

# Tribological Performance of Silicon Dioxide (SiO<sub>2</sub>) Nanoparticles as an Additive for Engine Lubrication Oil

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## Article Info

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## Abstract

A comparative oil degradation test was undertaken to determine the reliability of lubricating oil when additional SiO<sub>2</sub> nanoparticles were incorporated. A blend of palm biodiesel at 20 percent was used as fuel for a single-cylinder diesel engine. The test cycle consisted of running the engine with B20 biodiesel fuel alongside lubricating oil (SAE15W40) for 160h. With the aim to observe the effects of lubricating oil's tribological properties when the additional additive was incorporated, a similar test cycle was repeated by adding SiO<sub>2</sub> nanoparticles together with the lubricating oil (SAE15W40). Various tribological properties of lubricating oil, such as kinematic viscosity, density, total base number, and moisture content recorded at regular intervals to correlate the effect of fuel chemistry on lubricating oil performance and engine life. When comparing the two different setups, it was evident that lubricating oil (SAE15W40) with SiO<sub>2</sub> nanoparticles exhibited greater kinematic viscosity and density versus the lubricating oil (SAE15W40) without SiO<sub>2</sub> nanoparticles. The amount of debris resulting from engine wear was measured using the Rotating Disk Electrode – Atomic Emission Spectroscopy. By analyzing the lubricating oil samples drawn from the engine, it was observed that lubricating oil (SAE15W40) without SiO<sub>2</sub> nanoparticles contained higher metal concentration from engine wear, and further exemplified in ferrography tests, whereby said lubrication oil demonstrated significant deterioration.

**Keywords:** Biodiesel, Nanoparticles, Single-Cylinder Diesel Engine, Tribological.

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## 1. INTRODUCTION

For medium to heavy-duty applications, diesel engines are primarily used as power sources due to good thermal performance, lower fuel usage, and ability to withstand pressure and wear [1]. With close to 90% of global palm production, Malaysia is the second-largest producer of palm oil after Indonesia [2]. As vehicle ownership expands, demand for petroleum is expected to grow exponentially in the transportation sector for the

coming years. Because of the decline of fossil supplies and the subsequent deterioration of the atmosphere and global warming, worldwide attention extended to alternative fuels. At the present stage of technological development, biodiesel is the most widely renewable alternative to diesel fuels and is also the most commonly used transportation fuel [3]. The government of Malaysia is moving towards using a more sustainable option for energy, which is biodiesel. It will move further down the biodiesel route with biodiesel blend B30

arriving by 2025 [4]. By June 2021, the B20 biodiesel plan for the transport sector should be introduced throughout Malaysia. The benefits of using biodiesel in the automotive sector are well known in previous literature [5 & 6].

However, with long-term duration of running the engine, biodiesel happens to cause many problems, such as injector clogging, increasing water content, carbon deposit, and contamination of lubricants [7]. Because of that, proper lubrication is important to boost the engine's useful life, since it protects different engine reciprocating parts from fatigue, and often lowers energy usage by increasing the friction between engine parts [8].

Most researchers and scientists around the globe have performed very few explorations in biodiesel engine tribology analysis. Gopal and Raj [9] have studied the effect of 20% of Pongamia oil on the degradation of lubricating oil in diesel engines for 256h. The findings indicate that Pongamia biodiesel has lower lubricating properties due to its corrosiveness, oxidation, and residue formation. Dhar and Agarwal [3] conducted an endurance test for 200h using a medium-duty diesel engine equipped with 20% of biodiesel blend from Karanja. From the study, it was revealed that biodiesel had poor lubrication properties because if it contained more oxidation than the diesel fuel, the existence of wear trace metals was also higher for the Karanja biodiesel blend. Gulzar et al. [10] studied the effects of 20% of Jatropha and 20% of palm biodiesel on a diesel engine for 200h engine running duration. The test showed that the residue of fuel from B20 petrol improved in relation to diesel fuel. In addition, B20 fuels induced high corrosion rates and accelerated oxidation to reduce the lifetime of lubricating oil throughout the engine durability test.

As a result of reduced utilization of biodiesel in a diesel engine that affected the lubricating oil, recently, nanoparticles are commonly studied to improve the tribology of lubricating oil [11]. A variety of nanoparticles, such as Molybdenum disulfide ( $\text{MoS}_2$ ), Silica ( $\text{SiO}_2$ ), Alumina ( $\text{Al}_2\text{O}_3$ ), Copper oxide ( $\text{CuO}$ ), and Titanium oxide ( $\text{TiO}_2$ )

have studied in terms of lubricating oil [12–15]. Besides these, metallic nanoparticles have also used as an additive in lubricating oil such as Copper (Cu), Iron (Fe), and Zinc (Zn) [16]. A study by Kotia et al. [13] on the  $\text{Al}_2\text{O}_3$  nanoparticle lubricating oil and performance evaluation in diesel engines found that  $\text{Al}_2\text{O}_3$  nanoparticles were chemically stable because of the fresh lubrication oil absorbance value in FTIR was close to nano lubricants. Besides that, the density range of nano lubricants was approximately uniform. However, the viscosity value of tests did not meet the viscosity prediction models. Patil et al. [17] have examined the behavior of  $\text{SiO}_2$  nanoparticles as additives in Paraffin based SN-500 base oil and resulted in nanoparticles to improve friction coefficient with 17% to 66% of reduction in lubricating oil compared to fresh lubricating oil. The improvement of tribological properties was also reported, and nanoparticles reduced shearing stress. Thus, this paper will emphasize the use of silicon dioxide ( $\text{SiO}_2$ ) nanoparticles as the additives in lubricating oil will give a good effect towards properties of lubricating oil or otherwise.

## 2. LUBRICANT PREPARATION

Silica ( $\text{SiO}_2$ ) nanoparticles have been used in this experiment as an additive in lubricating oil. The most widely used nanoparticles for previous research was in the range of 20-150 nm [18]. For this experiment, a 150nm of Silica has used to be added with lubricating oil. The size of the Silica nanoparticles has determined using Anton Paar Litesizer 500 Particle Analyzer. The result of the test is shown in Fig. 1. A mineral lubricating oil (SAE15W40) that commonly used in a heavy-duty diesel application has been used as a base lubricating oil in this experiment. 0.5% of silica nanoparticles are added with lubricating oil as an additive and become n- $\text{SiO}_2$ . To achieve the stability and agglomeration between these two types of materials, an ultrasonic bath have been used at 40°C with 1h operation. Fig. 2 and Fig. 3 showed a lubricating oil before and after the

sonication process. To make sure that there is no de-agglomeration of the lubricating oil, a sediment test has been conducted for two weeks to see whether there is no sediment remaining in the lubricating oil. Since detrimental effects on a vehicle's engine can start to emerge within two weeks of inactivity [19], a similar time frame was taken for the sediment test. Due to the fact that the engine is not running, there will be no buildup of sediment.

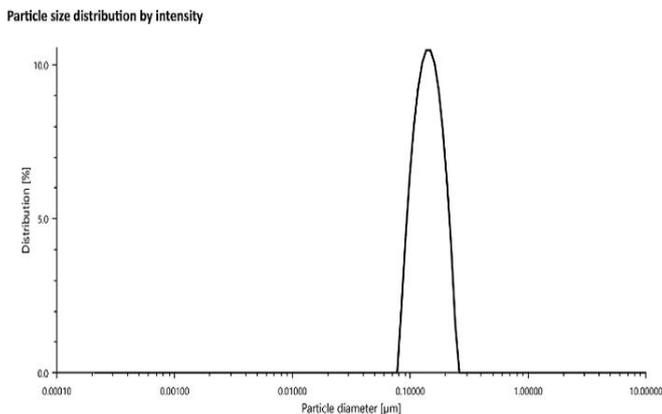


Fig. 1: Particle size of Silica ( $\text{SiO}_2$ )

### 3. METHODS OF TESTING

The experiment started with an endurance experiment for 160h using a hydraulic engine dynamometer, coupled with a single-cylinder diesel engine. A variety of experimental works have been carried out to describe the lubricating oil properties such as density, kinematic viscosity, moisture content, total base number, oxidation, ferrography, and rde-aes. These properties were compared between two types of lubricating oil: 1) Lubricating oil (SAE15W40), which is a baseline, and 2) Lubricating oil (SAE15W40) added with Silica ( $\text{SiO}_2$ ) nanoparticles which is n- $\text{SiO}_2$ . The manufacturer of the engine has suggested using the lubricating oil SAE15W40.

The extended duration endurance test was conducted using air-cooled, four-stroke, and single-cylinder compression ignition engine to study the effects of Silica nanoparticles in the lubricating oil on the degradation of lubricating oil using biodiesel blend B20. The specification of the test engine is

shown in Table 1. A hydraulic engine dynamometer was used as a test bench in this research. The dynamometer was equipped with a high-speed hydraulic gear pump and controlled flow by using a flow control valve. The dynamometer was also integrated with a high-speed rotary encoder to capture the rotation of the engine (rpm) linked to the control panel. A detailed description of the dynamometer is mentioned in Table 2. After several hours of preliminary running, the engine was set for a long-term engine performance evaluation. The durability test was carried out at a steady speed of 1800rpm for 160h with an interval of 40h Fig. 4 shows a schematic diagram of the experimental operation.

The samples of the lubricating oil were obtained from the engine per 40h to be analyzed. During the first phase of the process, the engine was fitted with a fresh lubricant (SAE15W40) and, every 40h, a sample of up to 100ml was obtained from the oil sump. After the sample was taken, 100ml of fresh lube was added to the oil sump to reach a minimum dipstick level as per ASTM D6750. A similar long-term endurance test was repeated for the second phase, and the engine was equipped with lubricating oil (SAE15W40) added with silica nanoparticles.

The experiments were carried out on samples of the lubricating oil to determine the comparative characteristic of lubricating oil consisting of the measurement of density, kinematic viscosity, moisture content, total base number (TBN), ferrography and rde-aes. For density, the analysis was performed using a pycnometer (ISOLAB). The viscosity was measured using a kinematic viscometer (ISL Automated Oil Bath Houillon Viscometer) at the temperature of 40°C and 100°C. The moisture content of the lubricating oil was determined by moisture analyzer (Mettler Toledo HB43-S). The titration method was used to determine TBN using Mettler Toledo T70 with an automated sampler. For determination of wear particle concentration, the samples were analyzed using direct reading ferrography (Predict DRF – Direct Read Ferrograph). RDE-AES measurement

apparatus (SpectrOil M RDE Atomic Emission Spectroscopy) was utilized to measure the 21 elements in lubricating oil consisting of iron, chromium, aluminium, copper, lead, tin, silver, nickel, silicon, sodium, potassium, boron, molybdenum, magnesium, calcium, barium, phosphorus, zinc, cadmium, vanadium, and titanium.

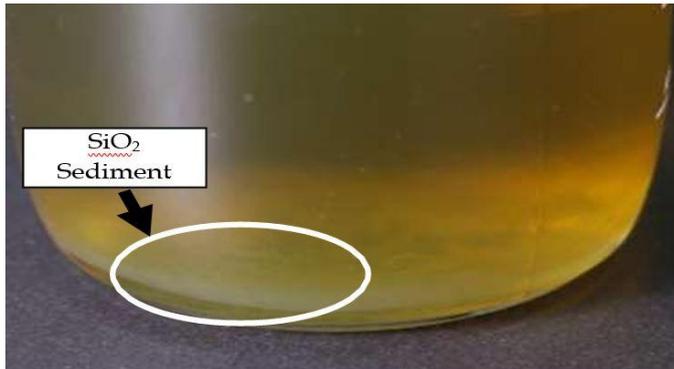


Fig. 2: Lubricating oil before sonication process



Fig. 3: Lubricating oil after sonication process

engine

Engine Type	Yanmar L70N
Engine Displacement, cc	320
Number of cylinders	1
Bore, mm	78
Stroke, mm	67
Engine speed, rpm	3600
Output speed kW(hp)	4.9(6.7)

Table 2: Specification of dynamometer

Dynamometer Type	Hydraulic Dynamometer
Pump	Gear pump
Oil Cooler	Air oil cooler
Medium	Hydraulic oil
Range (rpm)	0 – 4,000
Pressure (Bar)	0 – 400

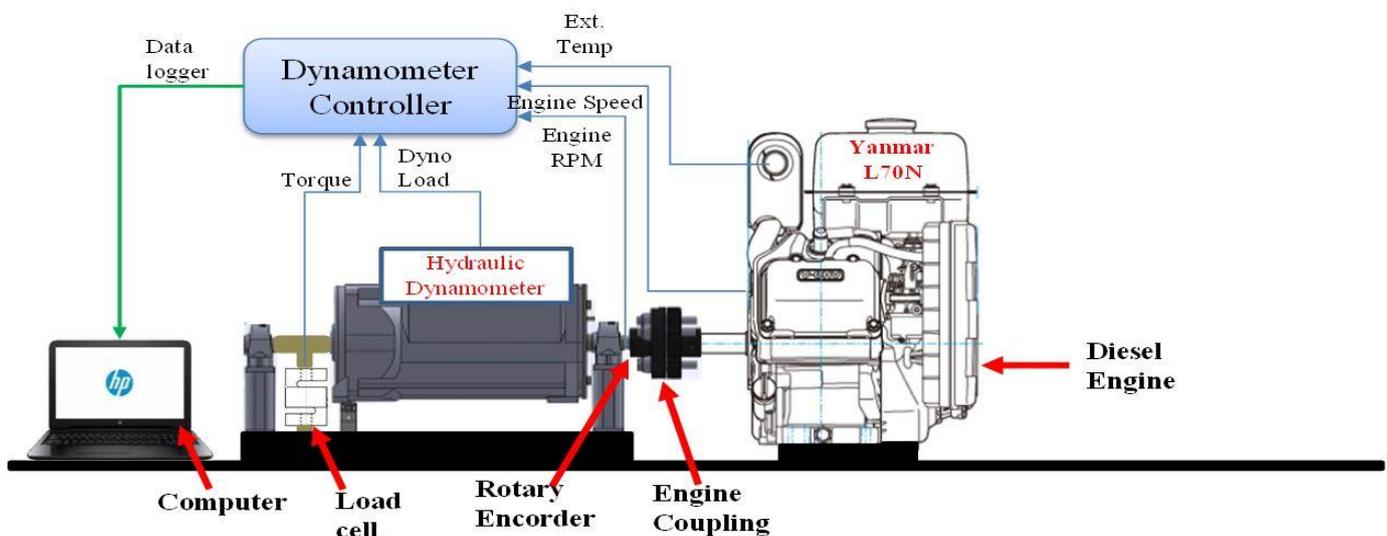


Fig. 4: Schematic Diagram of the experimental setup

Table 1:  
Specification of test

## 4. RESULTS AND DISCUSSION

Lubricant tribological properties (SAE15W40) were obtained by performing a 160h long-term engine endurance evaluation in a diesel engine fueled with palm biodiesel blend, also known as B20. The tribological properties of the engine such as density, kinematic viscosity, moisture content, total base number, ferrography, and rde-aes were also monitored for the baseline, which are lubricating oil (SAE15W40) and lubricating oil (SAE15W40) added with Silica ( $\text{SiO}_2$ ) nanoparticles, also known as n- $\text{SiO}_2$ .

### 4.1 Density

The density of lubricating oil study indicates the degree of corrosion from wear metal fuel residue. Increased lubricating oil density is significant corrosion of wear, fuel contamination, and moisture content increment [10]. Fig. 5 indicates the density difference between two types of lubricating oil, which are baseline and n- $\text{SiO}_2$ . The sample was collected at an interval of 40h from the usage of biodiesel blend B20. Initially, the density for fresh oil was recorded at about  $0.874 \text{ g/cm}^3$  for baseline, while for n- $\text{SiO}_2$  lubricating oil indicated about  $0.879 \text{ g/cm}^3$ . The value for the baseline is similar to the manufacturer description. According to the standard, the lower and upper limit was set to be 0.70 and 0.95, respectively. During the test run under 40 h, the lubrication oil with n- $\text{SiO}_2$  started to increase gradually up to 1% compared to the baseline. The n- $\text{SiO}_2$  also showed a higher rate of change during the entire endurance test began at 40 h onwards, which can be reached up to 4.6%. Increased density could be attributed to increased wear on engine components at a higher rate on engine activity. These conditions might be due to the addition of  $\text{SiO}_2$  nanoparticles onto lubricating oil that caused increases in density. Another factor that contributes to the increase of viscosity is oxidation, where it suspected from the use of biodiesel B20 fuel, which contains a higher rate of oxygen content. This oxygen content in B20 fuel

was reported by Putradamazman et. al. [20]. Therefore, as oxidation progresses, the density of the oil increases [21]. Overall, both densities did not reach the upper and lower limit standards.

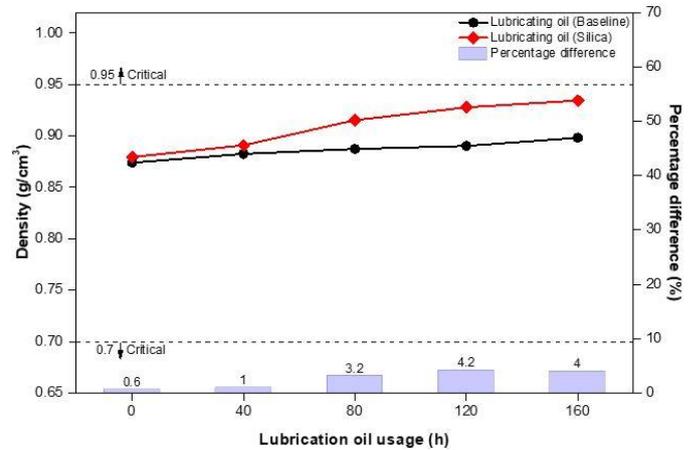


Fig. 5: Density of lubricating oil with usage

### 4.2 Kinematic Viscosity

The changes in the kinematic viscosity of lubricating oil from both samples shown in Fig. 6 and Fig. 7. These viscosities measured at  $40^\circ\text{C}$  and  $100^\circ\text{C}$  as per the ASTM D 445 standard testing procedure viscometer. The lower and upper limits were set at 98.9 cSt and 126.3 cSt for  $40^\circ\text{C}$ , while 12.5 cSt and 16.3 cSt for  $100^\circ\text{C}$ . The value of the baseline kinematic viscosity is quantitatively 2%, equivalent to the manufacturing specification. By incorporating n- $\text{SiO}_2$ , the kinematic viscosity is significantly increased from 1.3% to 6.2% for fresh oil at both temperatures relative to the baseline. The use of n- $\text{SiO}_2$  shows that the kinematic viscosity is risen rapidly and has started at a 40h endurance test onwards to the above critical limit for both temperatures ( $40^\circ\text{C}$  and  $100^\circ\text{C}$ ). In the case of kinematic viscosity measured at  $40^\circ\text{C}$ , the percentage difference rapidly increased in a range of 16.6% to 37.1%, equivalence to the baseline. Meanwhile, for kinematic viscosity measured at  $100^\circ\text{C}$ , an almost double increment of percentage difference compared to the baseline. However, the data upon reaching engine runtime of 120h and 160h respectively cannot be analyzed as it had exceeded the limit of the machine in reading the level of lubricating oil. This resulted in the processing of data only up to the nearest engine

runtime of 80 hours. These phenomena may have occurred due to the abnormal hydrodynamics film state, which caused by the extremely high temperature, engine load, and oxidation progress [22].

More fuel dilution and moisture content are also one of the factors for the degradation of the kinematic viscosity of lubricating oil. It was also expected that the viscosity of the lubricating oil would improve with respect to the introduction of Silica nanoparticles as an additive to the wear of debris in the engine. Physical examination of the conditions of the engine oil reveals that the lubricating oil tends to be sticky until the engine starts to stall and fails due to the rubbing issue, as a result of the addition of n-SiO<sub>2</sub> to the lubricating oil. Further analysis of engine conditions was performed and addressed in the engine monitoring section.

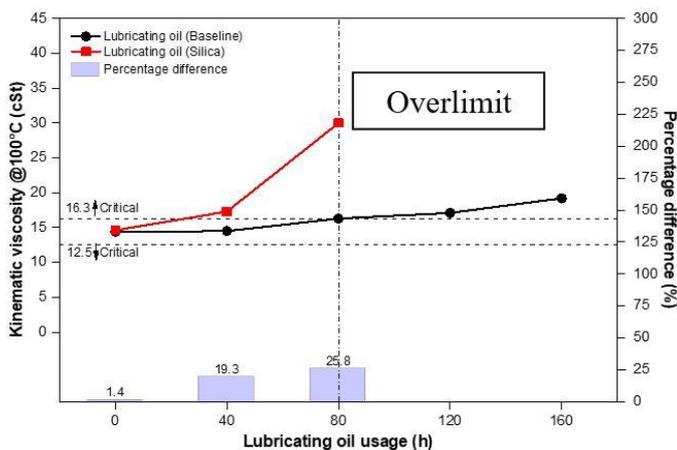


Fig. 6: Kinematic viscosity at 100°C of lubricating oil with usage

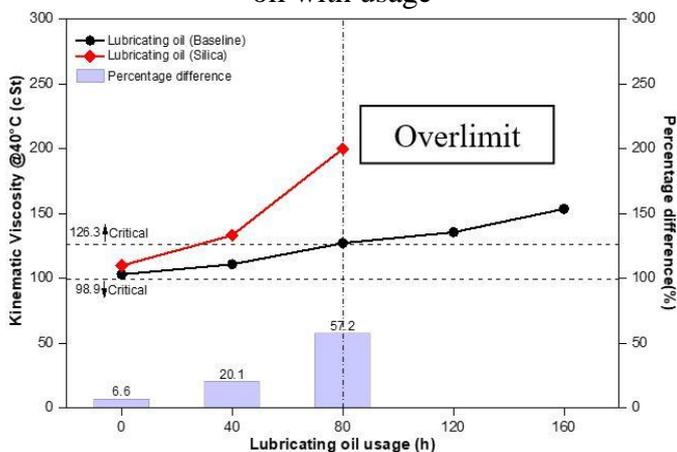


Fig. 7: Kinematic viscosity at 40°C of lubricating oil with usage

### 4.3 Total Base Number

Total Base Number (TBN) is one of the neutralization numbers commonly used to determine the amount of alkalinity remaining in the lubricant. It is an indicator of the capacity of the lubricant to neutralize corrosive acids produced during engine running. A low value of TBN provides a high concentration of lubricating oil free acids. As per ASTM D 664, TBN of collected lubricating oil samples was analyzed using the microscopic test. The experimental data for the TBN test are shown in Fig. 8. It has been shown that the total base number of lubricating oil SAE15W40 as a baseline and lubricating oil SAE15W40 has been applied to the SiO<sub>2</sub> nanoparticles. It can be indicated that the TBN of baseline samples collected decreased with use. The results showed that the lubricant oil added with n-SiO<sub>2</sub> began to increase slowly after 40h of endurance testing. Nonetheless, the percentage gap is small relative to the baseline and in acceptable critical limits. This trend of decrement of TBN is predicted, where the use of n-SiO<sub>2</sub> is able to lower the formation of corrosive acids in a lubricant as it breaks down [23].

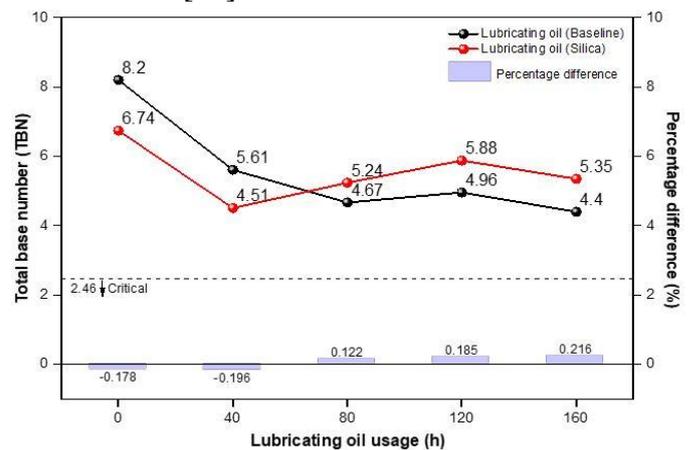


Fig. 8: TBN of lubricating oil with usage

### 4.4 Moisture content

Moisture content is also one of the essential roles to determine the quality of lubricant oil because it is the negative parameter that breaks the oil film intensity that can lead metal surfaces to corrosion, lubricant degradation, and weak lubrication. Fig. 9

shows the moisture content in lubricant as conducted in the engine dynamometer experiment. In the first phase, the moisture content highly increased until it reached 6900ppm, where it is above the critical limit. However, after 80h of engine running duration, the trend of moisture content started to reduce for both types of lubricants. The spike in the moisture level of lubricating oil used as an indicator of increased fuel dilution and accumulation of lubricating oil additives usually referred to as “additive drop out”. The lubricant added with n-SiO<sub>2</sub> indicates a substantial reduction in moisture content in the range of 8.7% to 41.2% compared to the baseline for increasing the sampling period. High moisture content in the lubricating oil could destruct the sealing arrangement between piston rings–liner interfaces. Therefore, the use of n-SiO<sub>2</sub> is able to overcome the moisture content caused by the biodiesel B20 fuel.

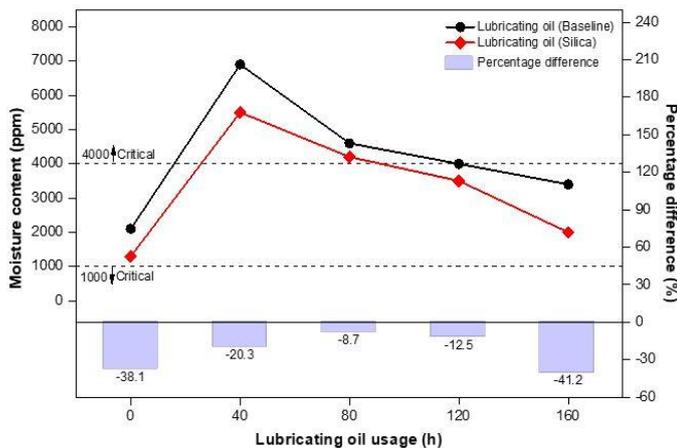


Fig. 9: Moisture content in lubricating oil with usage

#### 4.5 Ferrography

Fig. 10 shows the wear particle concentration in lubricating oil samples with usage. It was observed that wear particle in baseline was high, compared to n-SiO<sub>2</sub> under all the testing conditions. This condition may be due to the existence of Silica as an additive to provide excellent lubricity in reducing wear particles. In average, the lubricant added with n-SiO<sub>2</sub> shows the potentially reduced wear particle concentration, about 77.7%. The usage of baseline showed a failure less than 40h of

lubricating oil usage, because it passed the critical limit for wear particle concentration, while n-SiO<sub>2</sub> can prolong till 80h of an endurance test.

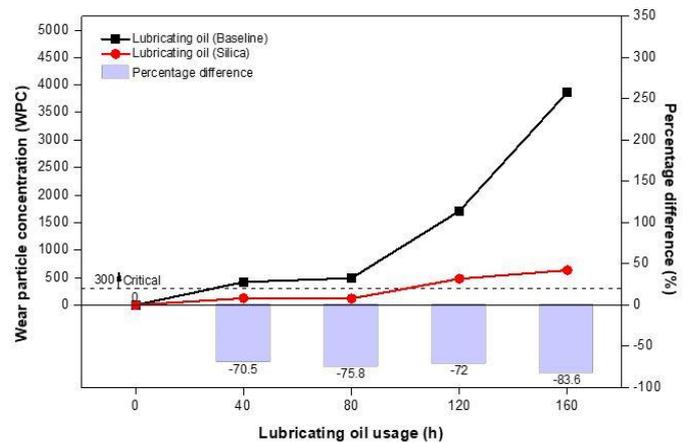


Fig. 10: Wear particles concentration of lubricating oil with usage

#### 4.6 RDE-AES

Up to 21 wear elements, contaminations and additives can be accurately and reproducibly detected by the AES. The elements include Iron, Chromium, Tin, Copper, Lead, Nickel, Aluminium, Molybdenum, Silicon, Sodium, Potassium, Boron, Magnesium, Calcium, Phosphorus, Zinc, Barium, Boron, Silver, Vanadium, and Titanium. For this study, four wear elements were discussed, which are Aluminium, Chromium, Copper, and Zinc.

##### I) Aluminium

Traces of aluminium was found in the lubricating oil and was attributed to be from piston wear, pushrod, oil pump, bearings, and crankcase finish. The content of aluminium in the baseline oil samples, based on Fig. 11, demonstrated marginal changes when compared to the lubricating oil with n-SiO<sub>2</sub>. A change in trend occurred after 80h of usage as the lubricating oil with additive began to demonstrate reduction in aluminium concentration while the baseline continues to rise and approach the critical line at 160h. It was observed that the aluminium content build up started between 12.7% and 20% during 80h endurance test onwards. The percentage difference also recorded in average of 30% increment compared to the n-SiO<sub>2</sub>. This was

due to the wear effects of components, namely the piston and bearings. However, both of the lubricating oil did not reach the critical limit that has been set.

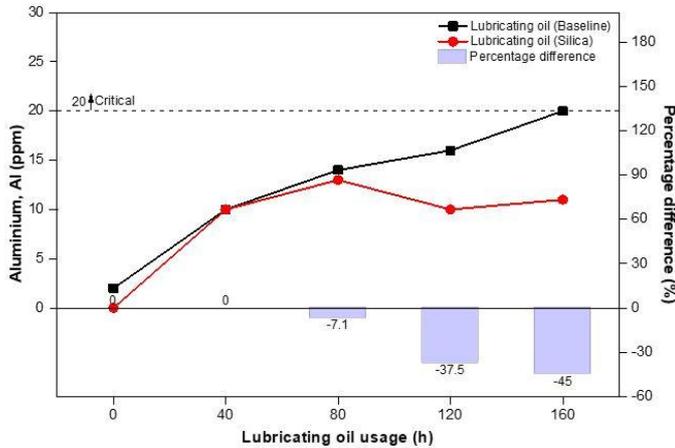


Fig. 11: Aluminium content I lubricating oil with usage

## II) Iron

Fig. 12 shows the concentration of iron debris that is present in the lubricating oil with respect to the hours of usage. Iron concentration occurred due to wearing effects from multiple parts within the diesel engine, most likely the piston, piston rings, cylinder head, valves, camshafts, crankshaft, cylinder block, valve guide, wrist pin, bearings, as well as rust from the surroundings. When comparing both the baseline and n-SiO<sub>2</sub>, it is revealed that the lubricating oil without n-SiO<sub>2</sub> additive has a higher iron concentration. This in turn, suggests that n-SiO<sub>2</sub> will result in providing better lubricating benefits due to the lower rate of iron concentration. At 80h of usage, the baseline has 46.4% more iron concentration and continues to increase as usage reaches to 160h.

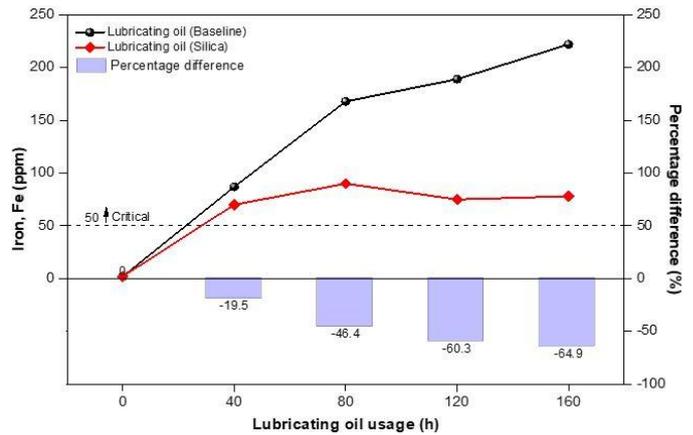


Fig. 12: Iron concentration in lubricating oil with usage

## III) Copper

The concentration of copper in lubricating oil is presented in Fig. 13. The traces of this element are attributed from injector shields, thrust washes, valve guides, connecting rod, and piston rings as well wear effects in the bushings and bearings. Similar to Fig. 9, the concentration for copper within lubricating oil with n-SiO<sub>2</sub> is lower compared to the baseline. While the concentration differs at 25% after 40h, the concentration of copper becomes much more prevalent after 80h with the baseline containing almost 71% more parts per million versus n-SiO<sub>2</sub> infused lubricating oil. Such effect was due to the silica nanoparticles forming a protective layer between the moving parts to reduce friction and component wear. The patterns specifically defined that the concentration of copper increased dramatically with growing time sampling.

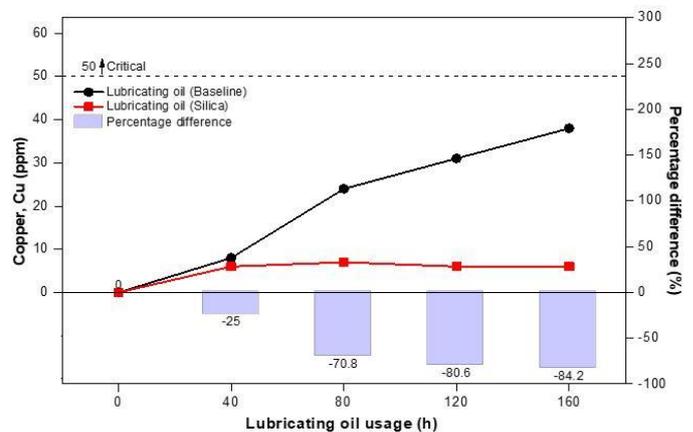


Fig. 13: Copper content in lubricating oil with usage

#### IV) Chromium

Fig. 14 shows the concentration in parts per million (ppm) for Chromium. This condition can originate from the effects of wear on rings, shaft, gear and chromium-plated liner, as well as cooling system leakage. It is shown that the baseline has a greater content of the element when compared to the n-SiO<sub>2</sub>, due to the higher wear of internal engine components. This is further reinforced by the experimental results of RDE-AES as the test indicated that the lubricating oil with n-SiO<sub>2</sub> had lower wear debris concentration.

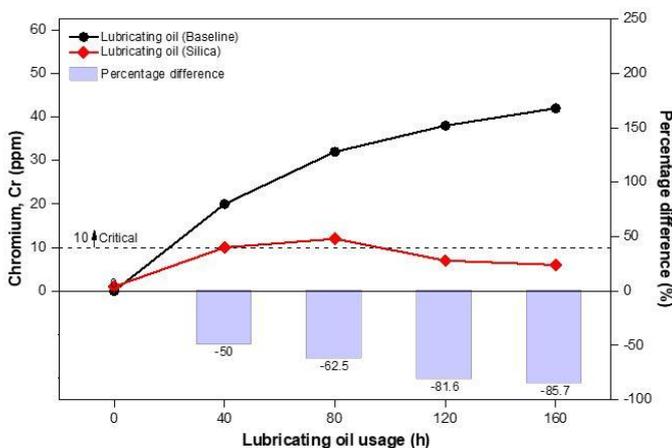


Fig. 14: Chromium content in lubricating oil with usage

#### 5. ENGINE CONDITION MONITORING

The stipulated run time for the experiment was 160 hours for each condition, where the engine starts to fail. Therefore, an investigation was conducted to observe the lubricating oil condition and the engine components condition. After an investigation on the engine, it is found that the components of the engine such as injector, cylinder block, piston and combustion chamber are in good condition. However, the piston ring was seen to be damaged. The piston ring of the diesel engine underwent a thinning process. This condition may be due to the increased viscosity of the lubricating oil as a result from the addition of silica particles. After several hours, the lubricating oil introduced additional friction upon the piston ring and wearing the component out as the increased viscosity oil is

pushed inside the engine's chamber and that what's make the engine fault. Fig. 15 shows the piston ring of the engine after 160h running condition. For the n-SiO<sub>2</sub>, it can be seen that the lubricating oil turns into a rubbing condition after several running hours. This condition also due to the increased viscosity of the lubricating oil.

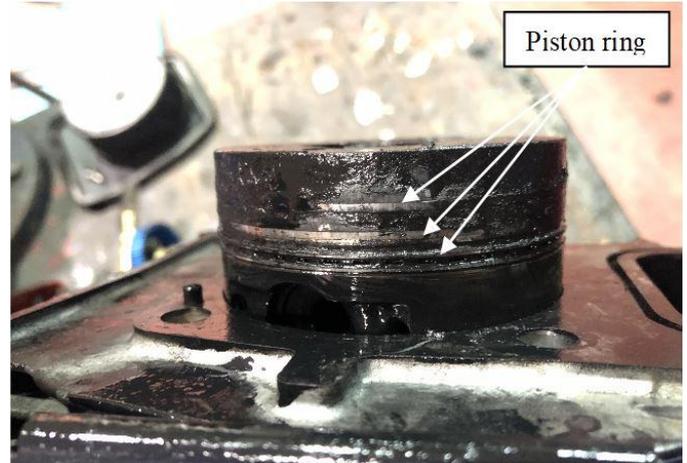


Fig. 15: Piston ring of the diesel engine

#### 6. CONCLUSION

In this study, the tribological performance of Silicon Dioxide (SiO<sub>2</sub>) nanoparticles as an additive for engine lubricant oil has been investigated. Based on the experimental results, the following conclusion can be drawn:

- The n-SiO<sub>2</sub> shows the potential for improvement in lubricant tribology, which protects the contact surface from wears and tears resulting in reduced concentrations of aluminum (up to 45%), iron (up to 64%), copper (up to 84%) and chromium (up to 84%) compared to the baseline oil. However, the n-SiO<sub>2</sub> as an additive in engine lubricant oil, however, has the potential to impair oil characteristics such as density (up to 4%), kinematic viscosity (almost double) and TBN (less significant) for endurance test compared to the baseline oil.
- Variation in viscosity of n-SiO<sub>2</sub> and baseline indicates the possibility of higher

oxidation and polymerization of lubricating oil drawn from the biodiesel fueled engine.

- The addition of SiO<sub>2</sub> induces friction in lubricating oil and thus limits the use of the piston ring.

Consequently, the use of n-SiO<sub>2</sub> in the long-term endurance test has been shown to improve the lubricity properties (wears and tears) but required to improve the viscosity of the oil film.

## 7. ACKNOWLEDGEMENT

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