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Competitive Molecular Interaction between Zinc Dialkydithiophosphate (ZDDP) and Methyl Oleate along Boundary Lubrication Regime

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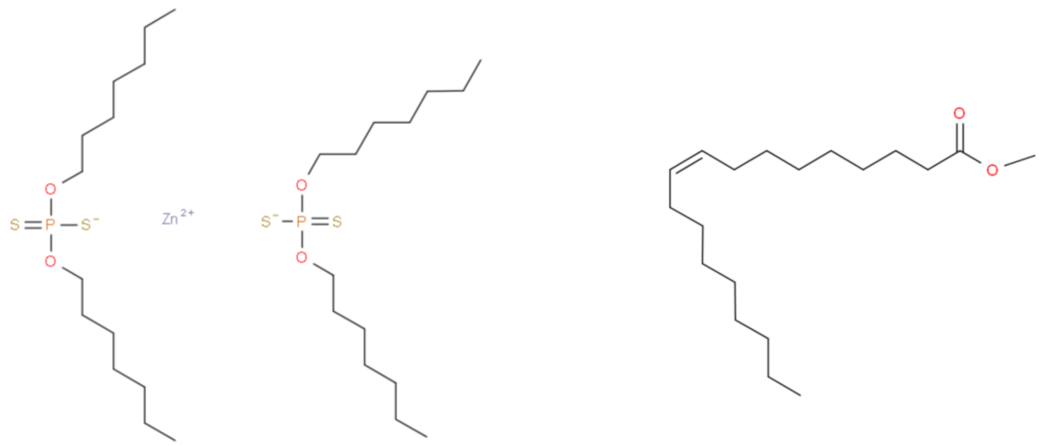
Abstract. Fatty acid methyl ester (FAME) possesses good lubricity properties, prompting numerous research work to explore their potential as lubricant additives. However, fully formulated lubricants consist of additive packages, which includes essential anti-wear agents, such as zinc dialkyldithiophosphate (ZDDP). Adding FAME into a lubricant could lead to adverse tribological effects if the competitive molecular interaction between different additives are not well understood. Therefore, the present study determines the tribological impact of molecular interaction between ZDDP and methyl oleate along boundary lubrication regime. Lateral force microscopy, coupled with fluid imaging approach, is adopted, allowing for the analysis to focus on asperity level interaction. A silicon nitride tip is used to slide against a mirror-polished steel substrate while being fully submerged in the tested fluids. The tested fluids are mixtures of ZDDP and methyl oleate, blended at different volumetric percentages. It is observed that the lowest friction force is measured for ZDDP-methyl oleate mixture containing 70-vol% of methyl oleate. Interestingly, the friction force measured for such mixture is found to be lower than that of neat methyl oleate. This finding indicates that an optimum blending ratio between FAME and ZDDP is essential in achieving better boundary lubrication performance for tribological conjunctions.

1. Introduction

Fatty acid methyl ester (FAME) is commonly used as an alternative biodegradable fuel in compression ignition engines. Such application has resulted in significant emissions reduction from compression ignition engines [1, 2]. More importantly, FAME is also known to have good lubricity properties [3], which has been evidenced by the improved fuel lubricity after being added to low-sulphur petrol-diesel. Typically, tribological properties of FAME have been investigated using tribometers, such as the high frequency reciprocating rig (HFRR)[4], four-ball tester [5], pin-on-disk [6] and ball-on-disk [7] type tribometers. Coefficient of friction and wear scar properties are commonly reported for FAME derived from different vegetable oils. Alternatively, based on the classical Stribeck curve analysis, for various types of tested vegetable oil and animal fat derived FAMEs, Hamdan et al. found that FAME has good friction modifier property, which delays the onset of mixed and boundary lubrication regime [6].

To date, most of the studies of FAME lubricity focuses on its tribological properties with little emphasis on the use of FAME as an additive. When being considered as lubricant additive, it is essential to be able to understand the molecular interaction of FAME with other types of additives, such as anti-wear agents. This is because the lack of such fundamental knowledge could lead to less desired tribological performances due to the competitive interactions between various types of additives. As an example, in a recent study on FAME dilution of engine lubricants, Hamdan et al. showed that the existence of FAME in the engine lubricants does in fact enhance the friction modifier effect of the lubricant [7]. However, care must also be taken because beyond a certain threshold amount of FAME dilution, adverse tribological performance are observed, mainly due to reduced load carrying ability of the lubrication film, which could result in more significant wear.

The present study intends to determine the tribological properties of anti-wear agent in the presence of FAME along boundary lubrication regime. The anti-wear agent selected in this study is zinc dialkyldithiophosphate while the selected FAME is in the form of methyl oleate. The selection of methyl oleate is because this type of FAME has been shown to consistently produce better tribological properties in terms of wear scar diameter and coefficient of friction as compared to the other types of FAME [3]. The molecular structures for ZDDP and methyl oleate are given in Figure 1. It is shown that ZDDP has a much more complex structure as compared to the fairly linear structure of methyl oleate.



(a) (b)

Figure 1. Molecular structure for (a) zinc dialkyldithiophosphate, $C_{28}H_{60}O_4P_2S_4Zn$ (ZDDP) and (b) methyl oleate, $C_{19}H_{36}$ (MO) (generated from http://www.chemspider.com)

2. Experimental Approach

In the present study, commercially available ZDDP and methyl oleate are obtained. Typical friction measurements using tribometers often produces results that couples macro-, micro- and nanotribological effects. To isolate only the boundary lubrication characteristics of the tested fluids, it is imperative that measurements are done at relevant length scale, which is at asperity level. Therefore, lateral force microscopy coupled with fluid imaging approach is adopted, allowing for the boundary lubrication properties of the ZDDP and methyl oleate mixtures to be investigated at asperity level. The asperity level friction measurement approach in this study follows the procedure proposed by Chong and Ng [8]. A silicon AFM probe with tip radius of 10 nm is used to slide against a mirror-polished stainless-steel substrate while being fully submerged in the tested fluids. The tested fluids are blends of ZDDP with methyl oleate mixtures at different volumetric percentages. During the test, applied normal load on the silicon AFM probe is varied between 1 nN and 10 nN at a constant sliding velocity of 10 $\mu m.s^{-1}$. The measured frictional parameters are then calibrated and converted into physical values following the method given in reference [9]. The setup of the friction measurement using lateral force microscopy approach is provided in Figure 2.

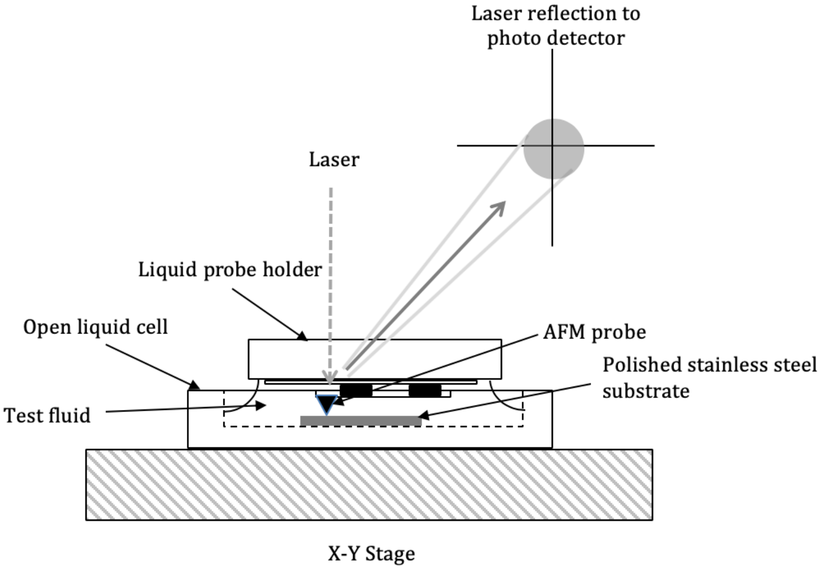


Figure 2. Schematic diagram for the lateral force microscopy setup based on fluid imaging approach

3. Results and Discussions

As mentioned above, the present study intends to determine the extent of competitive molecular interactions between ZDDP and methyl oleate along boundary lubrication regime. Before the friction test is conducted using lateral force microscopy, dynamic viscosity values for both ZDDP and methyl oleate is measured using a rheometer at different temperatures. The change of dynamic viscosities for ZDDP and methyl oleate with temperature is given in Figure 3. It is shown that ZDDP has a significantly higher viscosity when compared with methyl oleate. For Newtonian fluids, shear stress is proportional to the viscosity of the fluid. Therefore, hydrodynamically, ZDDP is expected to generate higher friction than methyl oleate. On top of this, adding methyl oleate into ZDDP is expected to result in a mixture with lower viscosity value, possibly leading to lower frictional losses.

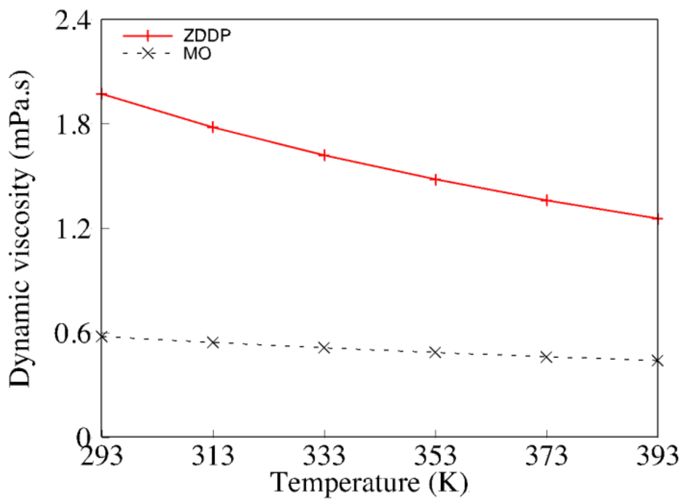


Figure 3. Measured dynamic viscosity for zinc dialkyldithiophosphate (ZDDP) and methyl oleate (MO) at different temperatures

However, along boundary lubrication regime, lubricants are most often known to operate under Non-Newtonian behaviour. The proportional relationship between shear stress and viscosity is no longer valid along this lubrication regime. Therefore, measuring friction force at asperity level is essential in obtaining the tribological behaviour of lubricants along boundary lubrication regime. Figure 4 shows the friction force measured for different ZDDP-methyl oleate mixtures at applied normal loads between 1 nN and 10 nN at 1 $\mu m.s^{-1}$. It is observed that all the measured friction forces increase linearly with larger applied normal loads. Neat ZDDP is shown to generate the highest friction force. When the volumetric percentage of methyl oleate is increased from 30-vol% to 70-vol%, friction force is found to reduce significantly. More interestingly, the friction force even drops lower than that of neat methyl oleate for ZDDP-methyl oleate mixtures with 50-vol% and 70-vol% methyl oleate. The trend observed indicates that the addition of methyl oleate molecules at an appropriate amount not only complements the tribological behaviour of the contact lubricated by ZDDP, it could also result in a much-improved frictional performance as observed in Figure 4.

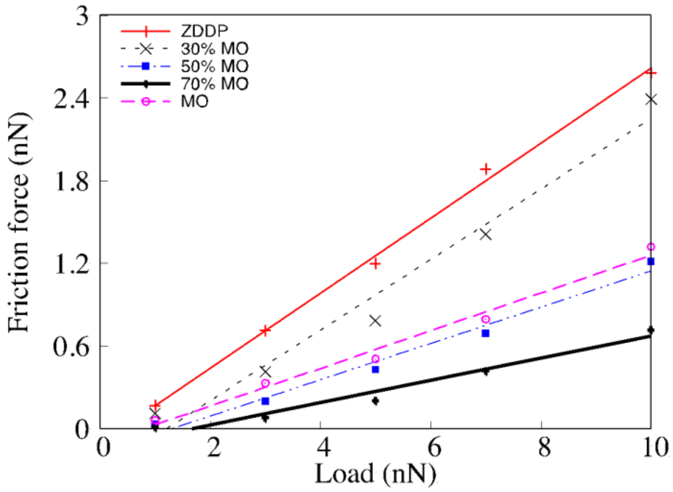


Figure 4. Measured friction force for zinc dialkyldithiophosphate (ZDDP) added with different vol% of methyl oleate (MO)

Figure 5 illustrates the coefficient of friction (CoF) for ZDDP-methyl oleate mixtures obtained from the friction force-load curve measured in Figure 4. The CoF also indicates the change in friction force with applied normal load. At asperity level, neat ZDDP lubricated contact generates the largest CoF value at 0.272. However, the addition of methyl oleate to ZDDP is shown to lead to a drop in CoF. Such reduction in CoF reaches a minimum value of 0.081 with the addition of 70-vol% methyl oleate to the ZDDP-methyl oleate mixture. Increase in the amount of methyl oleate beyond this volumetric percentage is shown to no further reduce the CoF value of the mixture. The minimum CoF value is also depicted to be lower than that of neat methyl oleate. Again, such tribological improvement indicates that both molecules of ZDDP and methyl oleate is capable of complementing each other's boundary lubrication properties so long as the blending ratio is properly optimised. Similar trend is also being reported for ZDDP containing SAE grade engine lubricants when diluted with methyl esters [8].

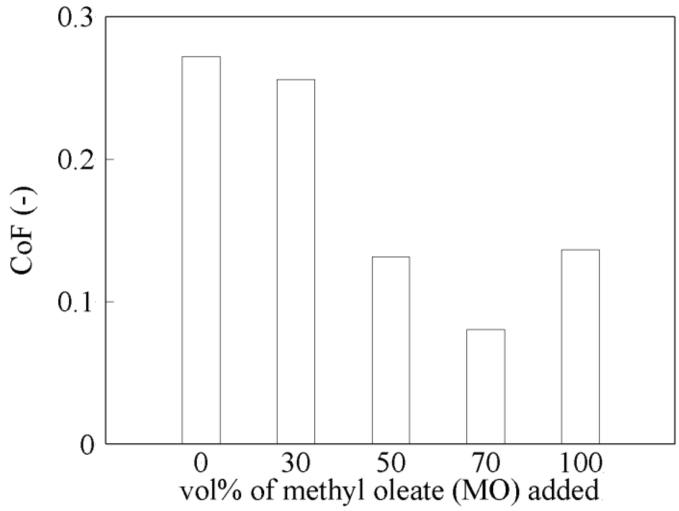


Figure 5. Coefficient of friction (CoF) variation for zinc dialkyldithiophosphate (ZDDP) added with different vol% of methyl oleate (MO)

4. Conclusion

The present study emphasises on the molecular interaction between ZDDP and methyl oleate along boundary lubrication regime at asperity level. Frictional properties are measured using lateral force microscopy coupled with fluid imaging for mixtures of ZDDP and methyl oleate at different volumetric percentages. It is observed that friction forces reduce when the amount of methyl oleate increases in the ZDDP-methyl oleate mixture. More interestingly, the addition of methyl oleate at 50-vol% and 70-vol% resulted in friction forces lower than that of the neat methyl oleate. When comparing the coefficient of friction (CoF) values, the lowest value is achieved for the ZDDP-methyl oleate mixture with 70-vol% methyl oleate, which is 0.081. This value is lower than the CoF of neat methyl oleate at 0.137. The results indicate that a much improved tribological performance along boundary lubrication regime could be obtained as long as an optimum blending ratio between ZDDP and methyl oleate is determined. This finding allows for a platform to further investigate the feasibility of using FAME as lubricant additives.

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