Identification of Organic Deposits Formed in Injection Components Used in Diesel Cycle

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ABSTRACT

The search for sustainable alternatives in the automobile industry has driven the use of renewable fuels, such as ethanol, to replace diesel in some engines. In the future, the interaction of ethanol with the components of the Diesel injection system may result in the formation of unwanted deposits, affecting the performance and durability of these systems. This work aims at an investigation focused on the formation of deposits in critical components of the injection of diesel engines. For this, samples of components subjected to real conditions of use will be extracted. The characterization of these samples will be performed using techniques that include confocal microscopy and scanning electron microscopy with energy dispersive spectroscopy (SEM – EDS). The results will allow us to understand the formation of deposits in the systems with the use of Diesel. In addition, these results will be compared with those obtained in future characterizations of samples tested with the use of ethanol. The analysis of the results will allow the selection of materials and coatings that are more suitable for the observed damage mechanisms, accelerated by wear, corrosion or synergy between these phenomena.

INTRODUCTION

The automotive industry is one of the main sectors of the global economy and holds relevant representative in Brazil, contributing approximately 2.5% to the national GDP [1]. However, this sector is also a major contributor to the emission of air pollutants, mainly due to the combustion of fossil fuels such as diesel and gasoline. Among the primary pollutants released through this combustion process are carbon monoxide (CO), carbon dioxide (CO_2), and nitrogen oxides (NO_x), all of them contributing directly in global warming and the deterioration of air quality in urban centers [2].

Due to the growing environmental concerns and the necessity to reduce GHG (greenhouse gas) emissions, sustainable alternatives have been extensively studied. One if these alternatives is the use of biofuels, such as ethanol, which offers environmental and economic advantages. Ethanol can be produced through the fermentation of plant-based biomass, thereby decreasing the petroleum-derived fuels dependence and supporting the development of the agricultural sector. Additionally, ethanol combustion in internal combustion engines (ICE) generates lower CO_2 emissions compared to fossil fuels, making it a viable solution for reducing the carbon footprint of the automotive industry [3].

However, despite its advantages, the use of ethanol in internal combustion engines also presents several challenges, predominantly due to its physical-chemical properties. The ethanol has high affinity for water, a condition that can lead to the formation of acids, such as acetic acid, which promotes corrosion of metallic engine components [4]. Besides, studies have shown that metals such as aluminum and iron, when exposed to ethanol-gasoline blends, tend to develop oxide deposits, such as Al_2O_3 and Fe_2O_3, which can compromise fuel injection system performance and reduce the service life of engine components [5].

In this context, studying the effects of ethanol on ICE components is highly relevant. However, to evaluate the magnitude of these effects, it is essential, initially, understand the interactions between diesel fuel and engine components. This provides a baseline for comparison and serves as a reference point for further analysis. The formation of organic deposits on fuel injection system components in diesel engines is a critical factor that affects the performance and durability. These deposits tend to accumulate in areas such as injector needle tips, as depicted in Figure 1, impacting the fuel atomization pattern and the combustion efficiency [6].

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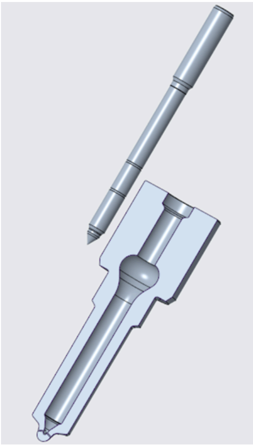

Figure 1. Schematic representation of an injection system (Authors)

According to Silva (2015), three main potential causes of injector failures related to fuel properties are: excessive wear, abrasion, and deposit formation.

The excessive wear, or scuffing, occurs due to inadequate lubrication provided by the fuel, which depends on its additive content and composition, leading to alterations in its lubrication properties. Hong et al. (2021) also investigated this possibility in their study, where the lubricity of ethanol-diesel blends was examined and observed that an increase in ethanol concentration reduced the formation of protective tribofilms, resulting in a higher friction coefficient and accelerated wear. Hansen et al. (2005) reinforced this observation by investigating that engine operating on ethanol exhibited severe wear on the injectors, particularly due to the chemical interaction between the fuel and the materials in the injection system.

On the other hand, the abrasion is caused by solid particles present in the fuel, which lead to wear on the internal components of the injector, compromising its functionality. Finally, the formation of organic deposits results from the thermal and oxidative degradation of the fuel, obstructing and affecting the fuel atomization pattern [6].

Another important factor, mainly when using biodiesel, is the accumulation of carbon on the nozzle injector. However, this information is also relevant for commercial diesel application, since it contains a mandatory percentage of biodiesel. The carbon deposition can be associated to the incomplete combustion of the blend (diesel/biodiesel). Over time, these deposits can lead to operational issues, such as a decrease in engine performance and efficiency [6;9].

Thus, the objective of this study is to investigate the formation of deposits and the degradation of components in the injection system of diesel engines. To achieve this, tribological tests will be conducted under real conditions, and characterization will be performed using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), to understand the effects of the interaction between diesel and the injector nozzle needle.

EXPERIMENTAL PROCEDURES

In order to analyze the deposits formed by the action of diesel on the injection needle, three needles exposed to a real injection environment and a new needle were used for comparison purposes. All needles are made of high-speed steel (main alloy elements are tungsten, molybdenum and vanadium), while the body is made of a mechanical construction steel alloy with chromium and nickel, and both undergo heat treatments.

Using scanning electron microscopy (SEM), images of the surfaces of the samples were taken in order to observe the morphology of the new and used needles. Energy-dispersive X-ray spectroscopy (EDS) was also performed to analyze the composition of the samples before and after exposure to fuel, identifying the deposits formed from this interaction.

EXPERIMENTAL PROCESS - In order to analyze the formation of organic deposits on the needles, the tribological pair was subjected to a test in a real engine with the specifications listed in Table 1.

Table 1. Specifications of tests on the tribological pair in a real engine

Technical specification	
Pressure of operations	2000 bar
Temperature of operations	100 °C
Test duration	3000 h
Fuel	S10 commercial oil
Needle material	High speed steel with tungsten, molybdenum and vanadium
Nozzle material (body)	Steel alloy with chromium and nickel composition

SAMPLE CHARACTERIZATION - After undergoing the tests, the four samples were taken for analysis by scanning electron microscopy. The images were analyzed using a Zeiss microscope, model Evo MA15, located at the Multiuser Center for Material Characterization at UTFPR – Curitiba – PR, Brazil. The microscope has a 20 mm² EDS X - Max detector from Oxford Instruments. This detector was used for the EDS analyses of the new and used needles.

To measure the hardness, the samples were cut in order to access the cross section of each one. The samples were prepared metallographically up to the polishing stage with alumina in suspension with a particle size of 1 micrometer. The Vickers hardness value for a new sample was obtained through 5 measurements using microindentation, with a load of 1.96 N (HV0.2). From the measurements, the value of 753 ± 24 HV0.2 was obtained. This value is within the hardness range provided by the manufacturer, being 700 to 900 HV, typical for tempered and resold tool steels.

RESULTS

Figure 2 and Figure 3 show the images obtained by SEM for the four samples analyzed. In the new sample, it is possible to observe a region with a homogeneous appearance across the entire tip with the presence of scratches caused by the manufacturing process.

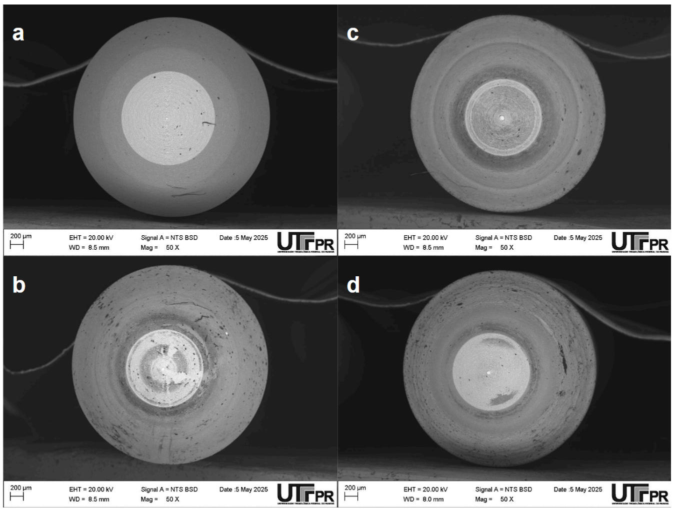

Figure 2. 50x SEM images of the needle top of: (a) fresh sample (b) sample 1 (c) sample 2 and (d) sample 3. (The authors.).

In the used samples, the visualization of these scratches, as well as the homogeneity of the part, is not so evident, where it is possible to observe parts more affected by the wear mechanisms. These regions appear as the darker tones in the images, in addition to showing some deeper grooves in the outermost part and black dots in some regions that may represent the parts affected by oxidation.

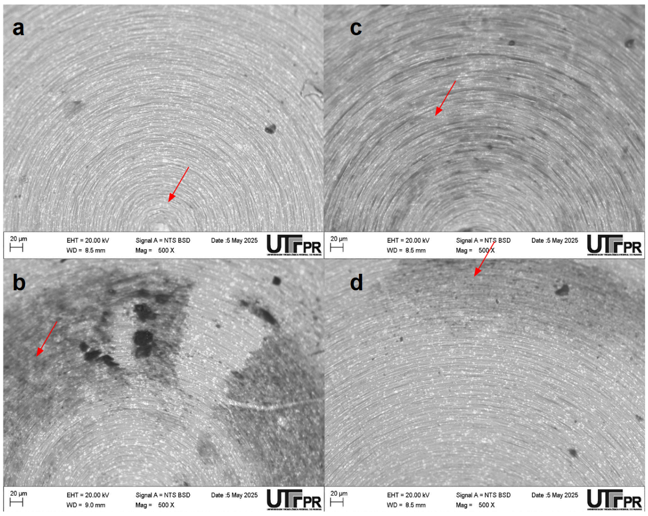

Figure 3. 500x SEM images of the needle top of: (a) fresh sample (b) sample 1 (c) sample 2 and (d) sample 3. (The authors.).

The three used samples showed signs of oxidation, which were more evident in sample 1. The scratches resulting from the needle manufacturing process remained in the three used samples. This may be an indication of the low loss of material from the nozzles during use.

Sample 1 showed more signs of oxidation and more wear. This may be related to the low capacity of the fuel to form a film that would reduce contact in this tribological pair, as well as contributing more to the corrosion process of this sample.

Figure 4 shows the points of the new sample that were used for EDS analysis.

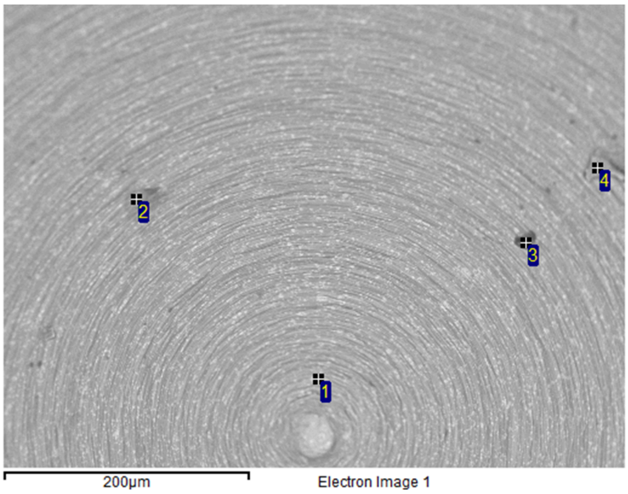

Figure 4. Points used for EDS analysis on the new sample. (The authors.)

Table 2 shows the results obtained by the analysis at the indicated points.

Table 2. Results of the chemical composition in percentage of the weight of the elements present in the new needle.

Elements	Points			
	1	2	3	4
C	12,03	31,96	4,66	5,33
O	1,41	6,77	-	0,6
Al	0,22	-	0,32	0,28
V	2,61	0,77	1,21	0,86
Cr	3,53	2,38	3,51	5,29
Fe	70,28	39,6	84	87,32
Mo	4,11	4,59	-	-
W	5,81	-	0,98	-
Na	-	-	0,3	-
S	-	-	1,25	-
Cl	-	-	0,59	-
K	-	-	0,73	-
Ca	-	-	2,47	-
N	-	6,76	-	-
Si	-	-	-	0,32

From these composition results obtained by EDS confirm the addition of alloying elements that are complex carbide formers, especially chromium, vanadium, molybdenum and tungsten, which are generally added to increase hardness and improve wear resistance. Figure 5 shows the points analyzed in the three used samples.

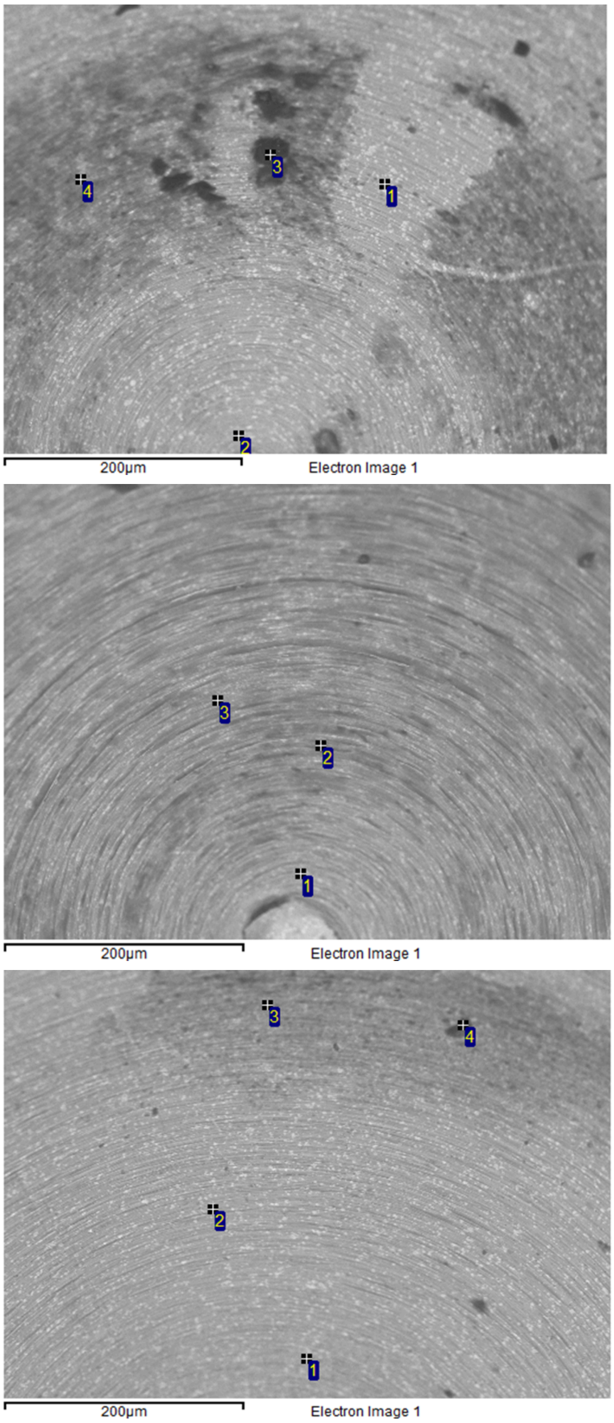

Figure 5. Points used for EDS analysis in samples 1, 2 and 3 respectively. (The authors.)

Tables 3 and 4 show the composition of the used samples considering the regions marked in Figure 5. In the case of sample 1, the darkest point, point 3, was not considered in the analysis because its composition does not present any percentage of some elements present in both the needle and the body, possibly due to the formation of an oxide or some contaminant.

Table 3. Results of the chemical composition in percentage of the weight of the elements present in the used needles of samples 1 and 2.

Element	Sample 1				Sample 2		
	Point				Point		
	1	2	3	4	1	2	3
C	17	8,36	-	33,47	19,3	46,1	32,34
O	3,34	3,55	43,41	9,95	8,95	13,95	13,59
Na	0,5	-	12,64	0,89	1,92	1,67	1,74
Ca	0,23	-	3,36	0,62	0,82	0,97	1,05
V	1,13	1,43	-	1,48	1,25	0,5	0,51
Cr	3,31	3,99	-	2,54	3	1,63	2,28
Mn	0,35	0,35	-	0,26	-	-	-
Fe	70	72,43	5,16	45,46	60,2	32,91	44,71
Mo	2,16	3,77	-	-	-	-	-
W	1,98	6,12	-	3,92	2,83	1,23	2,07
N	-	-	21,4	-	-	-	-
S	-	-	7,2	1,04	1,37	1,04	1,33
Cl	-	-	3,55	-	-	-	-
K	-	-	3,28	-	-	-	-
Al	-	-	-	0,16	-	-	-
Mg	-	-	-	-	0,36	-	0,37
Si	-	-	-	-	-	-	-
P	-	-	-	0,22	-	-	-

For the used samples, it is also possible to find traces of the needle's original materials, such as tungsten, vanadium and chromium, although in some cases this percentage is reduced. However, it is possible to observe the presence of oxygen at all points analyzed, even though the technique is not accurate in quantifying light elements. The presence of this element may be related to the formation of oxides in the darkened parts of the needles, resulting from the interaction of the tribological pair in the middle of commercial S10 diesel.

Table 4. Results of the chemical composition in percentage of the weight of the elements present in the used needles of sample 3.

Elements	Sample 3			
	Point			
	1	2	3	4
C	22,37	13,41	31,9	46,66
O	9,04	3,45	9,34	11,39
Na	0,75	-	1,27	2,54
Ca	0,77	-	0,73	0,88
V	3,42	0,92	4,57	1,01
Cr	2,67	3,61	2,56	1,68
Mn	0,3	0,6	0,26	-
Fe	38,25	71,22	37,17	24,4
Mo	8,95	3,17	5,34	5,44
W	13,46	3,22	6,85	5,86
N	-	-	-	-
S	-	-	-	-
Cl	-	-	-	-
K	-	-	-	-
Al	-	-	-	-
Mg	-	-	-	0,16
Si	-	0,4	-	-
P	-	-	-	-

Another point to be taken into consideration is the increase in deposits on the needles used. Previously cited studies indicate that some deposits involve carbon, and these are capable of demonstrating incomplete combustion of the fuel [6]. In this case, the technique is also not reliable for quantifying carbon, and other analyses are necessary to confirm its presence, but it is possible to observe the presence of the element in several points. The possibility of this type of deposition is viable for the analysis in question, since the fuel used has a percentage of approximately 14% biodiesel, which contains a higher amount of carbon. In this case, the accumulation on the needle was not evident to the naked eye without the use of SEM, but it can also be detrimental to engine operation in prolonged situations.

CONCLUSION

The use of commercial Diesel S10, at the parameters presented in the study, contributed to the oxidation process of the injector nozzles. Part of this contribution is due to the presence of oxygen from the biodiesel. This may also have contributed to the increase in the percentage of carbon in the used samples, which indicates the possibility of incomplete combustion of the fuel. The three samples showed signs of wear, which indicates that the film formed by the fuel was not sufficient to prevent contact between the tribological pair. Future studies will provide information on the real influence of biofuel on the oxidation of the needles, as well as on their abrasive wear.

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