LUBRICITY OF THE ETHYL ESTER SUNFLOWER OIL

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Abstract. *In Brazil has stepped up social, economic and technological incentives for biodiesel´s production through the various oilseed crop species and its utilization by the ethylic transesterification process. Biodiesel is responsible for restoring the lubricity of the ultra-low sulfur diesel fuel and, furthermore it is less polluting, and thus extends the life of diesel fuel injection system, (including injector nozzle). This property is extremely important from the point of view of the integrity of the injection system, since the diesel fuel is primarily responsible for lubrication of injector nozzle. Thus it is necessary that all diesel fuel meets a minimum limit of 460 µm maximum the Wear Scar Diameter (WSD) by HFRR – High Frequency Reciprocating Test Rig (ISO 12156-01). However, much has to be investigated in relationship to physicochemical properties of such blends and, that they can result in performance of components of the injection system. The lubricity of the fluids (Ethyl Ester of Sunflower Oil - B0, B5, B20, B50 and B100) was evaluated by the HFRR, according to ASTM D 6079-04. The thermoacoustic answers (contact temperature, sound pressure level and accumulated numbers of cycles) were obtained during these tests due to the coupling of a SPL meter and temperature sensors. All fluids offered values of the WSD lower 300 µm, but minimum values were found for B5 and B100 blends of sunflower oil, WSD <200 µm. Therefore, these renewable biofuels provide appropriate lubricity in any percentage blend, besides they have better performance than B0-Diesel (pure mineral diesel fuel).*

Keywords*:Biodiesel, ethyl ester of sunflower oil, HFRR, lubricity, wettability*

1. INTRODUCTION

When two surfaces in contact slip over each other under load, the interaction between their roughnesses is responsible for generating the contact forces that oppose the motion (known as frictional forces) which are part of their dissipated energies in the form of heat, noise and wear of the involved materials in contact. If into the surfaces there is material that serve as an interface between the contact surfaces and they are acting in order to reduce these frictional forces, it is said that the sliding is lubricated (Hutchings, 1992). According to Merriam-Webster Dictionary, lubricity is the ability to reduce friction; and fuel is a material applied to produce heat or mechanical energy by the burning process.

The lubricity issue is significant, because the advent of low-sulfur petrodiesel fuels and, more recently, ultralow-sulfur diesel (ULSD) fuels, as required by regulations in the United States, Europe, and elsewhere, has led to the failure of engine parts such as fuel injectors and pumps, because they are lubricated by the fuel itself. The poor lubricity of low-sulfur petrodiesel requires additives or blending with another fuel of sufficient lubricity to regain lubricity. The reason for the poor lubricity of low-sulfur petrodiesel is not the removal of the sulfur-containing compounds but rather that polar compounds with other heteroatoms such as oxygen and nitrogen are also reduced in low-sulfur petrodiesel (Wei and Spikes, 1986; Dimitrakis, 2003; Barbour *et al*., 2000).

To meet the established limits of wear scar in diesel fuel standards, 460 µm in European (EN 590-09) and 520 µm in U.S.A. (ASTM D 975) regulations, a variety of lubricity additives can be used,which have a high affinity to metallic surfaces forming a thin protective metal-metal contact layer. This lubricant film is formed by the adsorption of the polar molecules of the additives on the metal surface, which is negatively charged (Barbour *et al*., 2000).

Biodiesel is an alternative diesel fuel obtained through the transesterification of vegetable oils or other materials largely comprised of triacylglycerols (also known as triglycerides), such as animal fats or used frying oils, with hydric alcohols to give the corresponding alkyl esters (Knothe.and Dunn, 2001; Dunn and Knothe, 2001). In Brazil, the vegetable oils more commonly used for obtaining biodiesel are oils from soybean, castor bean fruit, sunflower, cotton, palm, and others. Furthermore, with the purpose of meeting the specifications of the Brazilian National Agency of

Petroleum, Natural Gas and Biofuels (ANP), antioxidant additives, from synthetic and natural origins, have been added to the biofuel (Tavares *et al*, 2011). Figure 1 shows the projection of the Brazilian biodiesel production, in million of m^3, according to FGV (Getúlio Vargas Foundation).

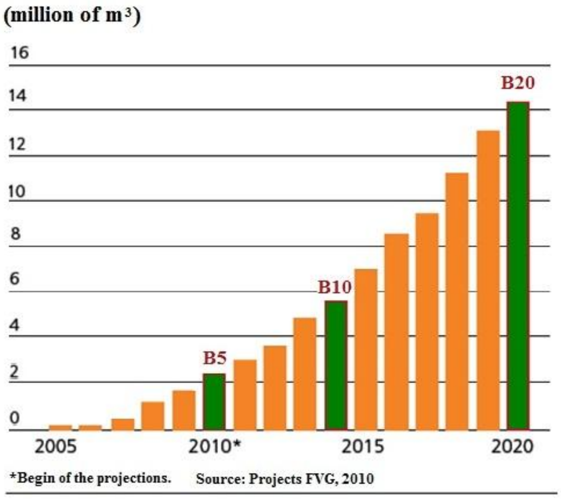


Figure 1. Projection of the Brazilian biodiesel production.

Previous literature states that low blend levels of biodiesel can restore lubricity to (ultra-)low-sulfur petroleum-derived diesel (petrodiesel) fuels, which have poor lubricity. And other advantages of biodiesel, compared to petrodiesel, include the reduction of most exhaust emissions, biodegradability, a higher flash point, and national origin (Knothe and Steidley, 2005). According Lapuerta *et al*. (2010), the impurities of biodiesel, such as monoglycerides and free fatty acids, are among the main variables affecting biodiesel lubricity. On the contrary, triglycerides almost have no effect on lubricity due to its poor solubility with diesel fuel. Ethyl esters have better lubricity than methyl esters, as reported by Kulkarni *et al.* (2007).

The higher is the degree of unsaturation in ester chain of a biodiesel, the smaller is its oxidation stability. Sunflower biodiesel obtained by the ethyl route possesses a high amount of unsaturated fatty acids, mainly oleic acid (C18:1) and linoleic acid (C18:2), thus being more prone to the oxidation process. Then these products cause corrosion in engine parts and formation of deposits, leading to the plugging of filters and injection systems (Tavares *et al*., 2011). The biodiesel obtained from sunflower oil is constituted of 98 to 99% triacylglycerides, displaying an elevated content of unsaturated fatty acids (around 83%), being 72% of linoleic acid and a small amount of linolenic acid (0.4%) (Jorge *et al*., 1998).

In this work, the blends of ethyl ester from sunflower oil were evaluated using HFRR equipment, where their lubricity properties were compared to the B0 and B5 - Off-Road Diesel. These blends were obtained by volumetric mixing of sunflower biodiesel (5 % and 20 %) with B0-Diesel (mineral conventional diesel fuel) and B00-SF (100% biodiesel from sunflower oil). Wettability tests were used to compare the fluid performance. Optical Microscope was used to exhibit and measure the wear scars and film lubricant formation on metallic ball surfaces. The roughness and waviness tests were used to show the cross section of wear track on the disks after to the HFRR tests.

2. EXPERIMENTAL

2.1 Fuel samples

A total of five fuel samples were evaluated in this work. The B0-Diesel (mineral conventional diesel fuel, 1200 ppm sulfur), i.e, petrodiesel which is produced by atmospheric distillation process with 1200 ppm sulfur by Petrobras (Brazilian Oil Company), and the Off-Road Diesel (B5 Biodiesel, 1100 ppm sulfur) which was acquired in the gas station of Natal City, Brazil, used like the comparison parameters. The biodiesel B00-SF was obtained by the process of ethylic transesterification from sunflower oil with potassium and ethanol catalyst 99.5%, made in the Laboratory of Technology Surfactants and of Separation Processes – Industrial Technologic Core of the Federal University of Rio Grande do Norte. The fuels B5-SF and B20-SF were resulting from the volumetric mixing between the ethyl ester from sunflower oil (B100-SF) with 5 % e 20 %, respectively, with B0-Diesel. Table 1 presents the adopted classification, and the composition of the studied fuels. In Table 2 is presented some physicochemical analyses as density, viscosity, copper strip corrosion, cetane number and flashpoint for these fuels.

Table 1. Description of the fuels.

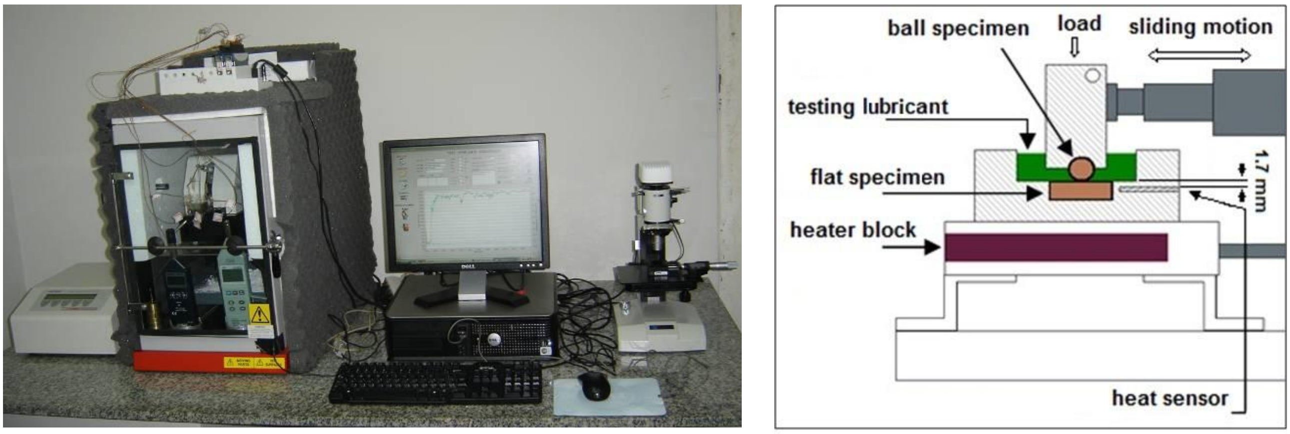
Fuels	Description
B0-Diesel	Mineral conventional diesel fuel, 100 % of diesel oil (no biodiesel), 1200 ppm of sulfur
Off-Road Diesel	B5 off-road diesel, 1100 ppm of sulfur. Available at gas stations of the Brazil since 2010
B5-SF	5 % ethyl ester of sunflower oil + 95 % Mineral conventional diesel
B20-SF	20 % ethyl ester of sunflower oil + 80 % Mineral conventional diesel
B100-SF	100 % ethyl ester of sunflower oil

Table 2. Physicochemical properties of the fuels.

Fuels	Density (Kg/m^3)	Viscosity at 40 °C (Pa.s)	Copper strip corrosion	Cetane number	Flashpoint (°C)
B0-Diesel	821	0.0025	1a	52	36.0
Off-Road Diesel	838	0.0030	unmeasured	42	43.0
B5-SF	830	0.0030	1a	58	41.5
B20-SF	847	0.0032	1b	62	44.0
B100-SF	889	0.0049	1b	55	80.0

2.2 HFRR test

Lubricity property of the fuels was evaluated using the *High Frequency Reciprocating Test Rig* (HFRR) from PCS Instruments®, as shown in Fig. 2. HFRR method is located in the GET (Group of Tribology Studies and Structural Integrity, UFRN, Natal – RN, Brazil). It is a ball-on-disk test to measure the friction and wear under boundary lubrication conditions using a highly stressed ball-on-disk contact. A hard steel ball (570 – 750 HV) of 6.0 mm diameter reciprocates on a softer steel disk (190 – 210 HV) of 10 mm diameter under the fully submerged fuel condition (2.0 ± 0.2 mL) at normal load of 1.96 ± 0.01 N and a 1.00 ± 0.02 mm stroke length at a frequency of 50 ± 1 Hz for 75 min, and the fuel temperature was kept at 60± 2 °C according to the ADTM D-6079-04, where the heating of the contact is measured at 1.7 mm distance of the ball-on-disk contact. Coefficient of friction was measured by a piezoelectric force transducer and the formation of electrically insulating films at the sliding contact was measured by the electron cyclotron resonance technique (ECR).



a) b)

Figure 2. HFRR tribotest: a) picture of equipment b) schematic diagram of HFRR.

The repeatability of the data provided in the test HFRR (friction coefficient, percentage of interfacial lubricant film, temperature and wear scar diameter) were evaluated using seven replicates for each fuel. After testing, the excess of the fuel is removed from the ball support, and the dimensions of the wear scar diameter formed in the surface of the ball were measured in the optical microscope with magnification of 100 times. Arithmetic average of the diameters of the elliptical scar (WSD number) describes the wear in the ball, to whom is associated the fuel lubricity degree. High WSD values indicate a greater wear of the ball and, therefore, a fuel with lower lubricity or vice-versa (JOAQUIM, 2007).

To ensure the relative humidity 30 % above inside the HFRR test chamber was used desiccant potassium carbonate (Anhydrous K_2CO_3). A thermo-hygrometer portable digital Instrutherm HTR-157 was used to measure the air relative humidity, before and after the HFRR lubricity tests. A data acquisition board from National Instruments® was coupled to the HFRR equipment, in which two modules containing four calibrated K thermocouples were inserted on it.

During the HFRR lubricity test, the sound pressure level (SPL) was measured by digital SPL meter, model SL-4012, positioned at 10.5±0.1 cm distance of the ball-disk contact and coupled to computer through its interface. To minimize any interference from outside the HFRR system, steaks of 7 cm thick of styrofoam plates were placed in the humidity and temperature control camber where is located the mechanics unit of the HFRR.

2.3 Ball and disk characterization

The tribological couple, HFRR standard, is composed by ball and flat disk of AISI 52100 steel (SAE 52100 or DIN 100Cr6). The technique of X-Ray Fluorescence was applied to characterize the chemical composition of AISI 52100 steel disk, indicated on the Tab. 3.

Table 3. Chemical composition by weight (%) from the AISI 52100 steel disk.

Fe	C	Mn	Cr	S	Si
Bal.	0.98	0.413	1.46	0.013	0.546

Based on the ASTM D-6079 – 04 standard, the roughness values (Ra – arithmetic average roughness) will be between Ra=0.02 μm for disk and; Ra=0.05 μm for ball. The surface conditions of the AISI 52100 steel disks were evaluated by roughness tests using a portable rugosimeter from Taylor Hobson®, model Surtronic 25. For each disk were performed five measuremets in the non-worn suface and two, in the transversal section of the worn surface. The results of surface roughness Ra and waviness Wa (μm) were calculated through the profile generated and stored on the computer by its own interface.

Vickers microhardness tests were performed for both balls and disks. The microhardness tests consists of applying the Vickers indenter (diamond pyramid with square base and apical angle of 136°) on the sample surface during 15 seconds with the following loads: 50 gf or 0.49 N ($HV_{0.05}$), for the surfaces of the disks; e 200 gf or 1.96 N ($HV_{0.2}$), for the surfaces of the balls. Table 4 shows the averages microhardness HV of the non-worn ball and disks sufaces.

Table 4. Microhardness HV averages of the non-worn ball and disk surfaces.

Average Values	B100-SF	B20-SF	B5-SF	Off-Road Diesel	B0-Diesel
$\mathbf{HV_{0.2}}$ (Ball)	589 – 750	530 – 640	558 – 641	552 – 750	543 – 627
$\mathbf{HV_{0.05}}$ (Disk)	166 – 181	165 – 182	168 – 182	179 – 208	177 – 197

2.4 Wettability test

The wettability is governed by both the surface free energy and the surface geometric structure. Therefore, the surface wettability can be modulated by changes in one or two of these factors (Tang *et al.*, 2010).

Bhattacharya *et al.* (2008) describe the wettability of a liquid as a function of surface energies at the interfaces: solid-gas, liquid-gas and solid-liquid. Surface energy across an interface or surface tension at the interface is a measure of the energy required to form a unit area of a new surface at the interface. The intermolecular bonds or cohesive forces between liquid molecules promote the surface tension.

The adhesion forces between the liquid and the second substance will compete against the cohesive forces of the liquid. The liquids with cohesive weak bands and strong attraction to another material (or predisposition to create bonds of membership) will tend to spread over the material, while liquid with strong cohesive bonds and weak forces of adhesion are likely to form a droplet in contact with another material. The contac angle can be related the surface energy by the Young equation (Eq. 1):

$$\sigma_{sg} = \sigma_{sl} + \sigma_{\lg}.\cos\theta \qquad (1)$$

where:

σ_{sg} = surface energy of the solid-gas interface;

σ_{sl} = surface energy of the solid-liquid interface;

$\sigma_{\lg}$ = surface energy of the liquid-gas interface; and

θ = solid-liquid contact angle.

Testing parameters of surface tension, by method of weight drop, and contact angle between fluid and HFRR disks are shown on the Tab. 5, which were measured by goniometer DSA Krüss at 25 °C. These volumes represent the amount of liquid required for drop formation and viewing of the contact angle. Samples of sunflower oil and ethanol, reference fluids, were used like criteria comparison, since they constitute the reagents to produce biodiesel.

Table 5. Parameters used to obtain of the wettability.

	B100-SF	B20-SF	B5-SF	Off-Road Diesel	B0-Diesel	Sunflower Oil	Ethanol
Density (Kg/m^3)	889	847	830	825	821	916	785
Voume for the Contact Angle (µL)	15	5	5	5	5	20	7
Volume to Surface Tension (µL)	5.5	4.0	4.5	4.5	4.6	15	9

3. RESULTS AND DISCUSSION

The five fuels samples were evaluated using HFRR test. Test condition without biodiesel, B0-Diesel, was used as reference in order to analyze the influence of ethyl ester sunflower oil (additive biodiesel) on wear of metallic surface. The following results will be presented and discussed about friction coefficient, temperature, sound pressure level, wear scar diameter (on ball), roughness (on disk) and wettability.

3.1 Wettability

Figure 3 presents graphs of surface tension and contact angle for the fluids studied, as well as sunflower oil and ethanol, which are reference fluids. The higher values of surface tension and contact angle were obtained for the B100-SF (32 mN/m) and its precursors sunflower oil and ethanol (33 and 31 mN/m, respectively). This can be explained by the density of the ethyl ester of sunflower (889 kg/m^3), relatively high when compared to other fuels (see Table 2). Same behaviour occurs for the contact angle, whose value obtained during the test for the B100-SF is practically constant (16-17 °) and all other fuels tend to 2-7.5°. According to these tests, are perceived that the fluids (SF-B5, B20-SF and Off-Road Diesel) have approached the wettability of the B0-Diesel. To the value of contact angle for ethanol shoul be considered its high volatility.

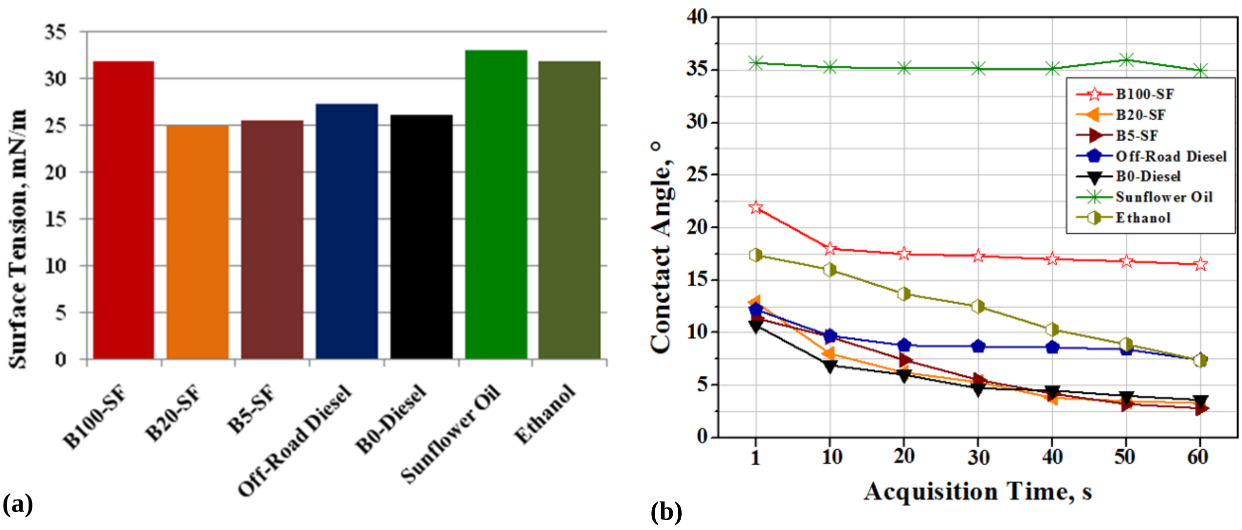


Figure 3. Wettability of the fluids: a) surface tension and b) contact angle.

3.2 Roughness and Waviness

According to ASTM D 6079-04, Ra roughness values for the disks before the HFRR lubricity tests have to be 0.02 µm, however it is observed that roughness values differ from the established value by this standard, like is shown on the Tab. 6., which presents the values of the roughness and waviness to non-worn and worn disk surfaces applied on the HFRR lubricity test of the fuels. It's important to verify that, despite the roughness of the disks tested with B0-Diesel be lower (before test), it can be seen that it promoted higher wear than other disks.

Table 6. Roughness Ra and waviness Wa averages of the non-worn and worn disk surfaces.

	Non-Worn Surface		Worn Surface	
Average Values	**Ra (μm)**	**Wa (μm)**	**Ra (μm)**	**Wa (μm)**
B0-Diesel	0.011 – 0.029	0.014 – 0.022	0.395 – 0.598	0.650 – 0.862
Off-Road Diesel	0.007 – 0.024	0.013 – 0.025	0.142 – 0.307	0.161 – 0.384
B5-SF	0.014 – 0.160	0.015 – 0.142	0.145 – 0.224	0.126 – 0.194
B20-SF	0.083 – 0.244	0.073 – 0.248	0.185 – 0.309	0.219 – 0.387
B100-SF	0.011 – 0.029	0.012 – 0.069	0.149 – 0.197	0.163 – 0.240

3.3. Lubricity

3.3.1. Friction coefficient, temperature, film formation and SPL

The formation of insulating films was measured using during HFRR test by means of the ECR. The surface coverage, caused by generation and removal of surface films, was measured under boundary lubrication conditions with a steel ball rubbing against a steel disk. For each fuel were executed seven tests and their data are exhibited in Fig. 4 through the box-plot graphs to (a) the heating of the contact; (b) the film formation behaviour of the fuels studied; (c) the sound pressure level and; (d) the friction coefficient obtained by the HFRR test.

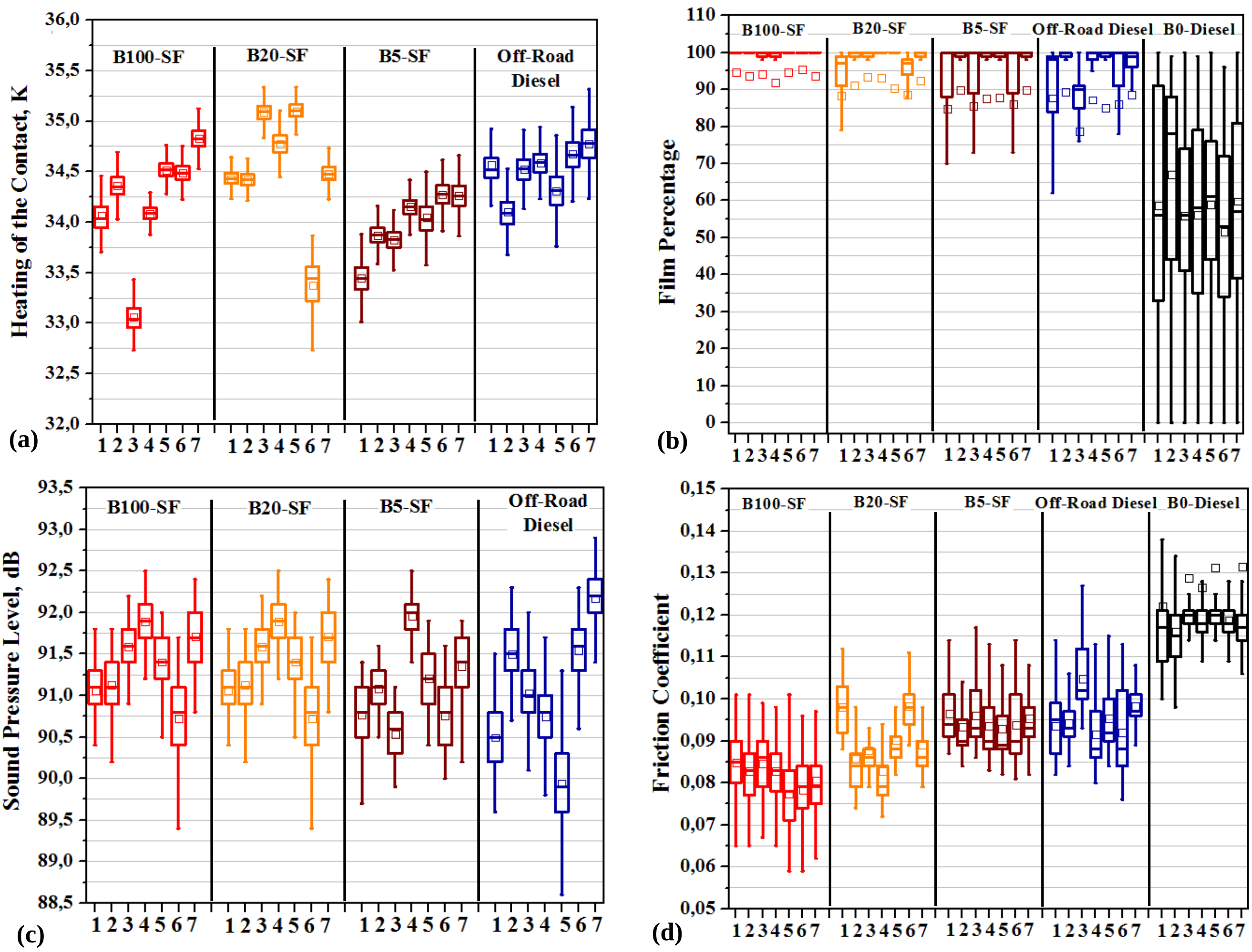


Figure 4: Results obtained by HFRR lubricity test: a) Heating of the contact, b) Film percentage, c) Sound pressure level and, d) Coefficient of Friction.

In Figure 4 (a) the graphs show that B20-SF presents higher heating than other fuels. The heating is also affected by friction and roughness; and according to Tab. 6, the B20-SF offered highest initial Ra. The sound level pressure levels showed similars fluctuations, range 88.6 - 92.9 dB. When biodiesels were used, there was a soldid film formation, displaying almost 100% film percentage, while the B0-Diesel offered more fluctuations during the tests. When the friction coefficients and film percentage for the seven tests to each sample fuels are recorded, it is noted that they are inversely proportional; i. e. the coefficient of friction corresponds well with the film formation (McQueen *et al.*, 2005). The high values of friction coefficients were observed to B0-Diesel. The films covering the rubbing surfaces affect the surface roughness and structure. Thus, friction behaviour demonstrated a corresponding response to the film formation between the contacts under the boundary lubrication conditions. When the full film was formed in the surface, the coefficient of friction showed a high values.

3.3.2. Wear scar

The worn volume values indicated that different wear mechanisms are acting in the contact. According to WSD number in the Fig. 5, B0-Diesel offers hight value and consequentely a smaller lubricity performance than the biodiesel fuels. An optical microscopy, with 100 x magnification, was used to examine the wear scar of the ball surfaces for each test. A selection of photomicrographs of the worn surfaces is presented in Fig. 6. On the left columm, the worn surfaces are shown and on the right, their respective profile roughness. The four variables measured in this study, grouped in windows of data acquisition (the heating of the contact, the sound pressure level, the percentage of lubricant film in the contact and the coefficient of friction) shown to be susceptible to the evolution of scars, or are parameters that correlate with the lubricity of biodiesel.

The positive influence of biodiesel in the wear can be seen due the *value maximum deph* and *area of the role* presented in the profiles and images of the scars on the balls (Fig. 6 – Right Columm), where B0-diesel confirms its low lubricity (higher WSD number and severe wear and higher maximum deph in profile than the biodiesel fuels). According to Hutchings (1992), the severe wear can be associated to debris formation and its separation from the surface, the rolling of debris particles between sliding surfaces is the cause of severe wear. Comparing the effect of biodiesel additive (B100-SF, B20-Sf, B5-SF and Off-Road Diesel), it is possible to observe that the biodiesels showed almost similar WSD and morphology, however they offered superior lubricity (WSD > 270 µm). Therefore, biodiesel blends are significant to improving the lubricating performance that is wear reduction when it is added at the oil diesel.

According to Xu *et al.* (2010), in their investigation about lubricity emulsified bio-oil, constated the lubrication mechanism could be attributed to the polar groups and oxygenic compounds making the micro-bio-oil drops absorbed in the surface of the frictional pairs and generating frictional chemical reaction that led to the boundary lubrication. Though, the existence of oxygen might accelerate the corrosion wear on the rubbing surface.

Despite the high sulfur content B0-Diesel (1200 ppm), this fuel had the greatest amount of wear scar (345 ± 15 µm) than the other biodiesel blends. Adding ethyl ester in only 5% to diesel is also sufficient to increase the lubricity of diesel with high sulfur content.

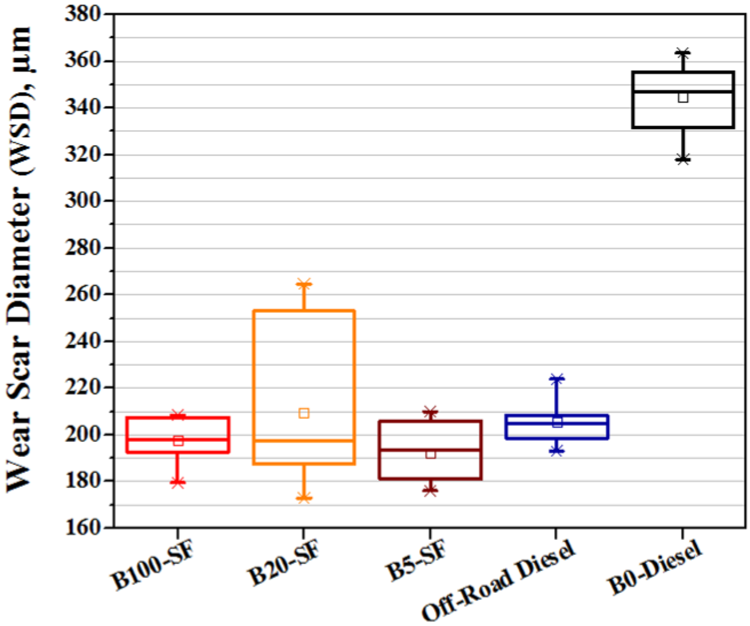


Figure 5. Lubricity of fuels: WSD number.

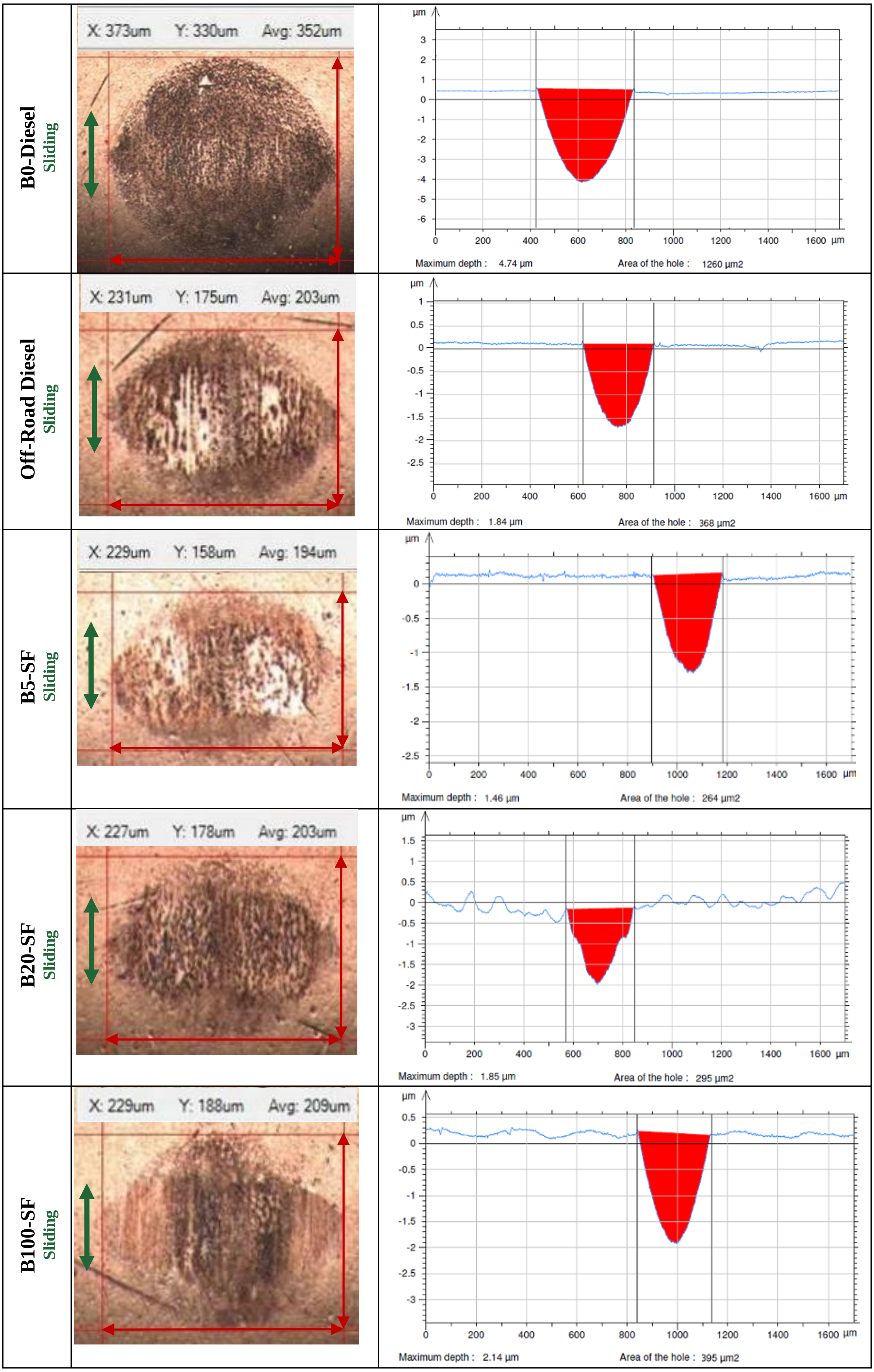


Figure 6. Wear scar of ball (left column) by optical microscopy and the profile roughness of the worn disk surfaces (right column) to the analised fuels.

4. CONCLUSIONS

According to the HFRR lubricity test results, can conclude:

- Biodiesel blends of sunflower oil and Off-Road Diesel showed higher lubricity with WSD numbers lower 270 µm. Although the high sulfur content (1200 ppm) of B0-Diesel, this fuel offered the greatest amount of WSD number (345 ± 15 µm) than other biodiesel blends. Biodiesel blends – like 5 % ethyl ester + B0-Diesel – were sufficient to improve the lubricity of high sulfur diesel fuel.
- Four types of variables (heating of the contact, sound pressure level, percentage of lubricant film and coefficient of friction), measured in this study, have shown to be susceptible to the scar evoluion, i.e, they are parameters that correlate with the lubricity of biodiesel. Insulating film formation was effective for all biodiesel blens, and the B0-Diesel showed greatest fluctuations during the tests. And the friction behaviour is lower for biodiesel blends than B0-Diesel.
- The wettability of fuel measured by contact angle, resulting from the biodiesel blends with the polished steel disks, converged to 19.5 ° ± 2.5 °, whereas in B0-Diesel, 7.5 ° ± 4.5°, leaving the B5-SF and B20-SF included in this last range.
- In general, renewable Biodiesels provide appropriate lubricity in any percentage blend, beyond they have better performance than B0-Diesel.

5. ACKNOWLEDGEMENTS

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7. Responsibility notice

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