolubricants purely as base oil. However, the production costs for biolubricants are estimated to be 1.5 to 5 times higher as compared to mineral oil-based lubricant [27]. In view of this limitation, for TMP esters, Rico et al. studied the wear prevention characteristics of polyalphaolefin (PAO) base oil added with TMPE and sunflower oil at different mass fractions using a four-ball tribotester [28]. In their study, they found that addition of TMPE to base oil (e.g. PAO) could act to reduce wear. Zulkifli et al. also evaluated friction and wear properties of typical lubricants added with palm oil-based TMPE at different proportions using a four-ball tester [29]. Along boundary lubrication regime, they observed that by adding 3-vol% of palm oil-based TMPE to the tested typical lubricant, a coefficient of friction reduction of up to 30% can be achieved. Along hydrodynamic lubrication regime, they witnessed friction reduction of up to 50% by adding 7-vol% of palm oil-based TMPE to the typical lubricant.

It is known that the effects of lubricant additives on machine elements depend on the lubrication regimes, especially along boundary lubrication regime, at the prevailing conditions at localized contacts [10]. The above mentioned studies, investigating the potential of TMPEs as lubricant additives, focus on friction and wear performances along boundary lubrication regime using typical tribometers, such as four ball tester. These measured frictional properties could possibly consist of contributions from both surface-to-surface interaction of asperities and shearing of boundary lubrication film that is a few molecular layers thick. In order to isolate the tribological properties of boundary lubrication film for TMPEs from direct surface asperity interactions, characterisation should be conducted at a relevant scale. This will allow for the determination of mechanisms governing the formation of this barrier in preventing direct surface-to-surface contact. Hence, the current study attempts to determine the boundary lubrication properties of palm oil-based TMPE at nano-scale using Lateral Force Microscopy (LFM) and fluid imaging. The interpretation of the measured nano-tribological properties of this TMPE are then conducted based on a thermal activation energy approach using Eyring's cage model. It is expected that the current nano-tribological investigation will further improve the fundamental understanding on the boundary lubrication properties of palm oil-based TMP ester.

2. Experimental approach

For the current study, laboratory grade palm oil-based trimethylolpropane ester (PTMPE) is synthesized from commercially available palm oil. It is also of the interest for this study to determine the boundary lubrication property change when converting palm oil (PO) to palm methyl ester (PME) and then finally to PTMPE. Therefore, nano-scale friction measurement is conducted for these lubricants: PO, PME and PTMPE, using LFM and fluid imaging.

2.1. Production of palm-based trimethylolpropane ester (PTMPE)

The production of polyol ester from palm oil (fatty acid composition as given in Table 1) can be achieved through a series of 3-step transesterification process as shown in Fig. 2, by converting PO into PME, and then into PTMPE [30]. PME is synthesized from Reactions 1–3:

$$\text{Reaction 1:Triglyceride} + \text{Methanol} \xleftrightarrow{\text{KOH}} \text{Methylester} + \text{Diglyceride}$$

$$\text{Reaction 2: Diglyceride} + \text{Methanol} \xleftrightarrow{\text{KOH}} \text{Methylester} + \text{Monoglyceride}$$