Tribological characteristics of biodiesel and silver nanoparticle mixture as additive for lubricant oil
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ABSTRACT
In recent times, there is an increased importance in sourcing for an alternative product that fully or partially replaces mineral oil, hence reducing the dependency on the environmentally harmful oil. Much effort has been focused on research and development of new types of lubricant oil additives. The use of additives to improve the lubricating capacity and durability of lubricant oils play an important role in wear and friction process of materials. This study looks into the possibility of partially replacing the mineral base additives with more environmentally friendly organic base oil. The aims of this research were to produce palm oil based biodiesel (methyl ester) and silver nanoparticles using “green methods” and combining them at different ratios to be added as additive into base oil lubricant. A total of eight oil samples tests were run to determine anti-wear and frictional properties using pin-on-disc tribology tester. The results showed that the 80:20 blend of lubricant oil to biodiesel and silver nanoparticles have better anti-wear properties than the base lubricant oil (commercially available, SAE 20W-50) on itself. The specific wear rate of the blend was 39.9% lower than that of the base oil and wear levels recorded by the pin-on-disc machine showed that the blend is comparable with the base oil in terms of stability. More importantly, the coefficient of friction for the 80:20 blend far outperforms the base oil with a considerably reduced friction value obtained throughout.

Recognizing the need for a more environmentally friendly lubricant, yet of comparable performance and cost-effectiveness, this project incorporated a mixture of biodiesel and silver nanoparticle into a mineral oil-based lubricant. Biodiesel and silver nanoparticle are ready candidates as both have proven to have excellent anti-wear and friction properties. Biodiesel, in fact, even cleans the engine very well as it lubricates, therefore making the combination very promising.

Biodiesel can be sourced from any form of vegetable or animal oils and is readily biodegradable, environmentally friendly and renewable. Although it has excellent anti-wear properties, it is however, not without shortcomings. Among other things, it has low oxidation and thermal stability, poor low-temperature properties and narrow range of available viscosities (Robertson and Randles, 1990). But within these few properties, its oxidation stability is the biggest factor in limiting its use as a commercial lubricant. Fox and Stachowiak (2006), have compiled a summary of oxidation compounds, analytical techniques and lubrication impact of the compounds on biodiesels. There are two stages of oxidation of the biodiesel being the primary and secondary stage. Found in the primary stage is the Hydroperoxide compound and it reportedly increases wear during boundary lubrication. All secondary oxidation compounds are decompositions of the Hydroperoxide compound found in the primary stage. The products can be categorized into volatile, non-volatile, high molecular weight and free fatty acid compounds. No conclusive results on lubrication came from volatile, non-volatile and high molecular weight compounds, by far. However, it was found that free fatty acids can improve the
boundary lubrication properties of vegetable oil. Also, there is reported reduction of oxidation level in biodiesel with the presence of additives. 4-Nonyl phenoxy acetic acid (NPAA), when added into palm diesel, reduces the oxidation level, increases anti-wear properties and reduces friction between test-surfaces (Kalam and Masjuki, 2008).

On the other hand, it has been recognized that nanoparticles are able to smoothen surfaces when at high temperatures due to sedimentation of the nanoparticles on the nucleate sites. Smoother surfaces will significantly reduce heat transfer coefficient thus proving beneficial as lubricants also functions as heat dissipaters in running components. Therefore, the potential of nanoparticles as additive in lubricants should be looked into.

Along with its excellent anti-wear and heat transfer properties, it also must be stressed that Wang et al. (2006) found that TiO$_2$ nanoparticles can be used as additives to enhance the solubility of the mineral oil in the hydrofluorocarbon (HFC) refrigerant. This property is very important for the silver nanoparticles to successfully infuse biodiesel into the base oil and keep it dispersed in a homogenous mixture. Other than their mechanical properties, nanoparticles like the silver nanoparticle have also antimicrobial abilities to add. Antimicrobial property is very useful in prolonging the shelf-life and stability of the biodiesel. As with any organically sourced compound and the fact that it is a form of oil, there is a slight tendency to go rancid and this can be avoided with help from the antimicrobial property of the silver nanoparticle.

The project will involve the production of biodiesel from waste cooking oil and production of silver nanoparticle using rapid and simple methods. Whereas the mineral oil that will serve as the base oil will be sourced from a commercially available lubricant. Both the biodiesel and silver nanoparticle will be blended together and various proportions of this mixture will be added to mineral based oil to study the effects of these additives on the lubrication properties. Keeping the note of an environmental friendly product in mind, the biodiesel and silver nanoparticles will be produced using methods that involve little or no toxic substance at all and are simple and rapid processes. The biodiesel used will be produced from waste cooking oil and the silver nanoparticle will be produced bio-synthetically using the bacterium Bacillus subtilis.

**Materials and Methods**

**Production of Biodiesel**

Biodiesel is derived from organic origins of either vegetable or animal sources. It consists of short chain alkyl esters (methyl or ethyl). The production of biodiesel involves a process called transesterification as shown in Fig. 1, that is, the exchanging of the alkoxy group of an ester compound with another alcohol. The biodiesel that will be used in this project will be produced using waste cooking oil as described previously (Saifuddin and Chua, 2004). This method requires shorter time compared to a conventional method because of the use of microwave irradiation. Most importantly it uses waste cooking oil as the feed source hence greatly reducing the cost of the biodiesel production.

**Preparation of Sodium Methoxide**

The catalyst—2.5 g (0.5% by weight of oil) of sodium hydroxide, was dissolved in 144 g of methanol (representing 6:1 molar ratio of anhydrous ethanol to oil) in a bottle. The bottled was then subjected to heat and content was stirred vigorously with cap closed with magnetic stirrer until catalysts were completely dissolved.

**Procedure for Transesterification**

The used cooking oil was filtered to remove food residues and solid precipitate. The oil and was then heated to approximately 110°C to remove excess moisture. (In the transesterification process it is important that the oil contains very minimal amount of water). The oil was then left to stand at room temperature until it reaches about 55°C. Sodium methoxide which was prepared earlier was then added into 500g of the oil and the mixture was stirred vigorously for 5 minutes. The mixture was then exposed to microwave irradiation at 50% exit power (2.45 GHz, at power output of about 550W in a cyclic mode) for 1 minute. The heating and stirring cycle was repeated for 5 times for a complete reaction. After that, the mixture was decanted by pouring the biodiesel layer into another container and leaving behind the glycerol. The biodiesel was then subjected to washing with warm water at least 3 times until the water runs clear. In between washing, the mixture could be further exposed to microwave irradiation to obtain better separation for ease of decantation.

**Production of Silver Nanoparticles (AgNP)**

Silver nanoparticles can be produced by various methods, the most common method being the chemical reduction of ions in solution. Other than that, there is the Sonication method, by Bio-synthesis, Laser ablation, Sol-gel and Colloid production method. But among all these methods, the bio-synthesis of nanoparticles is currently given more weight because it does not involve toxic chemicals in the synthesis protocol. The biosynthesis of Silver Nanoparticles was performed using the method described by Saifuddin, et al., (2009).

**Procedure for Bio-Synthesis of Silver Nanoparticles**

One Litre of Mueller-Hinton broth was prepared by adding 38g of Mueller-Hinton agar into 1 Litre of distilled water. The mixture was then autoclaved until it reaches 121°C and 20 psi, which took about 30 minutes. The media was allowed to cool to 55°C, when pressure is zero before the autoclave can be released. The broth was further let to cool.

To obtain the culture supernatant, 50mg of Bacillus subtilis was added into 1 Litre of the Mueller-Hinton broth and incubated for 24 hours on the shaker at 150 rpm. After incubation period, the culture was centrifuged in batches at 4,000 rpm for 20 minutes and the supernatant was collected. After that, 1 litre of aqueous solution of 1 mM silver nitrate (AgNO$_3$) was treated with 1 L of Bacillus subtilis supernatant solution in two 1 L beakers. The mixtures were then be placed in a domestic microwave oven and subjected to several short bursts of microwave irradiation at frequency of 2.45 GHz, at power output of about 550W in a cyclic mode (on 40s, off 15 s with stirring) to prevent overheating as well as aggregation of metals. The irradiation process was conducted for 15 cycles to ensure complete reaction. When the silver nanoparticle solution is ready, excess moisture was evaporated off in the drying oven for 3 days at 50°C, concentrating it to 50 mL thus obtaining a molarity of 0.2 mol.

**Preparation of Lubricant Samples**

The pin-on-disc tribo-tester, Ducom TR-20 requires a minimum sample volume of 3 liters. A total of eight samples were tested to obtain their coefficients of frictions and anti-wear properties as stated in Table 1.

**Test Conditions**

The tests was conducted in the Boundary lubrication regime. The solid surfaces will be so close together that appreciable contact between opposing surfaces is possible. The
friction and wear in boundary lubrication are determined predominantly by interaction between the solids and between the solids and the liquid. The bulk flow properties of the liquid play little or no part in the friction and wear behaviour.

Oils with wear reducing additives may exhibit better characteristics in boundary lubrication, but no advantages in hydrodynamic regime. Hence for better understanding of the anti-wear properties of the sample oils, the tests are conducted under high-load and low velocity conditions. The test parameters are listed in Table 2.

### Formulas for Friction and Wear

#### Friction

\[
F = \mu N
\]

**Eq. 1**

\[
\mu = \frac{F}{N}
\]

- \(F\) = Force applied on the pulley system (N)
- \(N\) = Normal force acting on pin (N)
- \(\mu\) = Coefficient of Friction

#### Wear Volume

\[
V = \frac{4m}{\rho}
\]

**(Eq. 2)**

- \(m\) = Mass difference, \(m_1 - m_2\) (kg)
- \(\rho\) = Density, \(\frac{m}{V}\) (kg/m³)

#### Specific Wear Rate

\[
k = \frac{V}{F_s}
\]

**(Eq. 3)**

- \(V\) = Wear volume (m³)
- \(F_s\) = Load applied (N)

### Experimental Procedure

The tribological tests were conducted on a Ducom TR-20 pin-on-disc machine available in Universiti Kebangsaan Malaysia (UKM), shown in Fig 2. The material for the pin was aluminium and was used for all the tests. The pin has been fixed on a holder, which has a provision for applying the load and is pressed against the rotating steel plate below it. An electronic balance having an accuracy of 0.1 mg with a maximum weighing capacity of 200 g was used to determine the mass of the pin before and after each run of tests. The weighing of the pin before and after each test was used as the measure of wear, according to the weight loss. The disc was slide against the pin situated at 4 cm radial distance at 0.417 m/s surface speed. The friction force was measured by a load cell attached to the pin holder (resolution 0.1 N) and the displacement of the pin was measured using a Syscon (Bangalore, India) displacement sensor (LVDT, resolution 1 µm, range = ±500 µm). The speed, frictional forces and displacement of the pin are recorded in the computer and friction force and coefficient, wear computed thereon. The wear test is conducted by keeping the speed, load and sliding distance as constant for all oil samples. Tests have been carried out for a sliding distance of 750 m and for each experimental point, 2-3 tests have been conducted to ensure repeatability.

### Results and Discussions

Information obtained from the tests includes level of Wear, Frictional Force and Coefficient of Friction. Subsequently, the Specific Wear Rate for each sample was calculated from the loss of mass of the pin before and after each run. The tests lasted 30 minutes per run. The amount of wear indicates the ability of the lubricant oil sample to form an oil film between the two sliding surfaces (aluminium and steel), keep them apart and well lubricated to prevent further corrosion.

![Fig. 2 Tribo-Test Run (Aluminium Pin Against Steel Plate)](image-url)

**Microwave Enhances Biodiesel Reaction Time and Properties**

It must be brought to attention that, in this study, microwave method has been chosen over the conventional method to produce biodiesel because it simply a more convenient, green and rapid process which produces a distinctively better biodiesel. Microwave irradiation increases the initial reaction rate overall comparing to conventional heating. Water content, solvent and reactants in the reaction mixture are subjected to particular microwave characteristics. One is the heat-transfer accomplished by dipole molecular rotation and ion conduction in regular alternating microwave field, which makes the heat-transfer efficiency higher than that of conventional heating. The other is electron spin oscillation of polar molecules caused by the special microwave energy level, which may delicately modulate the local configuration of the catalyst molecules to favor efficient binding of reactants according to the well known lock–key theory. The apparent activation energy (Ea) of this transesterification reaction decreases in microwave field, which is considered as one of the reasons resulting in the increase of initial reaction rate (Yadav and Lathi, 2004; Ipsita and Gupta, 2003).

In terms of Biodiesel properties, Huang et al. (2005) reported that there is microwave effect on substrate specificity of alcohol. Along with the fact that the increased reaction rate can be explained by the polarity and steric hindrance effects in the in reactant molecules, it is also this behavior the –OH groups that give rise to higher concentration of hydrogen bonding that increases the viscosity of the biodiesel. The electron spin oscillation of the polar –OH molecules, when exposed to microwave energy, tend to align themselves to the polarity of the microwave. This simple realignment creates higher instances where the –OH group in a molecule can be juxtaposed to another and forming the hydrogen bond. And as more of the formations occur, the viscosity in the biodiesel itself would be increased as the bonds at the molecular level provides resistance to flow. Similar results had been reported by Biswas et al., (2007) wherein dimerization of triacylglycerol molecules as a result of
heat treating or microwave irradiation of soybean oil may lead to a decrease in effective polar groups because of the configuration of the dimerized molecule. Although it was also reported that microwave irradiation shows promise to improve the cold-flow behavior of soybean oil, the treatment apparently will not produce superior vegetable oil-based lubricants. As such the biodiesel produced with this method would have to be blended with stock lubricants and tested for increased lubricity without much decline in resilience to the mechanical shear stress and heat that it will be subjected to in everyday usage.

**Pin-on-Disc Lubricant Test Results**

Figure 3 compares the level of wear for all lubricant samples. Most of the wear level stabilized towards the end of the run. The continued linear increment of samples 3 and 4, comprising of 100% Biodiesel and 100% Biodiesel + Silver Nanoparticles, suggests that no oil films can be formed between two layers to keep surfaces apart and prevent wear. The reason for this phenomenon is due to the fact that the viscosity of Biodiesel is very low compared to the standard lubricant oil. The viscosity is very much dependent on the amount of sulphur in the molecules.

When silver nanoparticles are added to the oil sample (Sample 4), it showed significant anti-wear properties by decreasing the wear level to 30 microns compared to that of 100% Biodiesel (Sample 3) with 59 micron wear. The same phenomenon occurred when silver nanoparticles were added to the 50% base oil + 50% Biodiesel blend (Sample 5), and when silver nanoparticles were added to 100% base oil (Sample 6). For the blend, it fared 18.8% better with less wear compared to Sample 2 with only 50% base oil + 50% Biodiesel. And for the base oil, the wear peaked at 10 microns without the nanoparticles and 8 microns, with them. This is due to nanoparticles acting as nanobearings between the surfaces of the aluminium pin and the steel plate. As mention earlier in the literature review, the nanoparticles tend to form sedimentation on the nucleate sites resulting in thin films that adheres to the surfaces. At nanoscale, the hardness of silver is comparable to the hardness of both aluminium and steel, making it an excellent bearing of sorts. The function of the silver nanoparticles as nanobearings would also greatly influence the coefficient of friction of the oil, because friction is greatly reduced when the surfaces slide past each other more easily, as can be seen in Fig. 4. As the blend move towards the 80:20 ratio of Base Oil to Biodiesel, the stability has greatly improved with the samples 7 and 8 both settling in the region just below 12 microns. And again, Sample 8 showed much lower wear, due to the presence of silver nanoparticles.

**Fig. 3 Wear level Computed for Aluminium Pin against Steel Plate for All Lubricant Sample, A Comparison Chart**

Fig. 4 shows the comparison of Coefficient of Frictions for all samples. Here it can be noticed that Samples 2, 4 and 3 which contain 50%, 100% + AgNP, and 100% Biodiesel all have appreciably lower coefficient of friction compared to 100% base oil (Sample 1), especially sample 4. This is mainly due to the fact that in boundary lubrication, the biodiesel has a very large influence on the lubricity of the oil (Rashmi and Biswas, 2009). Lubricity is greatly increased because the fatty acids in the biodiesel tend to migrate from the oil to the surface of the part where vacant sites are available. They adsorb and assemble a protective film till they are removed by subsequent contact with counter-surfaces. The assembly and desorption or wear and reassembly is a dynamic process. Furthermore, some other works report a reduction in friction for the fatty acids with humidity (Garoff and Zauscher, 2002). However, if a group of fatty acids in the adsorbed state is removed by the sliding of the surfaces and the adsorption kinetics does not allow the reassembly to occur before the next contact occurs, the film is not protective and the friction tends to be that corresponding to bare metallic contact (Rashmi and Biswas, 2009).

**Fig. 4 Coefficient of Friction Computed for Aluminium Pin against Steel Plate for All Samples, a Comparison Chart**

Sample 5, with 50% Base Oil + 50% Biodiesel and added 25 mL Silver Nanoparticles fared arguably better compared to Sample 2 which has only 50% Base Oil + 50% Biodiesel. In the same context, Sample 8, with 80% Base Oil and 20% Biodiesel and added 25 mL Silver Nanoparticles, has a much lower coefficient of friction than Sample 7 with only 80% Base Oil + 20% Biodiesel. This goes to prove that the addition of silver nanoparticles can improve lubricity significantly, especially in the boundary lubrication regime. As aforementioned, it is due to the function of nanoparticles as nanobearings between the two sliding surfaces that greatly decreases the amount of friction created.

Fig. 5 shows that using 100% Biodiesel (Sample 3) resulted in the highest specific wear rate. This is due to the fact that biodiesel is ‘thin’ and its viscosity is not sufficient to keep surfaces apart to reduce wear. And when Silver Nanoparticles are added (Sample 4), the specific wear rate was reduced by 27.5%. This shows that silver nanoparticles can help significantly improve anti-wear properties in a lubricant. When comparing Samples 2 and 5, Sample 5 showed a lower specific wear rate, a reduction of 53.8%, which is a significant amount. Again as mentioned previously, the nanoparticles in the lubricant oil has greatly improved lubricity by acting as tiny bearings to reduce sliding friction between the two aluminium and steel surfaces.

**Fig. 5 Specific Wear Rate Computed for Aluminium Pin against Steel Plate for All Lubricant Samples, a Comparison Chart**
Finally, when comparing Samples 6 and 8, with 100% Base Oil + 25mL AgNP and 80% Base Oil + 20% Biodiesel +25mL AgNP, the resulting specific wear rates are in fact the same. When combined with the results for wear (Fig. 3) and coefficient of friction (Fig. 4), it can be concluded preliminarily that Sample 8 is indeed a comparable lubricant to the SAE 20W-50 Base Oil. In fact, it even outperforms the Base Oil in terms of anti-friction properties, with a lower coefficient of friction. However, more work is needed to ensure that the oxidation level, deposition level and low temperature properties of the blend is up to par with any conventional lubricant oil. This study only focused pin-on-disc method which is macrotribology test and hence does not detail what happens in the microscopic level.

Conclusions
The project has proven to be very promising in both economic and environmental aspects.

- The materials and the bio-synthesis methods used in this study are all “green”, simple, and cheap.
- Biodiesel is derived from waste cooking oil which would otherwise end up in sewage systems polluting the waters. Furthermore, waste cooking oil is most often than not, can be obtained for free thus cutting the cost of production while the usage of microwave in the reaction is convenient, rapid and produces a more viscous biodiesel.
- The production of Silver Nanoparticles does not involve any costly ingredients as the cultures can be grown from batches and extensive amounts can be produced by using AgNO₃. The overall process does not involve toxic materials and the only active interaction is between the B. Subtilis culture and Silver Nitrate aqueous, making it a very safe method as the strain of bacteria is commonly found strain. It is also a very simple and quick method that can readily be improvised.
- These methods can be scaled-up easily if ever mass production is intended.
- Incorporating these components into mineral oil as a lubricant may in time, reduce the dependency on mineral oil lubricants.
- This study could be the starting point towards a replacement-free lubrication system. The wear rate of nanoparticles is comparably slower than that of mineral oil and if a working blend between silver nanoparticles as the nano-bearings and biodiesel as the flow medium can be achieved, lubricant change in machines can be minimized or better, eliminated.

From the results of the tests, Sample 8 performed better than the standard lubricant (SAE 20W-50) due to the addition of Biodiesel and Silver Nanoparticles.

This blend showed good anti-wear properties and even has a lower coefficient of friction than the base oil. In terms of stability, it is also at par with the base oil. In line with the advantages showed, further studies can be conducted on various aspects of the oil blend. Among them, to run the lubricant through the four-ball RCF machine to ascertain its anti-wear properties at the microscopic level and further delve into the interaction of the Silver Nanoparticles on the surface nucleate sites that makes it smoother, hence reducing friction.

A test run of a mineral-based oil lubricant with Biodiesel and Silver Nanoparticles additives can also be conducted to study its durability and its effect on machine endurance.

With enough interest on environmentally friendly materials, this resulting lubricant or others of similar advantages might one day be commonplace and fully take over the role of conventional mineral-based oil as the stock for industrial lubrication systems.

References
### Table 1 Sample Numbers and Corresponding Contents of Oil

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Content</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3l Mineral Oil (SAE 20W-50)</td>
<td>The benchmark. Other samples compare to this.</td>
</tr>
<tr>
<td>2</td>
<td>1.5l Mineral Oil + 1.5l Biodiesel</td>
<td>To determine level of lubricity when Biodiesel is mixed with mineral oil</td>
</tr>
<tr>
<td>3</td>
<td>3l Biodiesel</td>
<td>To determine lubricity of Biodiesel alone</td>
</tr>
<tr>
<td>4</td>
<td>3l Biodiesel + 25ml AgNP (0.2 Mol)</td>
<td>Determine lubricity when AgNP is added</td>
</tr>
<tr>
<td>5</td>
<td>1.5l Base Oil + 1.5l (Biodiesel + 25ml AgNP –0.2 Mol)</td>
<td>To determine how lubricity significantly increases compared to mineral oil alone or Biodiesel alone</td>
</tr>
<tr>
<td>6</td>
<td>3 l Base oil + 25ml AgNP—0.2mol</td>
<td>To determine wear reduction after AgNP is added to base oil</td>
</tr>
<tr>
<td>7</td>
<td>2l Base oil + 0.5l Biodiesel</td>
<td>Ratio that is determined after the outcome of test for sample 2</td>
</tr>
<tr>
<td>8</td>
<td>2l Base Oil + 0.5l Biodiesel + 25mL AgNP—0.2mol</td>
<td>Improvement of sample 8</td>
</tr>
</tbody>
</table>

### Table 2 Test Parameters Used for All Samples on the Pin-on-Disc Tribo-Tester (Ducom TR-20)

<table>
<thead>
<tr>
<th>Specimen (size)</th>
<th>Aluminium (6mm dia. x 32mm h)</th>
</tr>
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<tbody>
<tr>
<td>Load</td>
<td>98 N</td>
</tr>
<tr>
<td>Speed</td>
<td>200 rpm</td>
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<tr>
<td>Pressure</td>
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<tr>
<td>Temperature</td>
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<tr>
<td>Wear Disc Size</td>
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<tr>
<td>Wear Track Diameter</td>
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