Wear and friction behaviour of Si$_3$N$_4$ ceramics under diesel and biodiesel lubrication

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**ABSTRACT**

The wear and friction behaviour of self-mated silicon nitride pairs in lubricated ball-on-flat reciprocating sliding conditions is the subject of the present work, using diesel fuel and soybean biodiesels as lubricants. The results show that the friction coefficient is considerably higher for the diesel fuel than for biodiesels in the stationary regime (about 0.14 and 0.06, respectively). The wear coefficient values are in the range $10^{-8}$–$10^{-9}$ mm$^3$/N·m, denoting a mild wear regime, in agreement with the high lubricity of these fuels assessed by the ASTM D 6079 standard. The observed wear mechanisms were mainly mechanically dominated, consisting of transgranular and intergranular fractures, and the formation of a tribolayer by plastic deformation of the wear debris.

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**1. Introduction**

Ceramic materials based on silicon nitride (Si$_3$N$_4$) are well known technical ceramics of high performance due to their high hardness, toughness, strength, chemical stability and wear resistance. These properties allow the use of Si$_3$N$_4$ in various industrial applications, such as in cutting tools [1,2], mechanical seals [3,4], ball and roller bearings [5,6], turbine components, ignition parts and diesel engines [7–9].

In the case of the internal combustion engines, the operating pressures in the injection pump systems can reach values of up to 200 MPa, which allows a better fuel atomization, thereby controlling the combustion process and contributing to the reduction of pollutants emission into the atmosphere [10,11]. Considering that the trend is to increase the pressure, with the parts running faster and more accurately, new materials of lower weight, harder, more wear and corrosion resistant, capable of operating at higher temperatures and compatible with the fuel environment, are needed [10,12]. Then, materials with high dimensional stability, mechanical and heat resistant are required to withstand such working conditions, as it is the case of Si$_3$N$_4$ ceramics.

The lubrication regime in engine parts varies from boundary to hydrodynamic as in the case of mechanical seals and diesel pump plungers, respectively [13]. Due to geometric
defects, or during the start-up of engines, a very few amount of fuel is available in some points of contact, thus reducing the thickness of the lubricant film to molecular levels. Lubricant starvation may lead to seizure and adhesion of materials at the asperities, with subsequent rupture (scuffing) [13]. These phenomena usually occur at the contact of metallic materials, and are characterized by a sudden increase of the friction values. The substitution of metallic parts by ceramic materials is therefore an additional advantage because of its chemical inertness, resulting in higher resistance to adhesion that avoids seizure [8,9,13].

Data from an automotive parts producer have shown a wear reduction of 10 to 4 (on a scale of 0–10) when substituting metals by Si$_3$N$_4$ ceramics in the manufacturing of fuel injector plungers [9]. Another manufacturer showed that a conventional tool steel plunger can seize in 10 h or less when in presence of 1% water in the fuel, while the plungers made of zirconia operated for more than 300 h with 2% water without seizing [14].

Regarding the fuel properties, the most important is lubricity, a term used to describe the ability of a fuel in reducing friction and/or wear. For instance, the decrease of sulphur concentration in petrodiesel fuels diminishes their lubricity, which increases the wear of the engine components [15]. Biodiesel has better inherent lubricity and can be used as additive in concentrations as low as 1–2% for ultra-low sulphur diesel [16]. Blends of 5 and 20% are already used, and may reach 100% if certain adaptations are made in the fuel engine [17]. It is thus necessary to evaluate the tribological behaviour of the components materials that are in contact with these fuels.

The present work describes the study of the friction and wear of Si$_3$N$_4$ based ceramics using a commercial diesel, a soybean biodiesel fuel produced in the Laboratory of Engines and Fuels (Lamoc) of the National Institute of Metrology, Quality and Technology (Inmetro) and a commercial soybean biodiesel from Shell.

The test conditions were chosen to lead the tribosystem to work in the boundary lubrication regime. This condition consists in sliding the surfaces at extremely low speeds and very high contact pressures so that the incidence of hydrodynamic or elastohydrodynamic lubrication is reduced to a minimum [18].

### 2. Materials and methods

#### 2.1. Fabrication of Si$_3$N$_4$ samples

Si$_3$N$_4$ disc-shaped specimens (10 mm in diameter and 3 mm in thickness) were fully densified by pressureless sintering at a dwell temperature of 1750°C for 2 h, in an atmosphere of 0.1 MPa N$_2$, using aluminium and yttrium oxides as densification additives. The composition in weight percentage is: 89.3% of α-Si$_3$N$_4$ (M11, H.C. Starck), 7.0% of Y$_2$O$_3$ (C, H.C. Starck) and 3.7% of Al$_2$O$_3$ (CT 3000 SG, Alcoa).

After densification, the samples were ground (47 μm diamond wheel), lapped (15 μm diamond suspension) and mirror-polished (0.05 μm silica suspension) to an average surface roughness of Ra = 4.7 ± 0.4 nm (average of ten measurements in five samples, using a cut-off of 0.25 mm). The Si$_3$N$_4$ balls (5 mm in diameter), used as counter bodies, are commercialized by Coorstek and were used as received, presenting a Ra = 87 ± 21 nm (average of 18 measurements in nine balls, cut-off of 0.25 mm).

#### 2.2. Tribological tests

The self-mated tribological tests were conducted in a CETR UMT3 tribometer, with a reciprocating ball-on-plate configuration under 6 mm stroke and 1 Hz frequency. The tribosystems were tested under diesel and biodiesel lubrication, at ambient temperature. The applied load was 100 N and the total sliding distance approximately 780 m, equivalent to 18 h of testing. According to the Hertzian contact theory, the average and maximum initial pressure acting in the contact between the triboelements is 2.9 GPa and 4.4 GPa, respectively. For this calculation, the used values of Young’s modulus and Poisson’s ratio of Si$_3$N$_4$ were 300 GPa and 0.3, respectively.

The wear volume of the two triboelements ($V_d$) was estimated by 3D profilometry (FGI 830 Taylor Hobson profilometer), and the wear coefficient ($K_d$) calculated according to the equation: $K_d = V_d/P$·$x$, where $P$ is the applied load (N) and $x$ the sliding distance (m). The values of $K_d$ and coefficient of friction (COF) represent the average of at least three tests of repetition. Analysis of the wear mechanisms was made from observations by optical microscopy (OM) and scanning electron microscopy (SEM).

The lubricity of the fuels was determined by the ball-on-plate high frequency reciprocating rig (HFRR) test method, at the Laboratory of Fuels and Lubricants (Lacol) of the National Institute of Technology (INT), Brazil, according to ASTM D 6079 standard. The lubricity is determined by measuring the wear scar diameter of the ball with an optical microscope, taking the average of two measurements, one parallel and one orthogonal to the sliding direction. The HFRR test is performed with linear oscillatory motion of 1 mm stroke at 50 Hz and 1.96 N load, using an AISI 52100 steel ball bearing of 6 mm of diameter, nominal hardness of 62 HRC and a polished AISI 52100 steel disc with nominal hardness of 200 HV(30). In this study, the test temperature was 25°C. Two standard fluids were used as reference of high (ASTM D 6079 A – diesel fuel with 0.4 wt.% sulphur and kinematic viscosity of 2.4 mm$^2$/s at 40°C) and low lubricity (ASTM D 6079 B – iso-paraffinic hydrocarbon having a kinematic viscosity of 2.6 mm$^2$/s at 40°C), supplied by PCS Instruments.

#### 2.3. Fuel characteristics

The fuels used as lubricant in the tribological tests were commercial diesel from Chevron Co., a soybean methyl biodiesel fuel produced from commercial soybean oil following classical methodology [19] at Lamoc-Inmetro (BD Lamoc), and a soybean methyl biodiesel from Shell (BD Shell). The diesel fuel is a standard for calibration of the cetane number of the diesel engines, and its characteristics are given in Table 1. Fatty acid methyl esters (FAME), water content and free and total glycerin of both biodiesels were evaluated at Lacol-INT; by the methods EN14103, ASTM 6304 and ASTM D6584, respectively. The kinematic viscosity, $\nu$, was evaluated using the NBR 10441 method.
Table 1 – Fuel characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Diesel (Chevron)</th>
<th>Biodiesel (Commercial (Shell))</th>
<th>Biodiesel (Laboratory (Lamoc))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v = 2.5 \text{ mm}^2/\text{s}$ at 40°C</td>
<td>4.2</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Ester content (wt.%)</td>
<td>98.4</td>
<td>98.8</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturated: 63.5 C16:0</td>
<td>14.0</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td>Aromatics: 35.2 C18:0</td>
<td>4.3</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Olefins: 1.4 C18:2</td>
<td>25.5</td>
<td>25.1</td>
<td></td>
</tr>
<tr>
<td>Sulphur (0.03 wt.%)</td>
<td>47.5</td>
<td>47.4</td>
<td></td>
</tr>
<tr>
<td>Free glycerin (wt.%)</td>
<td>5.5</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>0.5</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>Diglyceride</td>
<td>0.16</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Triglyceride</td>
<td>0.10</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Water content (ppm)</td>
<td>871</td>
<td>559</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated percentage area of the respective bands of GLC (gas–liquid chromatography) plots.*

3. Results and discussion

3.1. Wear and friction analysis

Fig. 1a shows representative curves of the coefficient of friction (COF) as a function of the sliding distance for the three types of fuels. Fig. 1b presents the maximum and the average COF values for each fuel in the running-in and in the stationary regimes, respectively.

In the running-in period, the highest friction values, COF of 0.22, are achieved when the tribosystem is under BD Lamoc lubrication, followed by the BD Shell and Diesel fuels, both reaching maximum values of 0.17. Although the results of all tests were not presented, it was observed that the transitory regime occurs in a range between 250 m and 350 m, with some dispersion among the tests for the same fuel and disregarding the fuel type, attributed to shape deviations in the ceramic parts, ball and plate. At the stationary regime, the COF values drop significantly for both biodiesels, with a variation between $\Delta \mu = 0.10$ and $\Delta \mu = 0.13$, while this value is only $\Delta \mu = 0.03$ for the Diesel fuel. The lowest value, of 0.06, is achieved by the BD Shell, followed by the BD Lamoc, of 0.09, and Diesel, of 0.14.

The analysis of the wear coefficient ($K_d$) was made for both triboelements, ball and plate, and it is shown in Fig. 2a. It can be seen that the highest $K_d$ values (in $10^{-8} \text{ mm}^3/\text{Nm}$) were recorded for lubrication with BD Lamoc, with average values of 7.2 for the plate and 6.5 for the ball. On the other hand, the lubrication with BD Shell resulted in the lowest wear values, whose average values for the plate and the ball are 1.5 and 0.95, respectively. The distinct frictional behaviour of the two biodiesels can be related to a set of factors: (i) fatty acid (FAME) composition (namely carbon chain length and degree of unsaturation); (ii) diversity of species (fatty acids and contaminants); (iii) type and amount of contaminants (mono-, di- and tri-glycerides and presence of sulphur). Diversity, chain length and unsaturation degree of FAMEs are all characteristics that improve the frictional behaviour [16].

The fuel characteristics, presented in Table 1, show that the amount of FAMEs with the highest chain length (C18) with the high degree of unsaturation (namely C18:3) is higher in the case of the BD Lamoc biodiesel. So, this is not the reason for the lower lubricity of such biodiesel. Contrary to this, data at the Laboratory of Mass (Lamas) of Inmetro. The results of all these characterizations are given in Table 1.

![Graphs](image-url)

Fig. 1 – (a) Coefficient of friction (COF) as a function of sliding distance for each fuel; (b) maximum COF in the running-in regime and average COF values recorded in the stationary regime. The error bars correspond to standard deviations of the average values of 3–5 tests of repetition.
in Table 1 show a higher content of mono- and di-glycerides in the BD Shell, the most effective contributors to lubricity accordingly to Hu et al. [20].

It is worth noting that the order of the wear coefficients correlates well with the order of the COF values at the running-in period (Fig. 1), as the mechanical interactions between the two opponent surfaces are more intense at that stage. Also, the $K_d$ values of both triboelements do not show a clear trend among the fuels, being quite the same for each kind of fuel. In ball-on-plate reciprocating tribological tests, the ball remains in permanent contact with the opponent surface throughout the test, while the plate surface along the ball path is in intermittent contact, susceptible to an additional wear caused by fatigue contact. As it was not the case of the present work, it means that the wear mechanisms should be the same for both triboelements.

Fig. 2b shows the maximum depth of the wear track on the plate, an average of five measurements for each track and for each fuel. The average values ranged from 0.5 µm to 2.0 µm for BD Shell and BD Lamoc, respectively. This level of wear (of $10^{-8}-10^{-9}$ mm$^3$/N-m) denotes a mild to very mild wear regime, coherent with lubricated systems of high wear resistance [21]. It should be considered that the initial contact pressures are very high, in the order of 4 GPa, as evaluated by the Hertzian contact equation. Such condition was chosen to evaluate the tribosystems in extreme mechanical stress, although the contact pressures in the real automotive components do not exceed 600–1300 MPa [22,23].

![Fig. 2](image1.png)

**Fig. 2** – (a) Wear coefficient ($K_d$) of the balls and plates for each kind of fuel; (b) maximum depth of the wear tracks.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>BD Lamoc</th>
<th>BD Shell</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_d$ (mm$^3$.N$^{-1}$.m$^{-1}$)</td>
<td>1.0E-07</td>
<td>8.0E-08</td>
<td>6.0E-08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel</th>
<th>BD Lamoc</th>
<th>BD Shell</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum depth (µm)</td>
<td>2.0</td>
<td>0.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel</th>
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<tbody>
<tr>
<td>BD Lamoc</td>
<td>BD Shell</td>
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<tr>
<td>Diesel</td>
<td>Diesel</td>
</tr>
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</table>

![Fig. 3](image2.png)

**Fig. 3** – Lubricity of the fluids evaluated by the HFRR method: (a) WSD (wear scar diameter) and (b) COF (coefficient of friction) and film percentage for the reference fluids of high and low lubricity; (c) WSD and (d) COF and film percentage for each kind of fuel.
3.2. Standard HFRR test evaluation of fuels lubricity

The HFRR method was used to assess the lubricity of the fuels. This technique also gives information about the friction coefficient and the percentage of lubricant film that forms at the contacting bodies during the friction test. Although they are not considered to the evaluation of the fuel lubricity as described in the ASTM D6079 standard, their knowledge is important because some systems may operate under low wear regime, but with high friction, which can be detrimental in practical applications, as in diesel engines, where the fuel lubricates a set of components. The results of lubricity tests are shown in Fig. 3a and b for the fluids of high and low lubricity, used as references, and in Fig. 3c and 3d for Diesel and biodiesel fuels. In this method, the maximum wear scar diameter (WSD) acceptable for a lubricating fluid is 380 μm at 25 °C [16] as shown by the red line in Fig. 3a. The difference of the WSD values between the standard fluids of high and low lubricity (Fig. 3a) can be observed clearly, complemented by the low values of COF and high percentage of the lubricant film, in the first case, and the contrary, high COF values and low percentage of film, for the second case (Fig. 3b). It is thus evident in Fig. 3c and 3d that diesel and both biodiesel fuels are all fluids of high lubricity, as WSD does not surpass a value of about 220 μm, this maximum value corresponding to the BD Lamoc biodiesel. It is also interesting to note that the results in terms of rank of wear (BD Lamoc > Diesel > BD Shell) gotten from the HFRR method, which uses 52100 steel as the counterbodies material, followed the same trend of the results previously shown for the ball-on-plate one with Si₃N₄ tribo-pairs.

According to the literature, biodiesel fuels have higher lubricity than the diesel with low sulphur content, as shown in the work of Suarez [15], Knothe [16], Geller [24] and their respective co-workers. In their work, they found WSD values for diesel in the range of 400 to 650 μm, diminishing this value when adding biodiesel to the diesel fuel. WSD values of 150–300 μm were found for pure biodiesel, which vary with the biodiesel source. In the case of the present work, the diesel fuel presented a lower value of WSD than those found in the literature, and it is in the middle value of the two biodiesel fuels. It is probably due to the presence of other lubricant additives than

Fig. 4 – SEM micrographs of the Si₃N₄ ceramic: (a) original surface; (b) worn surface – BD Lamoc; (c) worn surface – BD Shell; (d) worn surface – diesel. Inset of the (d) energy dispersive X-ray spectroscopy of the adhered layer.
sulphur in that diesel (Table 1), whose content is considered low to be mentioned in the specification of the product.

The distinct lubricity of the two biodiesels is related to a set of factors above mentioned (Figs. 1 and 2). It is thought that the higher content of mono- and di-glycerides contributes to the higher lubricity of the BD Shell, as also verified by the HFRR method.

3.3. Wear mechanisms

The SEM micrograph of Fig. 4a presents the aspect of the mirror-polished surface of the Si3N4 plate. Dark β-Si3N4 grains of large aspect ratio are clearly seen, surrounded by the bright intergranular glassy phase. Fig. 4b, c and d are representative SEM micrographs of the wear tracks after testing under BD Lamoc, BD Shell and Diesel lubrication, respectively. The morphological aspects of the wear tracks are similar for all fuels and are characterized by a self-polishing abrasion mechanism, as it is still possible to recognize the polished surface morphology. Cracks along the grain boundaries are observed, with some grains presenting transgranular microfracture that leads to material chipping, as it can be seen in Fig. 4b and c. In some regions, as the one of Fig. 4b, a thin adhered layer is found, while in the others the surfaces appear clearer, as in the Fig. 4c, due to continuous formation and removal of the tribolayer. This layer is more evident in Fig. 4d, of the wear track formed under Diesel lubrication, where the direction of the sliding movement can be recognized (as indicated by the arrow). EDS analysis (inset of Fig. 4d) only detected the presence of elements that constitutes the ceramic material. This layer is thus probably formed by wear debris, which are plastically deformed by the tribological action.

It is known that the presence of tribolayers can reduce the wear damage as they are ‘sacrificial layers’ protecting the surface of the materials in contact [25]. This phenomenon is commonly observed in Si3N4 by the formation of an oxide layer when in tribological contact in the presence of air [21,25]. In the present work, and considering that the surface is submerged in fluid and not in direct contact with air, the oxides formation is not evident by the EDS analysis, as the percentages of the elements are very close to that of the original surface (not presented).

Because of their inertness, the adsorption of molecules on the ceramic surfaces is much lower comparatively to metals. On the other hand, the boundary lubrication caused by the action of tribolayers is more effective in ceramics than in metals [25] and, despite being formed by plastic deformation of debris, as it seems to be the case of the present work, this layer may have a fundamental role in the reduction of the wear of the Si3N4 ceramic, resulting in a mild wear for the three types of fuels studied.

In the running-in regime, friction values were in the range of COF 0.15–0.22, the lower values found for diesel and commercial biodiesel (BD Shell), and the highest one for the lab prepared biodiesel (BD Lamoc). At the stationary regime, COF dropped to 0.06 for BD Shell, 0.09 for BD Lamoc, and 0.14 for Diesel, the highest one at this regime.

The wear coefficient (k_d) was in the range of 10−8–10−9 mm²/N·m, denoting a mild wear to very mild regime, the ranking being BD Lamoc > Diesel > BD Shell. The main wear mechanisms were observed to be inter- and transgranular fracture and tribolayer formation on the ceramic surfaces.

Although the tribological behaviour of the Si3N4 pairs is similar under lubrication of the three tested fuels, it was possible to differentiate their friction and wear behaviour by this test. Biodiesels from the same source have different results in terms of lubricant ability, even though they are comparable to a Diesel of high lubricity, as shown by the HFRR method.

Conflicts of interest

The authors declare no conflicts of interest.

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