

# EFFECT OF INTERMEDIATE ESTERS TOWARDS BOUNDARY LUBRICITY OF PALM METHYL ESTER

Chiew Tin Lee\*, Hong Lian Low, and Mei Bao Lee

Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

## Article history

14<sup>th</sup> June 2023

Received in revised form

22<sup>nd</sup> October 2023

Accepted

23<sup>rd</sup> October 2023

Published

1<sup>st</sup> December 2023

\*Corresponding author  
ctlee5@graduate.utm.my

## ABSTRACT

Mechanism of methanolysis, using vegetable oil, methanol, and base-catalyze, is generally used to produce methyl ester. This method is also utilized for the kinetic study of the transesterification process based on the formation of fatty acid methyl esters to differentiate among the intermediate esters (e.g., triglyceride, diglyceride, monoglyceride, methyl esters). In the present study, the effect of intermediate ester content of palm oil transesterified with methanol, using potassium hydroxide as base-catalyze, was investigated. The operating conditions of transesterification used were the molar ratio of oil to methanol (1:7), the concentration of catalysis (1.0 wt% based on palm oil) with fixed reaction temperature of 55°C at reaction times of 0.5 and 60 minutes. A kinetic model was then adopted to determine the concentration of each intermediate esters. Boundary frictional analyses were conducted using lateral force microscopy (LFM) with different tip sliding velocities and applied normal loads. The experimental results obtained demonstrated that high triglyceride content exhibited better boundary frictional properties across tested tip sliding velocities and normal loads.

## KEYWORDS

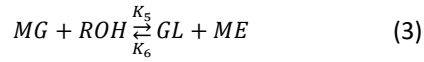
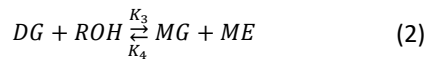
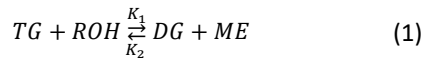
Transesterification; Lateral Force Microscopy; Frictional properties

## INTRODUCTION

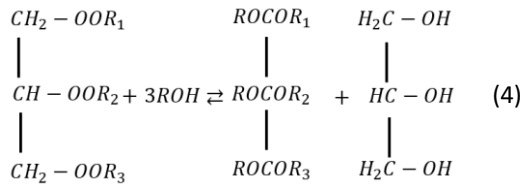
After use, the unregulated disposal of fossil fuel-based lubricants can lead to severe environmental contamination [1]. In addition, the diminishing fossil fuel reserves also increase the need to find an environmentally friendly alternative fuel. Thus, one of the most explored alternative resources to fossil fuel-based lubricants is derived from vegetable oil. Vegetable oil and animal fat are commonly used as a lubricant. However, the direct use of vegetable oil in machine elements, such as engines, poses various issues in the long run that are also coupled with high-temperature conditions [2]. Many studies have been conducted to align the physical and chemical properties of these alternative lubricants approximately to the performance of the fossil fuel-based ones.

Among these efforts, one of the more effective approaches is chemical modifications of vegetable oil transesterification. Transesterification of vegetable oil with methanol in a base-catalyze environment is commonly used to produce fatty acid methyl ester (FAME). Generally, FAME is a mono-methyl ester derived from the triglyceride structure of vegetable oil. As shown in equations (1)-(3), the transesterification process reverses three-step reaction because vegetable oil has three branches of the ester chain. First, the vegetable oil's triglyceride (TG) structure is converted into diglyceride (DG) and fatty acid mono-methyl ester. Then, the diglyceride will be further decomposed into monoglyceride (MG) and fatty acid mono-methyl ester. Eventually, monoglyceride is decomposed into fatty acid mono-methyl ester and glycerol [3-8]. The overall transesterification process occurs when one mole of oil is reacted with three mols of alcohol to produce FAME and glycerol, as shown in equation (4). According to the European standard for biodiesel (EN14214), the

yield of FAME higher than 96.5% is accepted as biodiesel [9].



Overall reaction,



$K_{1-6}$  are the reaction rate constants, and R is the alkyl group.

The triglyceride of natural oil may boost lubricity as a polar group in its structure can provide adequate boundary lubrication and act as anti-wear and friction additives for commercial lubricants [10]. Commercial lubricant's viscosity index (VI) has improved up to a maximum load of 500 N when added with 5% of palm oil methyl ester [11]. Goodrum and Geller [12] also studied the effect of lubricity for a commercial lubricant blended with castor methyl ester and Lesquerella oil methyl ester. They found that both methyl esters enhanced the lubricant's lubricity with a concentration of less than 1%. The high concentration of ricinolate acid was explained to be responsible for the lubricity-improving properties of the castor methyl ester.

Several kinetic studies [3-8] have also been reported in the literature, which focuses on the effect of operating conditions of transesterification, such as the molar ratio of oil to alcohol, reaction temperature, concentration, and type of catalyst. The concentration of each intermediate ester, which can play an essential role in determining the tribological behavior of the derived FAME, could be estimated using a kinetic model. Hu et al. [13] evaluated and compared the lubricity properties of refined and unrefined biodiesel. The effects of triglyceride (TG), diglyceride (DG), and monoglyceride (MG) on the lubricity properties of biodiesel were also examined. The lubricity properties of the biodiesel were evaluated by adding the derived biodiesels to base diesel and measuring the wear area diameter (WSD) obtained from using the High-Frequency Reciprocating Rig. The composition of the biodiesel was analyzed by gas chromatography (GC). Hu et al. found that unrefined biodiesel, consisting of more TG, DG, and

MG, had better lubricity properties than refined biodiesel.

Tribological characterization of a lubricant is usually measured using a high-speed reciprocating rig [13-15] and a ball/pin-on-disc tribometer [16]. These apparatuses are used to measure the friction force or wear scars. However, due to the significant influence of direct surface asperity interactions, these tribometers could not isolate the shearing of biodiesel lubricant film at the boundary lubrication regime. The tribofilm formed in this regime is not affected by the lubricant viscosity but is heavily dependent on the physical adsorption or chemical interaction between the lubricant and the surface. Thus, to isolate the shearing of boundary film, tribological characterization should be conducted at an atomic level. A study has been presented by Chong et al. [17], where they measured the friction force for biodiesels using Lateral Force Microscopy (LFM) and fluid imaging techniques. They observed that the CoF values for their tested biodiesels exhibited a trend that resembled the Stribeck curve, similarly reported by Maru et al. [16].

To further explore the boundary lubricity of FAME, this paper intends to provide an experimental elucidation on the efficiency of FAME as a substitute for petroleum-based lubricant, especially along with the boundary lubrication regime. The present study investigates the boundary lubrication properties of derived palm-oil-based FAME through different allowed reaction durations of the transesterification process. Subsequently, this is expected to allow for the potential correlation of boundary frictional properties with the concentration of intermediate esters in FAME, which is essential in determining the influence of these intermediate esters on the boundary frictional properties of FAME.

## METHODOLOGY

### Production of Palm Methyl Ester (FAME)

The experiments are designed to obtain various concentrations of intermediate ester and their respective boundary frictional properties. Different amounts of TG, DG, and MG can be obtained by controlling the reaction time during transesterification. In the present study, FAME is derived using refined bleach-deodorized (RBD) palm olein oil under a tested set of operating conditions. Based on the literature studies [3-8], a set of operating settings for transesterification was applied in this study. A 1:7 molar ratio of palm oil to

methanol was reacted with 1.0 wt.% of potassium hydroxide (KOH). Two different reaction times were selected, 0.5 and 60, representing two extreme transesterification conditions. In the following discussions, FAME reacted at 0.5 and 60 minutes, referred to as FAME-0.5 and FAME-60, respectively.

The present study conducted both cases at a fixed operating condition of 55 °C. After the reactions were completed based on the set reaction times, the mixtures were cooled to room temperature, with the top layer of FAME filtrated from glycerol. The mixtures were washed gently with water to remove the impurity and left in the oven overnight to evaporate the excess methanol and water. Figure 1 below illustrates the schematic diagram of the transesterification setup used in the present study.

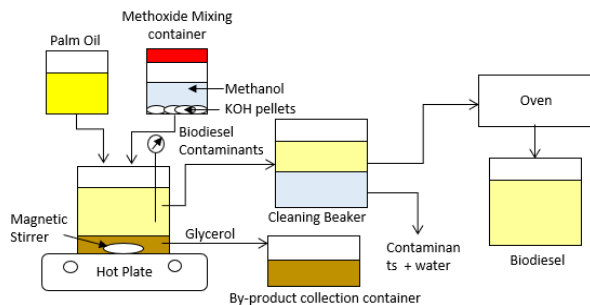


Figure 1: Schematic diagram for transesterification of palm oil

To determine the concentration of each intermediate esters (TG, DG, MG, FAME) for each case, a kinetic model developed by Darnoko and Cheryan [6], is adopted to determine the concentration of each intermediate esters. The macro model was created based on the above set of second-order equations. On the other hand, reaction rate constants proposed by Shahbazi et al. [5] were used together with the macro model.

### Viscosity measurement of FAME

The viscosity of the samples derived was determined according to ASTM D445. The kinematic viscosities of the samples were measured using a Brookfield Viscometer, model LVDV-II+Pro, at different temperature values, ranging from room temperature up to 100°C. The sample temperature was controlled and maintained at the required temperature using a temperature bath. Then, the dynamic viscosity is directly obtained from the analysis and converted into kinematic viscosity by dividing its density at the respective temperature. The viscosity index (VI) was also calculated for each sample of FAME according to ASTM D2270 [18].

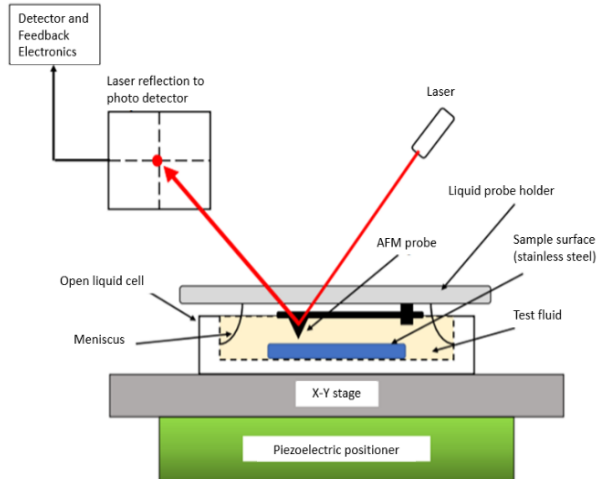
### Boundary friction measurement of FAME

The tribological properties of the derived biodiesels were investigated using Lateral Force Microscopy (LFM) (Park System XE-7 AFM), coupled with fluid imaging technique because the approach allows for the isolation of boundary film shearing from surface asperity interactions as compared to typical tribometer testing. Boundary frictional measurements were conducted using a silicon nitrate atomic force microscope (AFM) contact probe (tip radius = 10 nm) and silicon nitrate cantilever (PPP-CONTSCR 10M) of the resonant frequency of 23 kHz and spring stiffness of 0.2 N/m. For the friction test, the AFM tip was sliding on a stainless-steel substrate (composite surface roughness,  $S_q \sim 0.9$  nm) at varied applied normal loads (1-10 nN) and sliding velocities (2–200  $\mu\text{m/s}$ ) while being submerged in the studied FAME samples. Since the  $S_q$  value of the samples is comparatively smaller than the tip radius ( $\approx 10$  nm), the surface roughness can be assumed to be negligible during frictional measuring along with such tribological conjunction. Also, all substrate samples were cleaned using an alcohol pad and left to dry in a desiccator before running the experiments.

LFM measurement was started by scanning each sample's dry condition and adding the prepared FAME fluid samples slowly between the tip and the substrate contacts. During the set-up of the fluid imaging approach, an inlet meniscus has to be observed around the liquid probe holder, ensuring a full submersion of the AFM tip in the test fluid (see Figure 2) to minimize the meniscus forces' influence on the frictional contact conjunction during the measurement process [19]. It is to be noted that the AFM tip was first calibrated by scanning on a Silicon substrate with a known coefficient of boundary shear strength of 0.19 [17, 20]. Each fluid measurement was conducted using a new tip. The absolute average friction value (trace-and-retrace) was calculated for its applied normal load. The output from LFM is in the voltage signal. Therefore, the "Blind" calibration approach, proposed by Buenviaje et al. [21], was adopted to convert the trace-retrace voltage signal into friction force physical values. The calculated  $\alpha$  values were calculated based on the coefficient of boundary shear strength of the Silicon substrate, which is taken as 0.19. Then, all  $\alpha$  values were curve-fitted with the best power curve to obtain the respective value based on the power curve-fitted equation. The friction force could be converted into the required physical parameter using this calibration factor:

$$\alpha = \frac{F_f(V)}{F_n(nN)} \times \frac{1}{0.19} \quad (5)$$

$$F_f(nN) = \frac{F_f(V)}{\alpha_{cal}(V/nN)} \quad (6)$$

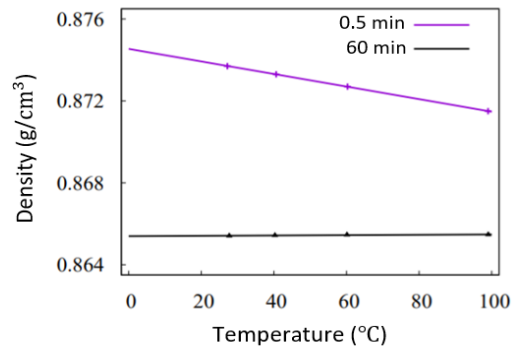


**Figure 2:** Lateral Force Microscopy (LFM) for varied applied normal loads (1–10 nN) and sliding velocities (2–200  $\mu\text{m/s}$ ) using the fluid imaging technique

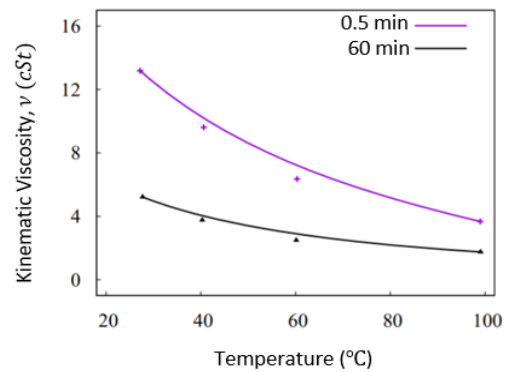
## RESULTS AND DISCUSSION

### Ester percentage and viscosity of FAME

Figure 3(a) shows the density of produced biodiesels measured at different temperatures. It is shown that the density reduces with temperature for both tested samples. At 40°C, FAME-60 possesses a density of 0.865  $\text{g/cm}^3$ , like the results observed by Demirbas [22]. Transesterification primarily aims to lower the viscosity of crude palm oil [22]. Such characteristic is evidenced in Figure 3(b), where the kinematic viscosity of FAME-0.5 is significantly higher than that measured for FAME-60, showing that the kinematic viscosity of vegetable oil decreases when the transesterification reaction progresses. The kinematic viscosity is also demonstrated to decrease as the temperature increases for both cases. However, the trend of FAME-0.5 dropped more dramatically compared to FAME-60 min, reflecting that a higher TG content is more susceptible to viscosity change with increasing temperature.



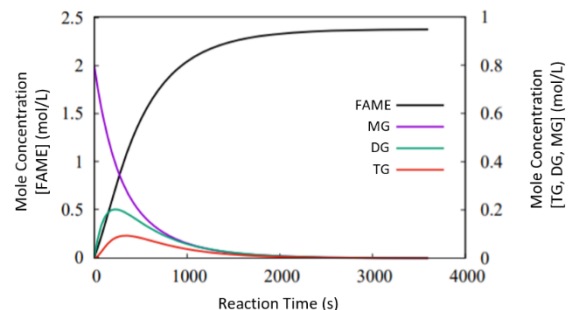
(a)



(b)

**Figure 3:** Density and kinematic viscosity–temperature relationships of test fluids

Figure 4 shows that the reaction begins with a very high reaction rate and slows down as the reaction reaches equilibrium. The trend can also be observed in many other studies related to palm oil transesterification [6]. It can be concluded that the highest number of intermediate esters exist at the first minute of the reaction. At the same time, there are the least amount of reaction intermediate esters after the reaction is complete



**Figure 4:** Transesterification process of palm oil

**Table 1:** Percentage of intermediate esters formed according to reaction time

	FAME-0.5		FAME-60	
	MC (mol/L)	% Int.Ester	MC (mol/L)	% Int.Ester
[FAME]	0.083	9.47	2.387	99.96
[TG]	0.721	82.01	3.78E-04	0.02
[DG]	0.069	7.84	4.00E-04	0.02
[MG]	0.006	0.68	2.66E-04	0.01
Ester yield (%)	3.48		99.91	

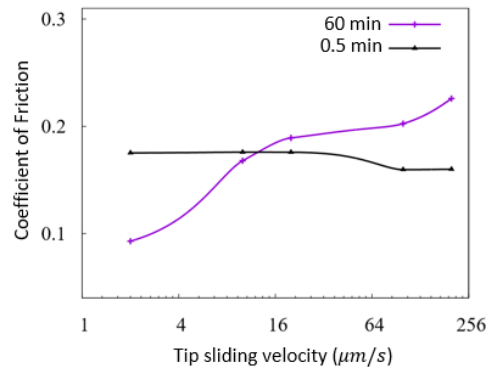
MC = mole concentration  
% Int. Ester = percentage of intermediate esters

Table 1 illustrates the percentage of each intermediate ester (TG, DG, MG, FAME) obtained at 0.5 (FAME-0.5) and 60 (FAME-60) minutes using the kinetic model developed by Darnoko and Cheryan [6]. The yield percentage of each intermediate ester is calculated based on the volume obtained. The reaction duration of 0.5 min shows a high concentration of TG (82.01%), while the reaction duration of 60 mins exhibits a high concentration of FAME (99.96%). With a reaction time of 60 minutes, approximately 0.02% of TG is estimated to be left behind in the mixture. According to the European standard for biodiesel (EN14214), such a high yield of 99.91% is accepted as biodiesel (>96.5%) [9]. From Table 1, it is clearly shown that there is only a slight difference in the molar concentration of DG (7.84% and 0.02%) and MG (0.68% and 0.01%) for both reaction times. On the other hand, a huge difference can be seen for FAME and TG, which are 9.47% ([FAME]-0.5 min), 99.96% ([FAME]-60 min), and 82.01% ([TG]-0.5 min) and 0.02% ([TG]-60 min). Thus, the boundary lubrication properties of FAME and biodiesel are more likely to be affected by the mole concentration of FAME and TG.

### Boundary friction analysis of FAME

Before conducting the frictional measurement of the test fluids using LFM, the force of adhesion of each test fluid was obtained from the force-displacement curve. As the AFM tip holder was entirely contained within an inlet meniscus, the surface energy of the fluid molecule was expected to be negligible throughout the measurement. Hence, the negative tensile stress (adhesion force) is not expected to be observed in the force-displacement curve for all operating conditions except for dry contact measurement [17]. At the boundary lubrication regime, lubrication typically involves shearing the boundary-absorbed thin film [23]. Through LFM, across the tested sliding velocities, FAME-0.5 is found to have generated a

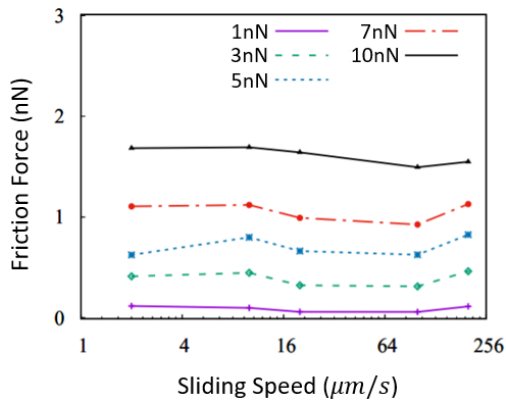
lower coefficient of friction (CoF) than FAME-60. By comparing both FAME-0.5 and FAME-60, the latter experienced a dramatic increase in CoF across the tested sliding velocities. At the same time, the CoF of the former remains relatively steady with a slight decline beyond 20  $\mu\text{m/s}$ . This demonstrated that high concentrations of FAME could potentially lack its ability to maintain an effective boundary film, leading to the increased CoF generated at higher sliding velocities. The intermediate esters possess free OH groups and could form hydrogen bonds that give ionic interaction with the metal surface [15]. Thus, as compared to FAME-60, a more significant amount of intermediate ester in FAME-0.5 (as shown in Table 1) is expected to be able to form a more stable boundary layer, corroborating with the measured CoF trend.



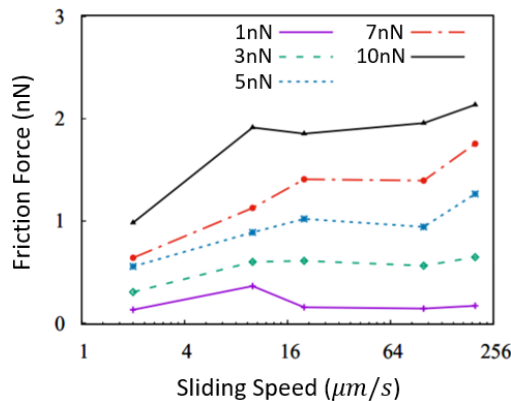
**Figure 5:** Coefficient of friction against tip sliding velocity for reaction duration of 0.5 (FAME-0.5) and 60 (FAME-60) mins.

The velocity and load dependence of the test FAME samples were also investigated. Figure 6 shows the friction force at a range of tip sliding velocities of (2–200  $\mu\text{m/s}$ ) and normal load (1–10 nN). It can be observed that the friction force is generally measured to be lower for FAME-0.5 as compared to FAME-60. When the sliding velocity increases, more lubricant molecules are expected to enter the confined space between the tip and the sample surface, which increases the chances of building up a more effective film. This phenomenon could explain the slight decrease of friction force at higher speeds for FAME-0.5, as illustrated in Figure 6(a), which could also be explained because of the higher content of TG in FAME-0.5 that allows for the formation of a more effective film as more lubricant enters the confined space compared to FAME-60, which has a lower amount of TG. The formation of such boundary films can mitigate excessive friction in boundary regimes of lubrication [24]. More importantly, the observed trend follows that real lubricants should comprise varying molecular

species (e.g., additives) that can promote desired contact characteristics [25].



(a) FAME-0.5



(b) FAME-60

**Figure 6:** Friction force against tip sliding velocity at different normal loadings for the reaction time of 0.5 and 60 mins.

## CONCLUSION

In the present study, the experimental results demonstrated that high content of triglycerides, TG, in FAME exhibited better boundary frictional properties across the tested tip sliding velocities and applied normal loads measured using LFM. The FAME-0.5 exhibited lower CoF and friction force at higher sliding velocities than FAME-60. This could be explained because the FAME-0.5 sample maintained a more effective film when the lubricant entered the confined space faster than FAME-60. This study shows that the more significant amount of reaction intermediate esters in FAME at the boundary lubrication regime could help maintain a more stable film at higher speeds. The high degree of non-polarity of the triglycerides found in the produced FAME is also expected to better adsorb onto the interaction surface, forming

an effective film to protect the surface better. The formation of such a boundary film can further separate the opposing surfaces in reducing friction, similarly observed through the measured boundary CoF properties.

## ACKNOWLEDGMENTS

We thank Universiti Teknologi Malaysia for sponsoring our doctorate studies through UTM Zamalah.

## REFERENCES

1. Willing, A., 2001. Lubricants based on renewable resources—an environmentally compatible alternative to mineral oil products. *Chemosphere*. 43(1): 89-98.
2. Venkatesan, M., Vikram, C., Naveenchandran, P., 2012. Performance and emission analysis of pongamia oil methyl ester with diesel blend. *Middle East Journal of Scientific Research*. 12(12): 1758-1765.
3. Liu, X., Piao, X., Wang, Y., Zhu, S., 2010. Model study on transesterification of soybean oil to biodiesel with methanol using solid base catalyst. *The Journal of Physical Chemistry A*. 114(11): 3750-3755.
4. Tubino, M., Junior, J. G. R., Bauerfeldt, G. F., 2016. Biodiesel synthesis: A study of the triglyceride methanolysis reaction with alkaline catalysts. *Catalysis Communications*. 75: 6-12.
5. Shahbazi, M. R., Khoshandam, B., Nasiri, M., Ghazvini, M., 2012. Biodiesel production via alkali-catalyzed transesterification of Malaysian RBD palm oil—Characterization, kinetics model. *Journal of the Taiwan institute of chemical engineers*. 43(4): 504-510.
6. Darnoko, D., Cheryan, M., 2000. Kinetics of palm oil transesterification in a batch reactor. *Journal of the American Oil Chemists' Society*. 77: 1263-1267.
7. Likozar, B., Levec, J., 2014. Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition. *Applied energy*. 123: 108-120.
8. Nouredini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. *Journal of the American Oil Chemists' Society*. 74: 1457-1463.
9. ASTM, A., 2008. Standard specification for biodiesel fuel (B100) blend stock for distillate fuels. *Annual book of ASTM standards*.
10. Maleque, M., Masjuki, H., Sapuan, S., 2003. Vegetable-based biodegradable lubricating oil additives. *Industrial lubrication and Tribology*.
11. Maleque, M. A., Masjuki, H. H., Haseeb, A., 2000. Effect of mechanical factors on tribological properties of palm oil methyl ester blended lubricant. *Wear*. 239(1): 117-125.

12. Goodrum, J. W., Geller, D. P., 2005. Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. *Bioresource technology*. 96(7): 851-855.
13. Hu, J., Du, Z., Li, C., Min, E., 2005. Study on the lubrication properties of biodiesel as fuel lubricity enhancers. *Fuel*. 84(12-13): 1601-1606.
14. Geller, D. P., Goodrum, J. W., 2004. Effects of specific fatty acid methyl esters on diesel fuel lubricity. *Fuel*. 83(17-18): 2351-2356.
15. Knothe, G., Steidley, K. R., 2005. Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. *Energy & fuels*. 19(3): 1192-1200.
16. Maru, M. M., Trommer, R. M., Almeida, F. A., Silva, R. F., Achete, C. A., 2013. Assessment of the lubricant behaviour of biodiesel fuels using Stribeck curves. *Fuel processing technology*. 116: 130-134.
17. Chong, W., Ng, J.-H., 2016. An atomic-scale approach for biodiesel boundary lubricity characterisation. *International Biodeterioration & Biodegradation*. 113: 34-43.
18. D, A., 2003. Standard practice for calculating viscosity index from kinematic viscosity at 40 and 100° C. *Annual Book of Standards*.
19. Leighton, M., Nicholls, T., De la Cruz, M., Rahmani, R., Rahnejat, H., 2017. Combined lubricant–surface system perspective: Multi-scale numerical–experimental investigation. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*. 231(7): 910-924.
20. Hamdan, S., Chong, W., Ng, J.-H., Chong, C., Zhang, H., 2018. Nano-tribological characterisation of palm oil-based trimethylolpropane ester for application as boundary lubricant. *Tribology International*. 127: 1-9.
21. Buenviaje, C., Ge, S.-R., Rafailovich, M., Overney, R., 1998. Atomic force microscopy calibration methods for lateral force, elasticity, and viscosity. *MRS Online Proceedings Library*. 522: 187-192.
22. Demirbas, A., 2008. Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel*. 87(8-9): 1743-1748.
23. Hamdan, S., Chong, W., Ng, J.-H., Ghazali, M., Wood, R., 2017. Influence of fatty acid methyl ester composition on tribological properties of vegetable oils and duck fat derived biodiesel. *Tribology International*. 113: 76-82.
24. Chong, W., Teodorescu, M., Rahnejat, H., 2012. Physio-chemical hydrodynamic mechanism underlying the formation of thin adsorbed boundary films. *Faraday discussions*. 156(1): 123-136.
25. Chong, W., Teodorescu, M., Rahnejat, H., 2011. Effect of lubricant molecular rheology on formation and shear of ultra-thin surface films. *Journal of Physics D: Applied Physics*. 44(16): 165302.