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Effect of oxidation and dilution of B30 palm oil biodiesel in pentaerythritol ester as engine bio-lubricant

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KEYWORDS

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ABSTRACT

Biodiesel and bio-lubricants became desirable options as alternative fuel and engine oil, respectively, to meet sustainability goals. However, their effects on the performance and longevity of engines are not well-established yet. The lubricity performance of engine oils is affected by oxidation and biodiesel dilution, potentially resulting in reduced efficiency and tribological characteristics. This research investigates the effect of oxidation on the physicochemical and tribological properties of aged pentaerythritol (PE) ester diluted with 0%, 1%, 5% and 10% palm oil biodiesel blend (B30) as well as 5% B30 + 0.2% antioxidant additive and compared to pure PE ester. The results showed that ageing and biodiesel dilution increased the kinematic and dynamic by 504.02-521.87% at 40 °C and 148.25-154.44% at 100 °C. Additionally, they significantly improved the coefficient of friction (from > 0.1 to less than 0.06) and the wear rate compared to unaged-undiluted PE ester. It was found that the antioxidant additive reduced the dynamic and kinematic viscosities which resulted in higher COF and wear rate compared to the aged and biodiesel diluted samples.

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1.0 INTRODUCTION

Engine oil plays a very important role in keeping the engine system working optimally and efficiently. The main functions of engine oil are to reduce wear on components such as bearings, pistons, piston rings, cylinder linings, valve trains and other moving parts of the engine which requires lubrication (al Sheikh Omar et al., 2021). Currently, biodegradable lubricating oils have received increasing attention as an environmentally friendly alternative to the current synthetic and mineral oils used as engine lubricants. Esters-based on synthetic and vegetable oils are the common options as environmentally friendly lubricants (Chan et al., 2018; Salimon et al., 2010). Pentaerythritol esters also known as PE ester is a chemical substance with many hydroxyl groups that have superior tribological characteristics such as high viscosity index and lubricity (Chen et al., 2022; El-Magly et al., 2013). Even though there have been several attempts to identify a suitable alternative to mineral-based oils in internal combustion engines, few research have emphasized the potential of ester-based bio lubricants as an aid to engine oil (Aziz et al., 2016). PE esters bio-lubricants are less toxic, biodegradable, and affordable when blended with mineral oil-based lubricants (Xu et al., 2019). However, esters are susceptible to oxidation which may affect their tribological characteristics.

Major automakers are concerned about tribological performance of diesel engines running by biodiesel blends. Biodiesels is fundamentally less oxidatively stable than ultra-low-sulfur diesel and they can readily create hydroperoxides, which in turn cause the synthesis of short chain acids or polymerization. These compounds deposit on the engine parts resulting in reduced tribological performance (Karavalakis et al., 2010; Uy et al., 2011). Additionally, they are concentrated in the oil sump causing higher biodiesel dilution levels due to their higher and narrower boiling range (325-375 ^{o}C) (Zdrodowski et al., 2010). Biodiesel dilution is decreasing engine oil viscosity and additives concentrations which negatively affect the lubricity of oil and its life, as well as increasing engine wear and piston deposits.

To the extent knowledge of the authors, no research addressed the effect of oxidation and biodiesel dilution with B30 blend on the physicochemical and tribological properties of PE ester bio lubricant. Thus, this research investigates the effect of dilution with 0%, 1%, 5% and 10% palm oil biodiesel blend (B30) as well as 5% B30 + 0.2% antioxidant additive and oxidation of PE ester by aging for 96 hrs. on its physicochemical and tribological properties for IC engines, then compared to pure PE ester without treatment.

2.0 EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Six samples – each of 250 ml – were prepared by mixing PE ester with B30 blend (using palm oil biodiesel) according to Table 1. For sample S5, 0.2%wt. of antioxidant from Ester of thiolate butylated hydroxytoluene was added. The recommended percentage for additives is 0.2-2%. In this research, the minimum of 0.2% antioxidant was used. This antioxidant can reduce the oxidation and prevent the aging of PE ester (Nath et al., 2018).

All the samples were artificially aged in the laboratory to mimic the engine oil operating conditions according to ASTM D4636-99. The samples were thermally aged at 160±3 °C with continuous stirring at 500 rpm for 96 hrs., Figure 1. A grey cast iron sample – as oxidation catalysis – was put into the mixture and air was supplied at a rate of 2 liter/hr to simulate the oxidation process of oil. A condenser was attached to minimize loss of oil due to evaporation during the aging process.

Table 1: Samples prepared for testing and investigation.

Sample	PE ester %	B30 %	Aging time, hrs.
S0	100	0	0
S1	100	0	96
S2	99	1	96
S3	95	5	96
S4	90	10	96
S5	94.8+ 0.2 antioxidant	5	96

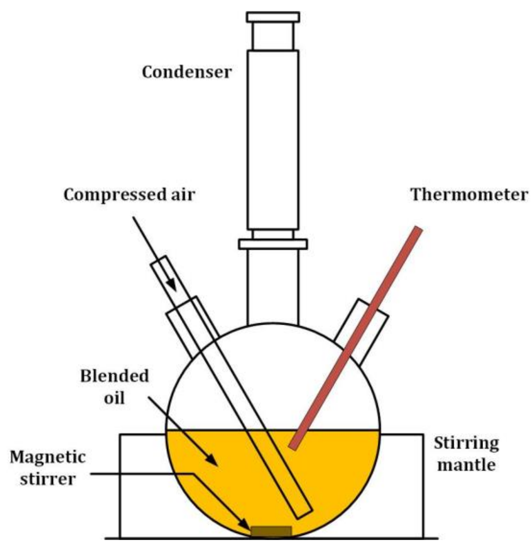

Figure 1: Schematic diagram of set up.

2.2 Physicochemical Characterization

The kinematic and dynamic viscosities of the prepared samples was measured using SVM 3000 Stabinger viscometer at standard temperatures of 40°C and 100°C. The viscosity index was calculated according to ASTM D2270. While the density was measured using SVM 3000 Stabinger Viscometer at a temperature of 15 °C.

Then, the total acid number (TAN) of the prepared samples was determined using the titration method. The titration was performed by adding phenolphthalein and KOH until neutralization and the TAN is calculated using Eq. (1) according to ASTM D974.

$$Total\ Acid\ Number\ (TAN)\left(mg\,\frac{KOH}{g}\right) = \frac{(A-B)M\times 56.1}{mass\ of\ sample\ (g)} \quad (1)$$

Where, A is the volume of KOH in mL, B is the KOH solution required for titration of the blank in mL, M = 0.1 (molarity of KOH) and 56.1 is the molarity weight of fatty acid.

2.3 Tribology Testing

High frequency reciprocating rig (HFRR), Figure 2, was employed to perform the tribology test according to ASTM D6079-18. The test comprises of a 6 mm hardened steel ball and 15 mm × 15 mm × 4 mm hardened steel plate submerged in 5±0.1 ml of prepared lubricant blend (the lubricant level was 3mm of ball diameter). The mating surfaces were polished to mirror-like to ensure the reliability of the results. The test conditions are set according to Table 2.

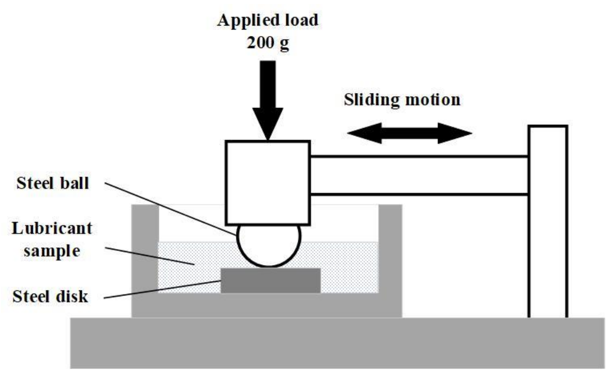

Figure 2: Schematic diagram of HFRR.

Table 2: Tribology test conditions.

Frequency, Hz	Load, N	Test duration, h	Stroke length, mm	Temperature, ^{o}C
10	2±0.1	1±0.01	3±0.05	27±2

The coefficient of friction (COF) formula is calculated according to Eq. (2):

$$\mu = \frac{f}{N} \quad (2)$$

Where: μ = coefficient of friction, f = frictional force in N, N = normal force in N.
After that, the lubricity of the prepared samples was assessed through weight loss of the steel ball and plate. Thus, the weight of steel ball and plate was measured before and after the test using precision scale (0.1 mg). After the test, the steel ball and plate were rinsed with ethanol and acetone, then ultrasonicated for 5 min. to remove the lubricant and any debris resulted from the wear.

2.4 Fourier-Transform Infrared Analysis

The prepared samples were analyzed using Fourier-Transform Infrared (FTIR, Spectrum 400, Perkin Elmer) to reveal their composition and resulted oxidation products such as aldehydes, carboxylic acids, and ketones. These substances can form strong organic acids which increase the wear rates. FTIR is not used to quantify the compounds formed due to thermal aging and biodiesel dilution.

3.0 RESULTS AND DISCUSSION

3.1 Physicochemical Characterization

The results of viscosity measurements are listed in Table 3. Sample S0 served as the baseline reference for the comparison between the diluted and aged samples. The results showed that the aged samples showed a dramatic increase in both kinematic and dynamic viscosities either at 40 or 100 ^{o}C. This can be attributed to polymerization and formation of hydroperoxides, aldehydes and ketones due to oxidation (Farfan-Cabrera et al., 2020). These compounds react forming carboxylic acid resulting in formation of high-molecular weight compounds that thickens the lubricant and increase the viscosity. Moreover, the viscosities increased as the level of biodiesel dilution increases. This is regarded to the oxidation of fatty acids contained in biodiesel which causes the degradation of the lubricant and increases the viscosity (Andreae et al., 2007; Karavalakis et al., 2010).

On the other side, the addition of antioxidant helped to reduce the increase in viscosity as shown by sample S5 which contained 0.2% antioxidant additive. This antioxidant effectively reduced the oxidation induced during the thermal aging process as confirmed previously (Nath et al., 2018). The antioxidant addition resulted in slight increase in the viscosity of S5 compared to S0 by 15.62-15.86% at 40 ^{o}C and 10.38-10.86% at 100 ^{o}C while the viscosities of samples S1, S2, S3 and S4 were increased by 504.02-521.87% at 40 ^{o}C and 148.25-154.44% at 100 ^{o}C.

It is noted that the density showed slight increase after thermal aging, in addition, the biodiesel dilution increased further the density of samples which caused by the formation of high-molecular weight compounds as indicated previously. However, the sample S5 showed the least increase in density implying that antioxidant helps in maintaining the physicochemical properties of the PE lubricant.

The aging and dilution increased the TAN compared to the baseline reference sample S0, Figure 3. It is noted that the aging – S1 – caused a slight increase in the TAN value, while the dilution showed a significant increase in the TAN values. Aging process results in peroxides and hydroperoxides which are the primary oxidation by-products. Additionally, these by-products undergo additional degradation in the existence of biodiesel to create shorter-chain molecules including low molecular weight acids, aldehydes, and ketones which significantly increase the TAN value. However, the addition of antioxidant reduces these reactions and decrease the TAN in the case of biodiesel dilution.

Table 3: Viscosity index, kinematic and dynamic viscosity, and density of prepared samples.

Property	Temp., ^{o}C	Sample					
		S0	S1	S2	S3	S4	S5
Kinematic viscosity, mm^2/s	40	68.471	174.510	270.990	413.580	413.580	79.170
	100	12.307	26.296	31.671	42.388	30.552	13.585
Dynamic viscosity, mPa.s	40	62.572	187.260	253.460	389.120	389.120	72.495
	100	10.769	19.622	28.398	38.312	27.401	11.938
Density, g/cm^2	15	0.9299	0.9398	0.9517	0.9569	0.9599	0.9316
Viscosity Index		179.7	173.7	158.5	155.4	104.5	176.2

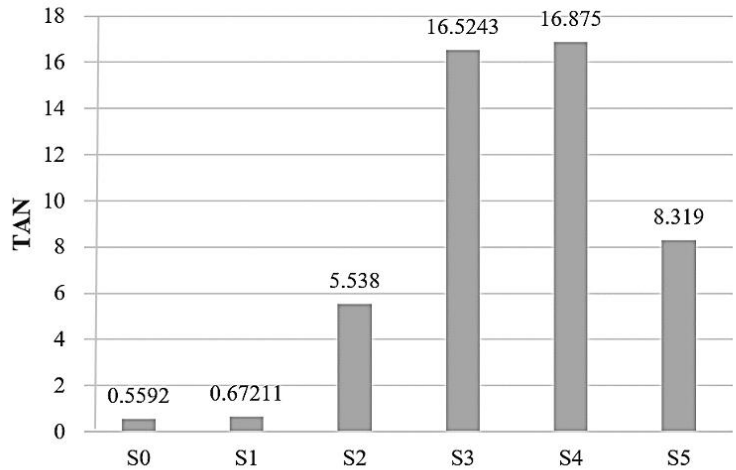

Figure 3: TAN values for the aged and diluted lubricant.

3.2 FTIR Analysis

Figure 4 shows FTIR spectra of aged and fuel-diluted samples. The recognized peaks are indicating the biodiesel dilution, besides the formation of ketones carboxylic acids (C=O), aldehydes and esters (C-O, C-H), while O-H groups are referred to the PE ester. These represent the compounds resulted from the thermal aging and biodiesel dilution. It is noted that as the biodiesel dilution increases, the transmittance increases which implies that the level of biodiesel dilution causes PE ester to degrade at a faster rate when higher levels of biodiesel dilution is present (Macián et al., 2012). This is regarded to the high molecular weight of the compounds formed.

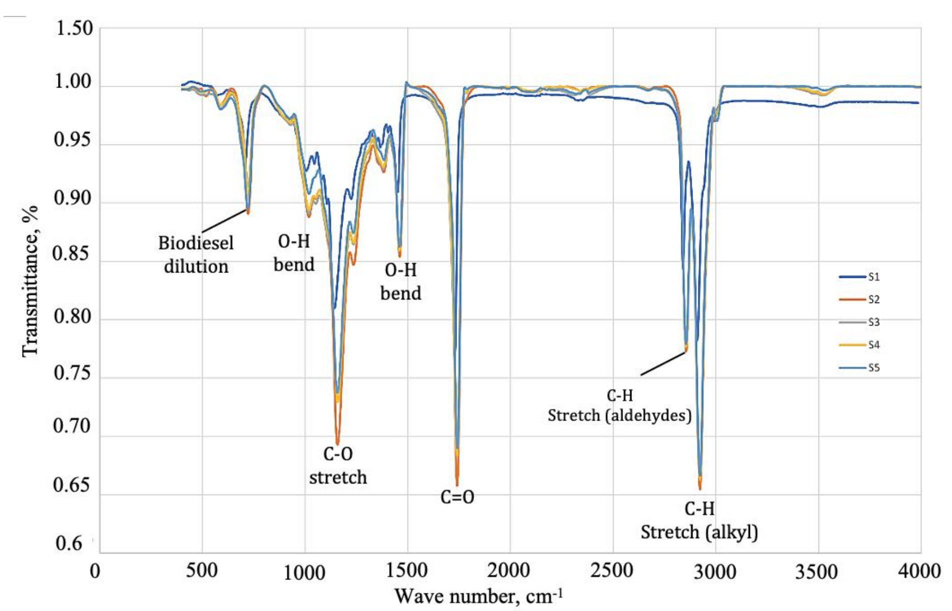

Figure 4: FTIR spectra of prepared samples.

3.3 Tribology Testing

Figure 5 shows results of COF with time. It is found that the highest COF was exhibited by S0 (an average COF > 0.1) and S5 (an average COF ≈ 0.08), while all other aged and diluted samples exhibited COF less than 0.06. This phenomenon occurs due to the "fluid friction" that is produced between lubricant layers. A high viscosity produces internal molecular friction which lead to less tribological performance.

These results imply that thermal aging and biodiesel dilution reduce the COF between mating surfaces as the dynamic and kinematic viscosities are increased, according to results presented in Table 3, which cause better coverage and stickiness to these mating surfaces. Additionally, the biodiesel improves the lubricity as indicated previously (Devlin et al., 2008; Hamdan et al., 2017).

The weight loss in tested plates under different lubricant samples is shown in Figure 6. Sample S0 showed the highest weight loss followed by S5 as they represented the lowest viscosity values. The alteration in weight loss – which is an indication for wear rate – is well related to the COF which is affected by the dynamic and kinematic viscosities. These results showed that increasing biodiesel dilution up to 5% improves the lubricity and tribological performance, while further increase to 10% degrades the lubricity and tribological performance (Hamdan et al., 2017).

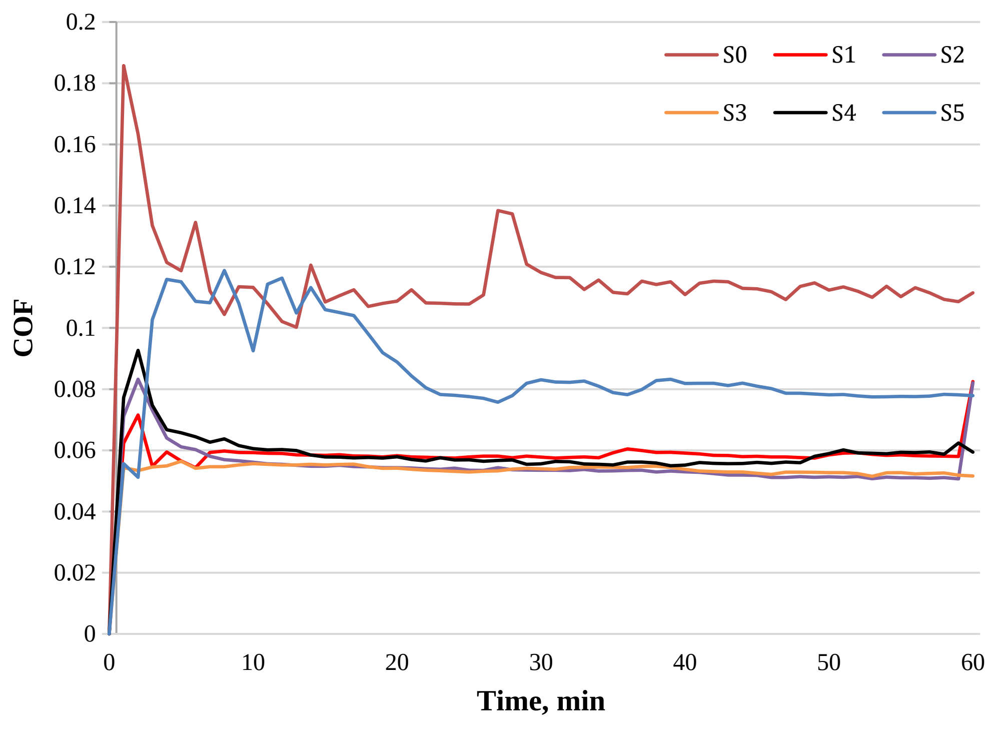

Figure 5: COF vs time for all samples.

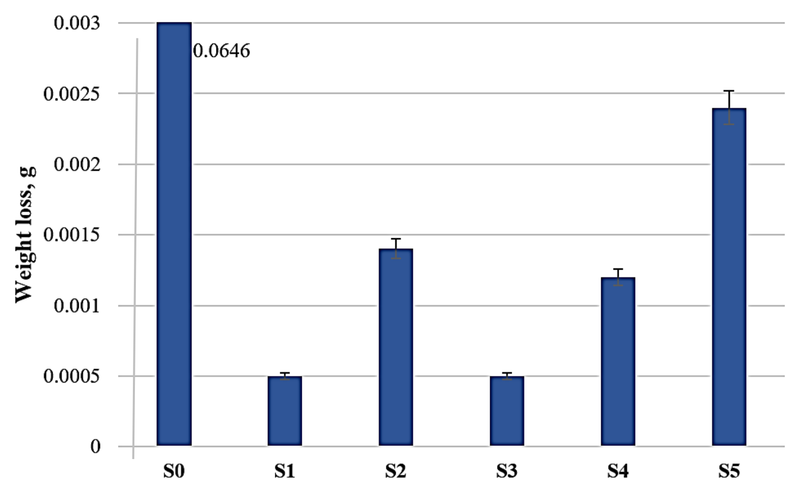

Figure 6: Weight loss of plate and ball due to wear test.

CONCLUSIONS

This research investigated the effect of B30 palm oil biodiesel dilution in aged pentaerythritol ester. The results showed that aging and increasing of biodiesel dilution caused the significantly increase of viscosity index, kinematic and dynamic viscosities, density, and TAN of lubricant samples. However, the addition of antioxidant hindered the increase in physicochemical properties due to less formation of high-weight molecular compounds. The biodiesel dilution caused the formation of carboxylic acids, aldehydes, and ketones – as confirmed by FTIR analysis – that significantly increased the TAN. The tribological test showed that unaged and undiluted oil exhibited the highest wear and COF followed by the sample S5 (aged, 5% biodiesel and 0.2% antioxidant), while the aged and diluted samples showed improved lubricity and less wear. This can be regarded to the higher viscosity of diluted and aged samples.

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