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Effect of Desulfurization of Diesel and its Blends with Biodiesel on Metallic Contact

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The current environmental scenario has required changes in fuel nature, in order to minimize the harmful effects caused by sulfur in diesel. However, reductions in sulfur content promote loss of its lubricity and consequently wear in the injection system of the diesel engine. This study aimed to investigate the influence of sulfur minimization on fuel lubricity and wear of metallic disks. The fuel tribological analysis was carried out in HFRR equipment in accordance with ASTM D 6079-04. The tested fuels were diesel oil with 50, 500 and 1800 ppm sulfur, and their blends of soybean and sunflower biodiesel (5, 20 and 100% in volume). The results showed an increase of disks wear with reduction of sulfur content when lubricated with pure diesel. This fact was decreased when biodiesel was added to all concentrations.

Keywords: *fuel, diesel, biodiesel, desulfurization, wear, steel*

1. Introduction

Due to environmental concerns, the EURO IV regulation from 2005 established a limit of 50 ppm of sulfur in automobile fuels[1]. However, that measure decreases fuel lubricity.

There are several methods to reduce gases emissions during the combustion of fossil fuels, such as the use of filters to reduce gas exhaustion, use of high quality fuel and increase of injection pressure of fuel[2]. However, if the lubricity is not adequate, the increase of injection pressure can cause problems in engines.

The introduction of low sulfur diesel fuel has caused some problems in fuel lubricating properties due to desulfurization process which eliminates not only the amount of sulfur in diesel fuel but also minimizes other compounds that help lubricity, such as poly aromatic, nitrogen and oxygen[3,4]. This reduction in lubricity can have a negative effect on injection systems. In order to avoid premature failure of equipment, several standards have been developed to ensure acceptable levels of lubricity to fuel. These standards are based on WSD (wear scar diameter) measure of the steel ball in contact with the fuel; the WSD should not exceed 460 μm[5] or 520 μm[6]. So, the diesel with low sulfur content requires suitable additives to restore its lubricating properties, stimulating the search for new formulations, among which biodiesel is an important alternative.

Biodiesel is defined as the mixture of mono-alkyl esters from vegetable oils or animal fats, produced by transesterification reactions. The fuel derived from fatty compounds by transesterification reaction has good lubricity due to oxygen concentrations and the presence of carboxylic acids[7,8].This is a determining factor in its use as an additive to conventional diesel.

Several studies have evaluated the lubricating properties of the biodiesel fuel in pure form and in mixture with diesel fuel[1,2,7,8,9]. In their research, Sukjit and Dearn[2] concluded that when a blend with 10% of rapeseed methyl ester and diesel was tested, a low value of WSD was found. Other biodiesels showed efficiency in reducing WSD, such as sunflower and olive biodiesel, when added to diesel at low concentrations (0.15 and 0.50 vol%)[7]. Although the addition of low concentration of biodiesel provides adequate results of diesel lubricity (WSD equal to 338 μm), mixtures of 5 and 10% biodiesel with diesel fuel (without a conventional lubricity additives) have lubricity values that are similar to conventional automobile diesel fuel[1].

This study evaluated the influence of desulfurization of diesel and biodiesel blends of soybean/sunflower on fuel lubricity, as well as on the wear of AISI 52100 steel disks.

2. Material and Methods

For synthesis of biodiesel were used soybean and sunflower vegetable oils, that were dried in oven at 110°C for 4 hours. The transesterification reactions were performed in a batch with a magnetic stirrer. The reaction mixture containing ethanol, the catalyst (KOH) and vegetable oil (soybean or sunflower oil), with the molar ration of alcohol/soybean oil/catalyst of 6:1:0.001 was stirred for one hour at environment temperature. After this time, the mixture was neutralized and washed many times with distilled water. The separation of different phases was carried out by gravity in a separator funnel and the biodiesel was dried for 4 hours at 110°C. The blends were prepared with diesel S1800, S500

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and S50 (ppm sulfur) in proportions of 5, 20 and 100% of soybean biodiesel / sunflower.

The kinematic viscosity was determined at 40°C using a reomether HAAKE MARS; the density was measured with pycnometer. Also, humidity[10] and flash point[11] were determined in triplicate for samples of soybean and sunflower oils and its biodiesel. The sulfur content in diesel (S50, S500 and S1800) was measured by sulfur analyzer[12,13,14].

The friction and wear performances were evaluated using the HFRR (High Frequency Reciprocating Rig) and according to[15]. The HFRR method 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 and Ra of 0.02 μm under the fully submerged fuel condition at normal load of 10 N and a 1mm stroke length at 20 Hz frequency for 60 min. Both ball and disk were made of AISI 52100 steel. The fuel temperature was kept at 50°C. The friction coefficient was measured by a piezoelectric force transducer and the formation of electrically insulating films at the sliding contact was measured by the ECR (Electrical Contact Resistance) technique. Both, ball and disk, were cleaned by ultrasonically agitated bath of acetone and toluene before and after the HFRR test.

After the test, the WSD was measured using the optical microscope, while the disk surface was analyzed by scanning electron microscopy.

3. Results and Discussion

Table 1 shows the physicochemical characterization of vegetable oils, biodiesel and diesels, while the sulfur content of diesel oils are present in Table 2. The results of density and kinematic viscosity were similar for both oil and biodiesel fuels. Whereas the humidity of vegetable oils was similar and greater than biodiesel, indicating hygroscopic character, and for this reason, these oils were dried before transesterification. The humidity may result in the saponification of the final product during the transesterification process. The flash point of soybean and sunflower oils show values lower than those described in the literature, which can be explained by the fact that the samples were dried before analysis. The biodiesels were according to the standards of ANP (Petroleum National Agency), except for acidity, whose values are under the maximum. The sulfur content was lower than limits (Table 2), regarding that low sulfur content decreases diesel lubricity.

Figures 1 and 2 show the friction coefficient behavior and percentage of film obtained during the tribological test lubricated by the studied fuels. Analyzing Figure 2, it is possible to confirm that sulfur presence in diesel is very important to reduce the friction, diesel with 1800 ppm of sulfur showed best performance in tribological test with lower friction coefficient than diesel with 500 and 50 ppm of sulfur. Also, it is observed similar behavior for diesel S500 and S50 until 2500 seconds of test, after this time diesel S50 gave better results. However, when biodiesel was added to diesel, an improvement in friction coefficient was observed for all blends. Also, increasing the biodiesel concentration it is possible to observe that friction coefficient decreases, independently of sulfur concentration and biodiesel type (sunflower or soybean). Better results of biodiesel addition was verified for mixture of diesel S50 and 20% biodiesel, while for other diesels (S1800 and S500) the concentration 5 and 20% showed close values. On the other hand, the biodiesel type influenced in decrease of friction coefficient, better results were observed for blends with sunflower biodiesel.

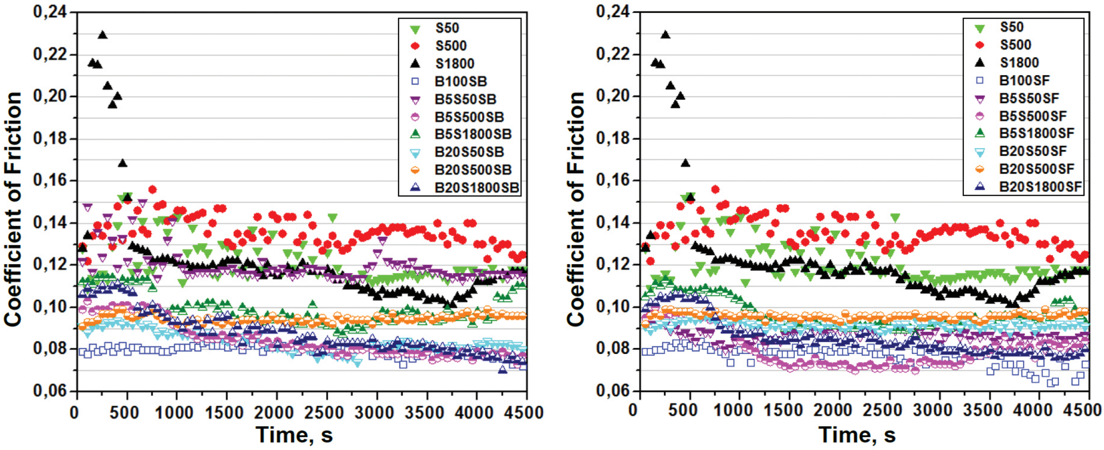
The surface coverage, caused by generation and removal of surface films, was measured under boundary lubrication conditions with a steel ball sliding against a steel disk by Electrical Contact Resistance during the test. The friction behavior shows a corresponding response to

Table 1. Physic-chemical characterization of fuels.

Oil	Biodiesel	Density (Kg/cm³)		Acidity value (mg KOH)		Humidity (%)		Flash Point (°C)		Viscosity (cSt) à 40°C	
Sunflower	B100-SF	912.2 ± 4.5e-5	874.5 ± 6.1e-5	1.07 ± 0.01	1.15 ± 0.01	0.035 ± 0.4e-5	0.009 ± 0.6e-5	212 ± 0.3	160 ± 0.2	37.05 ± 0.03	4.97 ± 0.05
Soybean	B100-SB	913.7 ± 1.5e-5	874.8 ± 1.4e-5	0.79 ± 0.02	1.10 ± 0.02	0.049 ± 0.5e-5	0.015 ± 0.7e-5	197 ± 0.2	180 ± 0.3	32.50 ± 0.04	4.85 ± 0.03
Diesel 1800		920 ± 5.6e-2		---		0.64 ± 2.2e-3		43 ± 0.1		3.0 ± 0.01	
Diesel 500		879 ± 1.2e-2		---		0.62 ± 2.5e-3		41 ± 0.2		1.14 ± 0.02	
Diesel 50		853.8 ± 2.7e-3		---		1.59 ± 2.2e-3		64.7 ± 0.1		1.1 ± 0.02	

Table 2. Sulfur content of diesel under study.

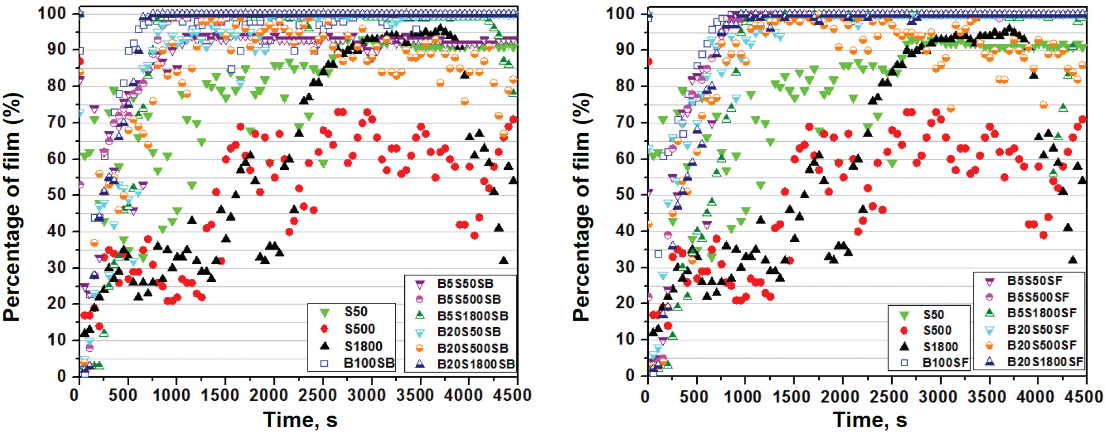
Sample	Sulfur content (ppm)	Limits (NBR 14533, ASTM D 4294 and 5453)[12,13,14]
Diesel S1800	1100	≤1800
Diesel S500	298	≤500
Diesel S50	7	≤50



(a)

(b)

Figure 1. Coefficient of friction of the contact disc-ball lubricated: a) for pure diesel and biodiesel from soybean and their blends, and b) for pure diesel and biodiesel from sunflower and their blends.



(a)

(b)

Figure 2. Percentage of film formation on disk surface: a) for pure diesel and biodiesel from soybean and their blends, and b) for pure diesel and biodiesel from sunflower and their blends.

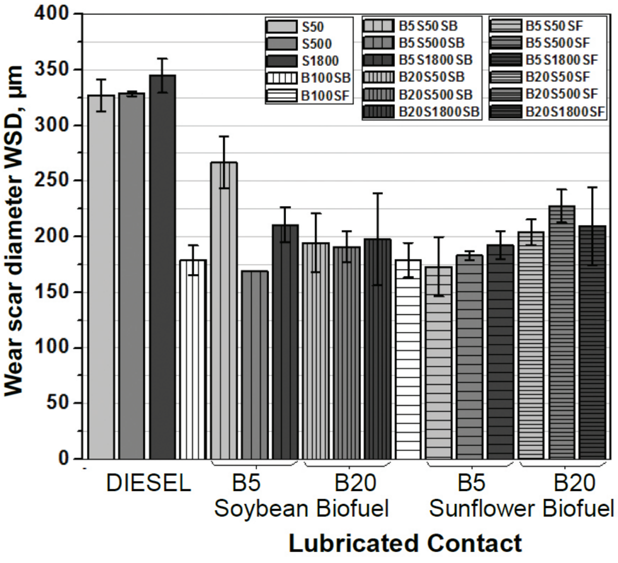


Figure 3. Diameter of wear scar of ball after HFRR test rig.

the film formation between the contacts under the boundary lubrication conditions; this fact was observed in Figure 1. The ability of diesel to form a film on the surface is lower than its blends with biodiesel as it is verified in Figure 2, confirming the high friction coefficient observed to diesel in Figure 1. A very good surface coverage was found for pure biodiesel almost 100% of coverage. However, the blends of diesel and biodiesel showed good ability to form film, specially the blends of diesel and sunflower biodiesel, indicating that sunflower biodiesel is more suitable to improve diesel lubricity.

The wear scar diameter results are shown in Figure 3. This value was measured after HFRR test using optical microscopic and a software of HFRR equipment. Note that all WSD are lower than the maximum value (460 μm) established by European regulation.

The wear of the ball is greater when in contact with diesel fuel. For this research WSD varied from 327 to 337 μm, depending of sulfur content, but statically these WSD are similar. Also, other important verification is that biodiesel, soybean and sunflower resulted in practically the same wear scar diameter (175 μm). When biodiesel is added to diesel, a significant decrease was observed in

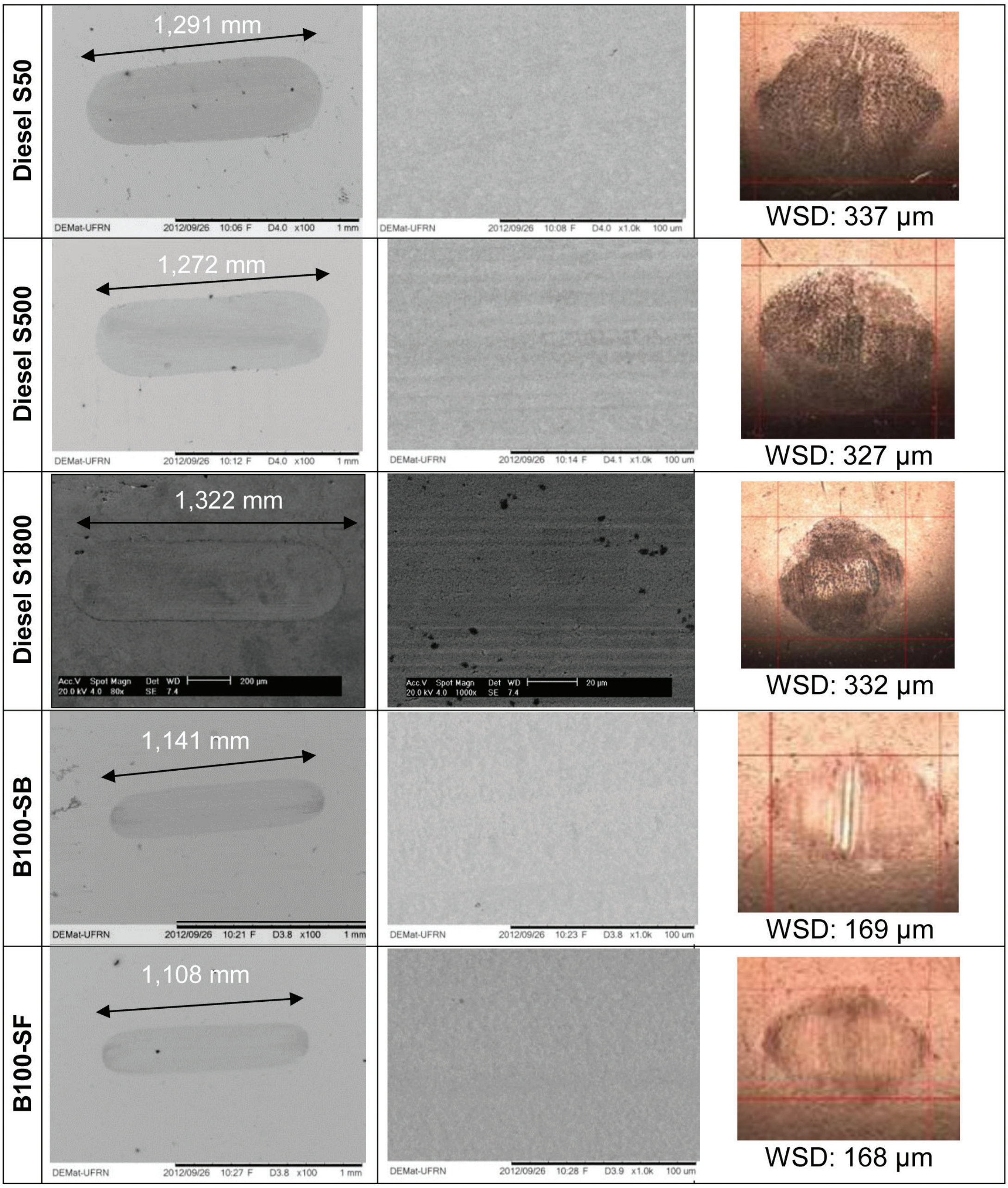


Figure 4. SEM the worn surfaces of the disks after testing lubricated by pure diesel blends of B5 (S50, S500 and S1800) and biodiesel from soybean and sunflower.

WSD, about 40%. This observation agreed with friction coefficient results. It is obvious that the addition of sunflower and soybean biodiesel improves fuel lubricity. However, the type of biodiesel and blends concentration (5 and 20%) did not have significant influence on WSD.

The images of worn disks and balls surfaces are shown in Figure 3, only for three types of diesels and biodiesels. These figures show the characteristic track of disk (left), worn surface area at 1000x (center) and the wear scar of the ball (right).

A scanning electron microscopy (SEM) was used to examine the disks surfaces after each test. A selection of micrographs of the worn surfaces is presented in Figure 3 (images in center of figure) and the influence of fuel in the

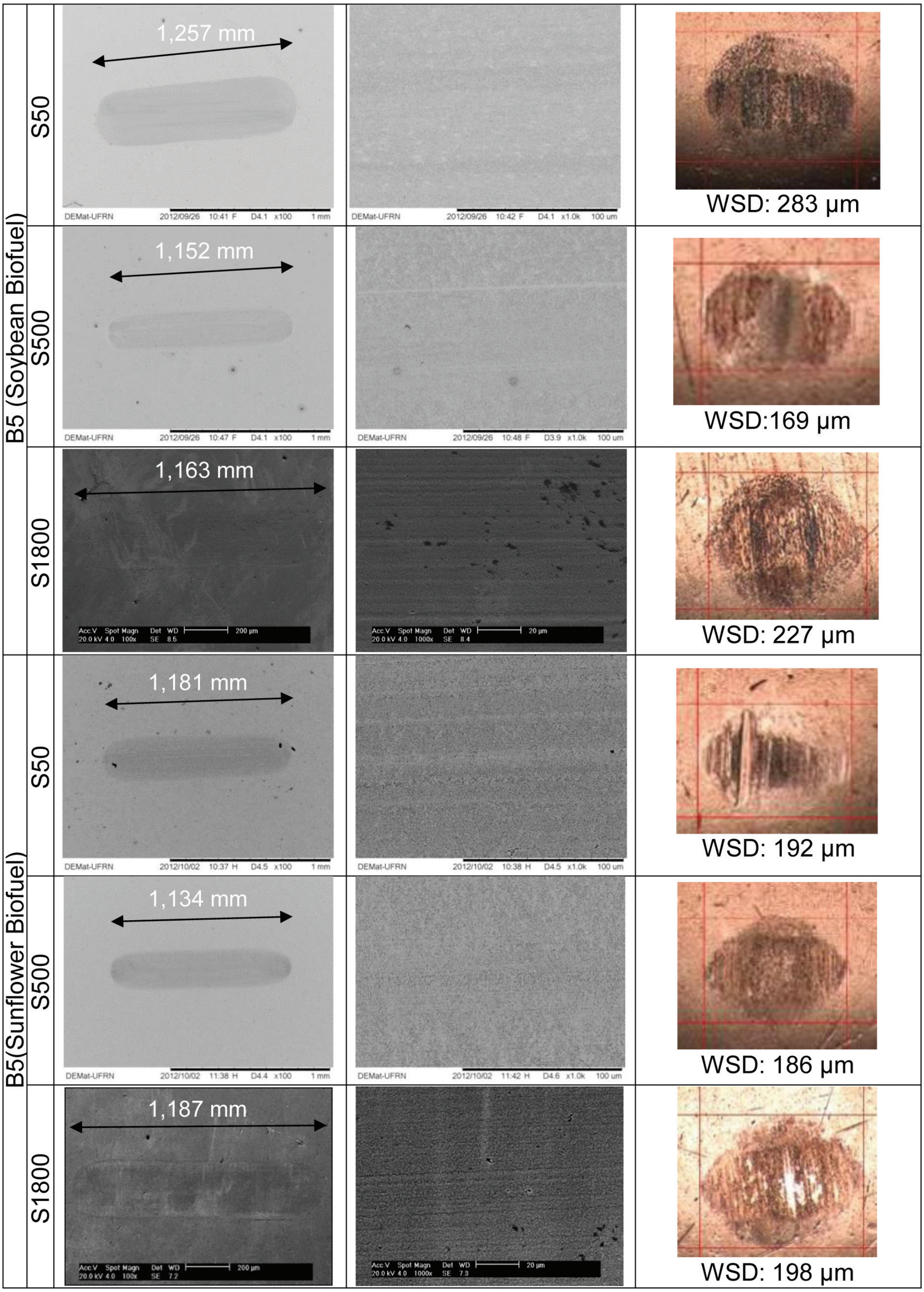


Figure 4. Continued...

wear can be seen in these figures. These images show the worn surface when diesel S50, S500 and S1800 were used as fuel and, in all situations, there are abrasive signals and it seems to be the main wear mechanism (Figure 3). According to[16] the severe wear can be associated to debris formation, their detachment from the surface and the rolling of debris particles between sliding surfaces. This wear mechanism was observed for disks lubricated with blends of diesel and biodiesel, and their tribological behavior is intermediate between pure diesel and pure biodiesel. Also, the length of the track in test lubricated with blends is smaller than lubricated with diesel. However, better results were found for

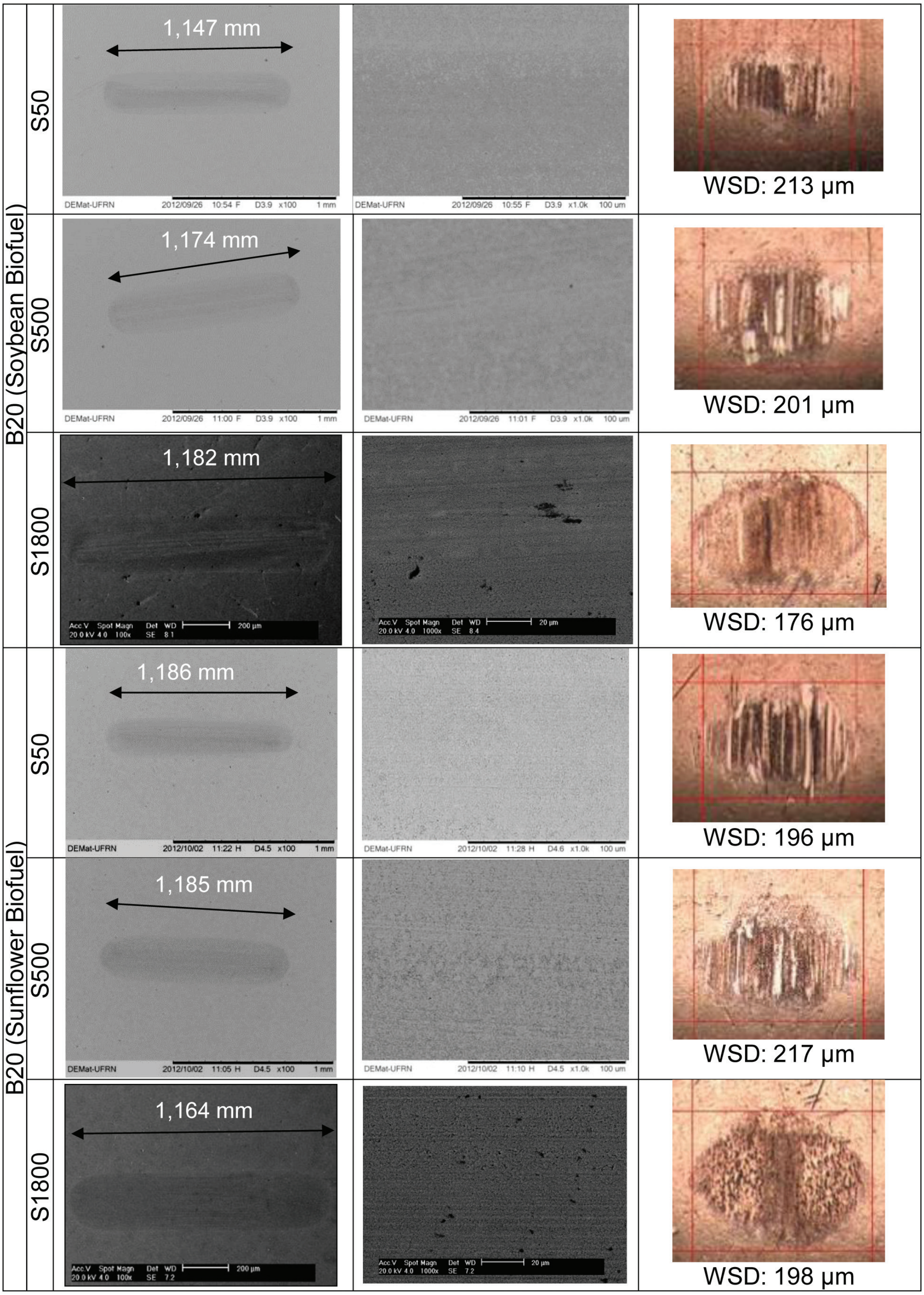


Figure 4. Continued...

tests with pure biodiesel 1.141 and 1.108 mm, for soybean and sunflower biodiesel, respectively (Figure 3).

The wear scar diameter of the ball was measured using software for analysis of ball optical microscopy image. Values of diameter at 0° and 90° on the scar lines (X and Y) were measured. Then, the mean diameter of the wear scar was obtained (Figure 3 on right). Considering that the ball was set on the equipment in perfect alignment and the movement of the disc is parallel to the surface in contact with the ball, there should be a uniform wear on it. Thus, the shape of the wear should be spherical (see Figure 3 for diesel S1800). However, elliptical shape were found on some ball surfaces as for tests of pure biodiesel. This difference of wear shape is not influenced by fuel type, but probably by the contact of tribological pair. The elliptical shape is formed when there is accumulation of material on the side of the worn track. Also, some severe abrasive signals were found in worn scar (see Figure 4 B100 soybean biodiesel), it could be caused by the rolling of debris particles between surfaces in contact. Because of this difference on wear scar of the ball, it is difficult to evaluate the lubricity only by WSD, so it is necessary to analyze the tribological response, such as friction coefficient.

4. Conclusions

The following conclusions can be drawn from this study:

- The properties of biodiesels are directly correlated with their respective base vegetable oils and they are according to ANP limits.
- The sulfur content has influence on diesel lubricity, low sulfur content gets worse lubricity, but this lubricity can be restored with biodiesel.
- Biodiesel showed better friction reduction performances than the different commercial diesels. However, blends of biodiesel and diesel present similar tribological performance and can be used as an excellent fuel.
- The lubricity evaluation should not be based only on WSD because of different shapes of wear scar but the friction coefficient should also be considered.

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