

Orbital: The Electronic Journal of Chemistry journal homepage: www.orbital.ufms.br

e-ISSN 1984-6428



FULL PAPER

| Vol 11 | | No. 5 | | July-September 2019 |

Study of Corrosion in Diesel Engine Piston by Soybean Biodiesel and its Mixtures

Fernanda Beatriz Aires de Freitas^a, Daniel Freitas Freire Martins^a, and Antonio Alex de Lima Silva^b

^aUFERSA – Federal University of the Semi-Arid, Campus Caraubas, Brazil. ^aUERN – University of the State of Rio Grande do Norte, Campus Mossoro, Brazil.

Article history: Received: 16 April 2019; revised: 29 July 2019; accepted: 30 July 2019. Available online: 30 September 2019. DOI: http://dx.doi.org/10.17807/orbital.v11i5.1404

Abstract:

Of the renewable energy sources, which are less polluting and with the same efficiency of petroleum products, we highlight biodiesel, a renewable and promising source of clean energy, which is now being added in small quantities to commercial diesel used in diesel cycle engine. However, it is necessary to evaluate several factors, so that the amount of biodiesel in the diesel is increased, among them the physicochemical properties of the biodiesel and its mixtures with the commercial diesel, so that they are according to specification of the National Petroleum Agency (ANP) besides the corrosion that it can cause to the constituents of the motor, when in contact. Thus, this work had as main objective to verify the existence of a corrosive process in diesel engine piston when in contact with commercial diesel, biodiesel, and its mixtures, in different proportions and temperatures. For this, initially accomplished the biodiesel synthesis and the characterizations physiochemical of the same. Posteriorly, got it fortyfour samples, which were immersed in the pure biodiesel (B100) and its mixtures with commercial diesel in the proportions of 7, 10, 20, 30, 40, 50, 60, 70, 80, and 90% in different temperatures, after the immersion tests, it was calculated the corrosion rate present and analysis of the samples with the help of the scanning electron microscopy (SEMA), that were analyzed through of the ImageJ program. After analysis, it can be concluded that the biodiesel synthesized had the properties within the limits established by the ANP, that the corrosion in the material that compose the engine piston in the studied period was low for all the mixtures used. Therefore, it is suggested that the biodiesel obtained in this work and itis respective mixtures are viable as alternative renewable sources to be applied as fuel in engines.

Keywords: biodiesel; corrosion; diesel cycle engine; piston

1. Introduction

Fossil fuels are of great importance in the Brazilian energy matrix since they are used in various segments of society. This fact is proven by the production of oil products in 2014, which reached 140.855 million m3 of these products, according to the ANP (National Agency of Petroleum, Natural Gas and Biofuels). However, some factors, such as energy, environmental, among others, have led to the search for renewable sources of fuels, fewer pollutants and with the efficiency of petroleum products [1].

The use of vegetable oil in the diesel engine is nothing new. The first experiences with compression-ignition engines were conducted with peanut oil. In 1900, the inventor of the diesel engine, Rudolf Diesel, drove an engine prototype at the Paris Universal Exhibition with the use of peanut oil, but the development of petroleum products and the wide supply of fossil fuels made this alternative unattractive to the economic point of view. In 1937, the Belgian scientist G. Chavenne discovered and patented transesterification process, which reduced the viscosity of vegetable oil and improved its combustion process inside the engine [2]. Thus, the name "biodiesel" was given to transesterified vegetable oil to describe its use as fuel in diesel cycle engines [3].

The use of biodiesel allows the control of pollutant emissions, increase efficiency and

replace fossil fuel, which is promising for research into the improvement of diesel engines. Therefore, the study of the partial substitution of diesel fuel by renewable fuels is of great relevance, and biodiesel is a promising alternative for such substitution [4].

From the economic point of view, biodiesel presents great viability, since it can be an important product for export and for the national energy independence, besides generating Jobs and income in the neediest regions, thus developing the primary sector.

Taking into consideration environmental issues, the use of biodiesel in internal combustion engines results in reduced emissions of unburnt hydrocarbons, carbon monoxide, sulfates, aromatic compounds, and particulate materials. The effect that increases according to the amount of biodiesel in the mixture with the diesel, being that in the pure biodiesel the reduction is even greater [6]. In addition, the addition of biodiesel in correct proportions in the fuel mixture brings benefits in terms of engine performance and specific fuel consumption [4].

However, even the use of these fuels is better from the environmental point of view, when in contact with metallic materials, such as the engine components, can cause corrosion of the same, causing enormous economic losses.

The metal corrosion is the transformation of a metal or alloy by a chemical or electrochemical interaction through a given exposure, resulting in formation of corrosion products and the energy release [7]. Thus, it is necessary to study the corrosive processes, especially when it is related to the use of fuels, which generates significant economic losses.

In diesel-cycle engines, for example, there is corrosion of the engine piston, which is very important for its operation, since it has the function of transmitting force by means of an alternating movement due to the internal pressure of the expanding gases to the crankshaft, through the pin and connecting rod, giving movement to the engine [8].

In this context, there is a need for studies on corrosive processes in diesel engines, so that biodiesel can be used as a source of clean, renewable and very promising energy, without significant losses for them.

Thus, this work aims to verify the existence of corrosive process in diesel engine piston when in contact with commercial diesel, biodiesel and its mixtures, in different proportions and temperatures.

2. Material and Methods

2.1 Biodiesel synthesis

The biodiesel synthesis was done using commercially characterized soybean oil. With this, the transesterification reaction was carried out by the metallic route with potassium hydroxide (KOH) as the catalyst [9].

The biodiesel synthesis conditions were those described by Marques [9], with oil / methyl alcohol molar ratio of 1: 6, reaction time of three hours and 2% of catalyst (KOH).

2.2 Preparation of the mixtures biodiesel / diesel

The biodiesel mixtures were prepared in different proportions of commercial diesel added to the biodiesel, where it was initially the pure biodiesel (B100) and 7% biodiesel with 93% of diesel, denominated by the symbol B7; in this representation the number indicates the percentage of biodiesel contained in the mixture. The same was done for the other necessary portions (B10, B20, B30, B40, B50, B60, B70, B80 and B90).

2.3 Physico-chemical analyzes of oil, biodiesel, commercial diesel and its mixtures

Soybean oil, biodiesel, commercial diesel and mixtures were analyzed according to the American Society of Testing and Materials (ASTM) [10 and 11] standards and methods described by the American Oil Chemists Society (AOCS) [12] for the following parameters: free fatty acids, water and sediments, acidity index, saponification index, specific mass, flash point, combustion point, sodium and potassium, moisture content and viscosity.

2.4 Collection of samples

For the cutting of the specimens, a lathe and

saw were used, in which the specimens necessary for the analysis were obtained, with dimensions of approximately 20 mm of base, 20 mm of height and 6 mm of thickness.

2.5 Immersion test

The immersion test was used to evaluate the possible damages generated by the corrosion of the material in contact with the biodiesel and its mixtures, during the ten months of the test.

After the characterization of the biodiesel and its mixtures, the test was started at the times of 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 days. For this, the fuels were placed in 50 mL beaker and in plastic pots, for controlled temperature and environment tests, respectively. Finally, the samples taken from the piston of the diesel engine were inserted in their due fuels. The procedure was performed in duplicate. At the end of each month the fuel was changed, washed, weighed and measured of the specimens in order to calculate the corrosion rate.

2.6 Corrosion rate

In determining the corrosion rate the mass loss is an important factor, since it is influenced by the exposed area and time of exposure, which when combined express the corrosion rate. Thus, with the aid of Equation 1, it is possible to determine the corrosion rate present in the test pieces in mpy (millesimal of an inch per year) [7].

$$mpy = \frac{\text{mass lost} \times 534}{\text{area} \times \text{time} \times \text{density of the material}}$$
Equation 1

Where the mass lost will be expressed in milligrams, the surface area exposed in square inches and the time in hours.

2.7 Density of the material

In order to calculate the corrosion rate, it is necessary to use the density of the material that is being exposed to corrosion. Volumetric density determination was performed using the parameters of ASTM D 792-08 [13], where three samples, previously washed, measured and weighed on a 210g digital scale were used. The calculation was done using Equation 2.

$$\rho = \frac{\mathbf{a} \times \eta}{(\mathbf{a} + \mathbf{w} - \mathbf{b})}$$
 Equation 2

where: ρ = Volumetric density (g/cm³); a = Weight of the dry sample (g); η = Density of the water at the test temperature at 28°C (0,992g/cm³); w = Weight of sinker partially immersed in water (g); b = Weight of the sample immersed with the sinker in water (g).

2.8 Scanning Electron Microscopy Analysis (SEMA)

The analyzes were performed at the Scanning Electron Microscopy Laboratory (SEML), Department of Plant Sciences, UFERSA. To achieve these, aluminum alloy samples, taken from the diesel engine piston, were cut into pieces approximately 0.2 cm wide. The samples were mounted on carbon stubs and were then observed in a scanning electron microscope, beam intensity of 20 kv, BSE and SE detectors, at the magnifications of 100x, 500x and 3kx. This is a technique that used by other authors for this purpose [14, 15, 16, 17 and 18].

The quantification of the number of pores present in the SEM images was performed through the ImageJ program, which creates an image that contrasts the lower relief areas, the higher relief areas, and then counts the pixels that are in lower relief, and converts to the scale that the user reports.

The pores determined using this technique can be the result of the corrosive process, evidenced by the formation of pites, that is, excavations with a depth greater than the diameter of the cavity.

3. Results and Discussion

3.1 Physico-chemical properties of soybean oil

The synthesis of biodiesel occurs after a transesterification reaction, which can be influenced by the properties of the oil, and may or may not generate a poor quality product [19]. In this way, some physicochemical properties of the used oil were determined, presented in the Table 1.

According to the results shown in Table 1, it was possible to verify the absence of water and

sediments in the oil under study, which was expected, since it is an edible oil, which goes through purification processes before being made available to the consumers.

Table 1. Physicochemical parameters determined for soybean oil.

| Analyzes | Soybean | Unit |
|----------------------|---------|------------|
| | Oil | |
| Free fatty acids | 0.53 | % |
| Water and sediments | 0 | % |
| Acidity level | 0.61 | mgKOH/g |
| Saponification index | 97.95 | mgKOH/g |
| Especific mass | 914.50 | kg/m³ |
| Flash point | 299 | °C |
| Combustion point | > 310 | °C |
| Sodium and potassium | 0 | mg/kg |
| Moisture content | 0.49 | % of water |
| Viscosity | 36.00 | mm²/s |

In relation to free fatty acids a satisfactory value was obtained, since, in order to have maximum yield in the reaction, the value must be less than 0.5% [5]. This parameter is of great importance, since the amount of free fatty acids influences directly the reaction of transesterification, being able to affect in the yield of the reaction and in the greater formation of byproducts.

The acid value was lower than 1 mg KOH/g, indicating, according to Farias [20], that oil neutralization is not necessary because, in this way, the reaction will proceed with greater efficiency.

Regarding the saponification index, the result obtained is in agreement with the one found by Marques [9] which was 95.83 mgKOH/g. It is known that high values of this parameter imply the occurrence of undesirable reactions in the transesterification, which may hinder the biodiesel washing process, thus affecting the final reaction yield [5].

The results of the specific mass are in agreement with the one found by Marques [9] that obtained value of 913.7 kg / m³. This parameter is directly related to the point of glow and combustion, where the higher the specific mass, the greater the energy required to produce glow and to combust.

High flash point and combustion are damaging to the engines, since the engine will have to

operate at higher temperatures than the conventional one, which can cause problems, like the degradation of its components. This is one of the reasons not to use oil as a fuel source. In a study carried out by Santos [5], values of 317.0 °C, 314.6 °C, 264.0 °C and 297.0 °C were obtained for the flash point of cotton, sunflower, oil palm and bovine tallow, respectively; and 319.3 °C, 320.0 °C, 269.3 °C and 303.0 °C for the combustion point of these same oils. As for the soybean oil in this work, the value of 299 °C and greater than 310 °C for flash point and combustion were found, respectively. Results consistent with the literature [9].

In relation to moisture, Silva [21] states that the ideal oil for the transesterification reaction should have a value below or equal to 0.5%. This, when in excess, promotes the deactivation of the catalyst and the formation of free fatty acids which, in turn, favors the saponification reaction, transforming the fatty acids into soap and forming water molecules [19]. Thus, as a function of the value obtained, to avoid the occurrence of undesirable reactions, before the synthesis, the oil to be used was dried in the oven to remove any percentage of moisture present.

The viscosity of the soybean oil presented a very high value, 36 mm²/s, due to the high molecular weight they present, which is the main reason why the oils are not used directly as fuel. This result is consistent with the literature, since values of 38.4 [19] and 33.7 mm²/s [20] are obtained.

Regarding the value of sodium and potassium, nothing was quantified, which was expected, since the soybean oil used is a commercial oil, which undergoes several procedures before being commercialized.

3.2 Physical and chemical properties of methyl biodiesel and its biodiesel / diesel blends

The quality of the produced biodiesel is of extreme importance for the good operation and longer life of the engine. Thus, it is necessary that it is within the specifications accepted for its use. In this sense, the physical and chemical analyzes of the biofuels derived from soybean oil in this work were compared with the specifications established by the ANP, as can be seen in Table 2.

Table 2. Physicochemical properties of soybean biodiesel.

| Analysis | Biodiesel | ANP Specifications | Unity |
|----------------------|-----------|--------------------|-------------------|
| Water and sediments | 0 | NC | % |
| Acidity level | 0.2589 | < 0.5 mgKOH/g | mgKOH/g |
| Saponification index | 92.12 | NC | mgKOH/g |
| Especific mass | 876.50 | 850 a 900 kg/m³ | kg/m ³ |
| Flash point | 180 | >100 °C min | °C |
| Combustion point | 194 | NC | °C |
| Sodium and potassium | 0 e 2.20 | 5 mg/kg | mg/kg |
| Moisture content | 0.0930 | NC | % of water |
| Viscosity | 3.6343 | 3.0 a 6.0 mm²/s | mm²/s |

¹NC – There is no specification in the resolution.

Analyzing Table 2, it was observed that biodiesel is within the norms established by the ANP. The water content and sediments present in the biodiesel were analyzed in triplicate, but nothing was recorded, thus showing that the washing and drying process used in the biodiesel synthesis was efficient.

In relation to the acidity index, acceptable values were obtained and according to the norms that limit it. The value obtained of 0.2589 mgKOH/g, is lower than the maximum value stipulated by ANP. This result is still in agreement with the literature, where values of 0.2379 [22], 0.28 [23] and 0.26 mgKOH/g [20] are found. Regarding the saponification index, it can be observed that the value obtained from this parameter for biodiesel has similar behavior to the oil used as raw material, and thus, a coherent value for the same.

As regards the specific mass, Cunha [22] carried out studies on biodiesel from soybean oil, obtaining a value of 883.5 kg/m³ being close to that found in this work, which was 876.5 kg/m³, and of according to the ANP standard that limits this value between 850 and 900 kg/m³. Comparing the value obtained in the biodiesel with that of the oil, it is observed that there was a decrease, which indicates the conversion of the carboxylic acids into methyl esters was efficient.

The flash point presented a value of 180°C, which is above the minimum allowed by the ANP of 100°C, meaning, greater safety of storage, handling and use of this fuel. According to Galvao [24], when you have a high flash point you have more security in the parameters mentioned above. This result is still in agreement with Farias [20] and Cunha [22], who in their works obtained values of 168 °C and 190 °C respectively.

With respect to the point of combustion, it had a value of 194 °C. For this parameter, the higher

the molecular weight, the greater the energy required to produce glow or combustion. High values of the combustion point imply that it is more difficult for the engines to burn the fuel, causing greater wear on the parts, since the engine will operate at higher temperatures [5].

Sodium and potassium presented values of 0 and 2.2 mg/kg respectively. Probably the value of potassium found was due to some problem in the process of washing the biodiesel after the synthesis process, leaving some small amount of potassium hydroxide that was used as a catalyst. However, the sum of these two parameters is still lower than allowed, since according to the ANP this figure can reach a maximum of 5 mg/kg.

Finally, it has viscosity, which is a property of great importance, since it has a direct relation with the mechanism of atomization (spraying) of the molecules in the initial stage of combustion and is a determinant point in the behavior of the engine, in which values higher than that established by the standard in force may impair the operation of the injection system, interfering with combustion and maximum engine power. In addition to being able to cause clogging and formation of deposits damaging the engine parts [20].

In this work, the viscosity presented a value of 3.6343 mm²/s, being within the allowed by the norm that is between 3.0 to 6.0 mm²/s. Cunha [22], also analyzed the viscosity of soybean oil biodiesel, obtaining a value of 4.6 mm²/s, also within the limit established by the ANP and similar to that obtained in the present work.

It is also necessary to point out that the value obtained for biodiesel was much lower than that of soybean oil, indicating that there was conversion of the oil into biodiesel, also indicated by the reduction in the specific mass value previously discussed. This result is very positive, since high values can generate problems such as

wear of lubricated parts of the injection system, leakage of the fuel pump and incorrect atomization in the chamber [25].

The characterization of biodiesel blends with commercial diesel is necessary to know how they all behave. CNPE Resolution 03/2015 states that for the commercialization of these mixtures it is necessary that they comply with the specifications established by the ANP. Also included in this resolution is the experimental use, specific or in events of diesel oil with biodiesel in proportions higher than 20% (B20) and equal to or less than 30% (B30), in captive fleets or road consumers served by a filling station, having that is within the allowed values.

In this work, commercial diesel and biodiesel were used in the proportions of 7, 10, 20, 30, 40, 50, 60, 70, 80 and 90%, called B7, B10, B20, B30,

B40, B50, B60, B70, B80 and B90, respectively. As previously mentioned, CNPE Resolution 03/2015 deals only with mixtures B8 to B30, so there is no specification for the others.

Therefore, even if there is no standard for the others, the results obtained in the characterizations of all the mixtures and that are arranged in Table 3, were compared and are in accordance with ANP specifications and CNPE Resolution 03/2015, the which do not differ significantly from each other at the level of values established for each parameter in common.

However, a high acidity index is observed in B7 (commercial diesel), a reduction of this index with the increase of the percentage of biodiesel added to the diesel, which shows that this acidity is not due to the synthesized biodiesel, but to commercial diesel used for analysis.

Table 3. Physical-chemical properties of commercial biodiesel/diesel mixtures.

| Mixtures | WS | Al | SI | М | FP | СР | Na | K | V |
|----------|----|--------|---------|-------|-----|-----|----|-----|--------|
| B7 | 0 | 0.8073 | 4.5499 | 837.4 | 62 | 75 | 0 | 0 | 3.9240 |
| B10 | 0 | 0.5407 | 11.0689 | 839.6 | 68 | 79 | 0 | 0.4 | 3.8615 |
| B20 | 0 | 0.5320 | 26.1701 | 842.1 | 71 | 82 | 0 | 1.0 | 3.8598 |
| B30 | 0 | 0.5397 | 32.1537 | 846.6 | 76 | 84 | 0 | 1.2 | 3.8032 |
| B40 | 0 | 0.5376 | 37.2971 | 850.5 | 76 | 92 | 0 | 1.3 | 3.7759 |
| B50 | 0 | 0.5151 | 49.8208 | 855.3 | 81 | 98 | 0 | 1.4 | 3.7728 |
| B60 | 0 | 0.5409 | 54.8519 | 859.2 | 88 | 102 | 0 | 1.6 | 3.6899 |
| B70 | 0 | 0.5332 | 68.0301 | 862.9 | 95 | 115 | 0 | 1.8 | 3.6873 |
| B80 | 0 | 0.4419 | 74.8876 | 867.5 | 115 | 140 | 0 | 2.0 | 3.6872 |
| B90 | 0 | 0.2639 | 83.7258 | 871.7 | 131 | 159 | 0 | 2.1 | 3.6864 |

WS (water and sediment), AI (acid index), SI (saponification index), M (specific mass), FP (flash point), CP (combustion point), Na (sodium), K (potassium) and V (viscosity).

3.3 Immersion test

In order to evaluate the possible damages caused by corrosion of the material (aluminum alloy) when immersed in biodiesel B100 and its mixtures with the commercial diesel B7 over time, the immersion test was carried out with the specimens to be analyzed at ambient temperature and under heating at 100 °C.

After the treatment of the samples and obtaining the mass and area, the test was started in the period of 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 days. For this, 100 mL beaker (tests with heating) and plastic pots (tests at ambient temperature), containers used to put 50 mL of the fuels were used. Then the specimens were immersed in biodiesel and its mixtures with commercial diesel and waited for the first set time

test. At the end of each month of the study, the measurement of the area of the test specimen and its weighing were done, thus obtaining the values of mass loss and the area for controlled and ambient temperature.

3.4 Corrosion rate

After the immersion time and with the obtained values of mass loss and surface area, the corrosion rate was calculated by Equation 1 in mpy (millesimal of an inch per year). In Figures 1 and 2, it is possible to visualize the results found in the test of corrosion by immersion in the period of ten months, under the two temperature conditions studied (ambient temperature and controlled temperature).

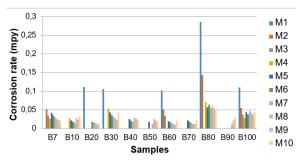


Figure 1. Corrosion rate (mpy) - Ambient temperature (M - Month).

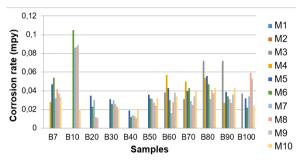


Figure 2. Corrosion rate (mpy) - Temperature controlled (M - Month).

According to the results obtained, it was possible to observe that there was no standard behavior, being independent of the percentage of the mixture to which the metal alloy was subjected, the exposure time and the temperature at which the system was submitted. The values obtained were very small, not allowing the confirmation that there was actually corrosion during the 10 months of exposure.

The variation presented is most probably due to experimental errors in the weighing procedure, in which, in most cases, the variation in the mass of the test specimen occurred in the third decimal place. Therefore, stabilization problems, variation in electric current, centralization of the test body in the balance plate, are actions that can cause small changes in the results obtained in the weighing process.

However, one should not rule out the existence, even if small, of some corrosive process in the material being studied. According to Gentil [7], when the attack is uniform and in a chemical environment, the metals can be divided into three groups, according to the corrosion rate and application, where the corrosion rate of less than 5 mpy are of materials with good resistance corrosion and are suitable for use in critical parts

of equipment; metals with values between 5 and 50 mpy can be used in cases where a high corrosion rate is tolerated as in tanks, pipes, valve bodies. When it is greater than 50 mpy the metals are few resistant to corrosion, is not recommended its use. Comparing the values found in the study months, it can be seen that in all months, temperatures and mixtures the corrosion rate was less than 5 mpy, so the material has good corrosion resistance.

In this way, it is possible to notice that the corrosion present in the specimens under analysis, if it occurred, was of low intensity, since its corrosion rate was inferior to 5mpy. Result consistent with that found in the literature, in a study by Rolim *et al.* [8], which uses for the synthesis of biodiesel, ethylene oil. In this, it is possible to see that the corrosion rate is very small, the material of low corrosivity and biodiesel being suitable for use in engines of this type.

Kaul *et al.* [26] also performed studies in this area, studying corrosion in the piston and piston liner caused by contact with biodiesel synthesized with different types of oil. In this work it was verified that only one of them (biodiesel of Salvadora oil) caused significant corrosion in pistons, due to the large amount of sulfur present in the piston.

Singh and Sharma [27] analyzed the corrosion effects of engine parts that come into contact with biodiesel and their blend with diesel, and obtained copper, aluminum, copper (bronze) alloys and elastomers, significant levels of corrosivity in biodiesel, corrosion was low in mixtures. Stainless steel samples showed significant corrosion resistance in biodiesel compared to copper, aluminum and copper alloys, but the level of corrosion was even higher than in petroleum diesel.

Ashraful *et al.* [28], carried out a study with the use of palm biodiesel and common diesel, evaluating the operation of this in the engine through emission behavior, part wear as well as lubrication characteristics. In their results the authors showed that blended fuel offers benefits in terms of reduced wear and friction. However, oxidation of fuel at higher temperatures affect some properties of fuels. Even so, it is still a viable alternative and promising future.

The corroded value of this work still shows us

that the synthesis used in the production of biodiesel is adequate, considering that the biodiesel obtained is in accordance with the standards established by the ANP. It was also observed that at controlled temperature the corrosion rate, although close, was somewhat lower than the ambient temperature. This may be due probably to the experimental errors discussed above, but also to the fact that the fuels exposed to ambient temperature have a small moisture content, which was eliminated with increasing temperature, offering an even less corrosive effect than ambient temperature.

3.5 Analysis by Scanning Electron Microscopy

After the tests of immersion and determination of the corrosion rate for each mixture and temperature, the initial and final test bodies were analyzed by Scanning Electron Microscopy (SEM) and then quantified the number of pores in each image. In the Figure 3, the images obtained in the SEM (with 100x and 500x magnification; and with arrows indicating one of the pores) only for the test specimen in the initial condition are shown, since there were not great variations in the images.

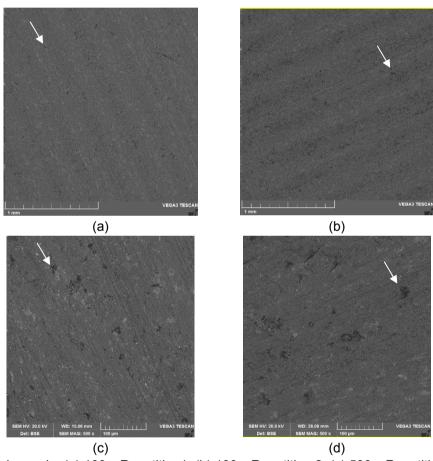


Figure 3. Initial sample. (a) 100x: Repetition1; (b) 100x: Repetition 2; (c) 500x: Repetition 1; (d) 500x: Repetition 2.

However, as this form of corrosion is localized, the results obtained will probably not present a definite pattern, a fact that can be verified by analyzing the results presented in Table 4. Thus, the number of pores found in this work can be from some corrosive attack, even if small, or simply, deformations exist on the surface of the specimens. Moreover, it is interesting to note that

this type of corrosion can be found in aluminum materials [29 and 30], metals [31], among others.

4. Conclusions

From the results obtained it can be concluded that with the increasing use of renewable sources

of fuel there is a search for methods that make it increasingly efficient. Since biodiesel is a renewable source, since it is an alternative fuel, it is necessary to carry out analyzes to obtain the ideal conditions for its use, with the quality standards within the current norms, thus acquiring safety and qualification so that it can go to the market and guarantee the functionality of the engine.

In this context, it was perceived that the synthesized biodiesel and its blends with the commercial diesel were with the properties according to the limits established by the ANP. In the results of the physical-chemical characterization of the soybean oil, it was evidenced that it was able to be used as raw material in the biodiesel production through the transesterification reaction.

It was still possible to observe in the calculation of the corrosion rate that the corrosion in the material of the engine piston in the studied period was low for all the mixtures used. In this context, it was not possible to verify a standard behavior, being independent of the percentage of the mixture to which the metal alloy was subjected, the exposure time and the temperature at which the system was submitted. However, a small difference can be observed between the corrosion rate at the controlled temperature and the ambient temperature, where the controlled temperature was slightly lower than the latter.

The corrosion value found in this work also shows that the synthesis used in the production of biodiesel was adequate, since the biodiesel obtained was in accordance with the standards established by the ANP. By analyzing the corrosion of the samples through images generated by scanning electron microscopy (SEM), small values of pore number were also obtained and without a well defined pattern for all the blends and temperatures studied.

Therefore, it is suggested, based on this study, that the biodiesel obtained in this work and their respective mixtures are viable as alternative renewable sources to be applied as fuel in diesel cycle engines.

Table 4. Pores ambient temperature and controlled.

| | Average % of pores | | | | |
|---------|---------------------|------------------------|--|--|--|
| | Ambient temperature | Temperature controlled | | | |
| Initial | 0.7835 | 0.7835 | | | |
| B7 | 1.2700 | 0.2210 | | | |
| B10 | 1.1125 | 0.3760 | | | |
| B20 | 0.7410 | 2.3930 | | | |
| B30 | 1.4190 | 1.3345 | | | |
| B40 | 0.6220 | 0.6850 | | | |
| B50 | 0.2975 | 1.2665 | | | |
| B60 | 0.8430 | 0.4630 | | | |
| B70 | 0.5185 | 0.5240 | | | |
| B80 | 1.1910 | 0.9395 | | | |
| B90 | 0.3040 | 0.4730 | | | |
| B100 | 0.5150 | 0.6880 | | | |

References and Notes

- [1] Valente, O.S. Desempenhos e emissões de um motor-gerador de energia elétrica usando biodiesel. Dissertação (Mestre em Engenharia mecânica). Belo Horizonte: Universidade Católica de Minas Gerais, 2007.
- [2] Knothe, G. Revista A&G 2002, 47, 222.
- [3] CERBIO, O biodiesel, Publicação da Divisão de Biocombustíveis – DBIO, Ano II, Ed. 12, Maio, 2006.
- [4] Bueno, A. V. Análise da Operação de Motores Diesel com Misturas Parciais de Biodiesel. Tese (Doutorado em Engenharia Mecânica) – Campinas: Universidade

Estadual de Campinas, 2006. [Link]

- [5] Santos, A. G. D. Avaliação da estabilidade térmica e oxidativa do biodiesel de algodão, girassol, dendê e sebo bovino. Dissertação (Mestre em Química) Natal – RN: Universidade Federal do Rio Grande do Norte, 2010. [Link]
- [6] Cortez, L. A. B. et al. (Org.). Biomassa para energia. Campinas: Editora da UNICAMP, 2008. [Link]
- [7] Gentil, V. Corrosão. 5 edição. Rio de Janeiro: LTC, 2007.
- [8] Rolim, A. L.; Rolim, M. J.; Barroso, R. F. A influência do biodiesel na corrosão do pistão do motor

- [Monography]. Centro Universitário Positivo. Curitiba, 2007. [Link]
- [9] Marques, H. G. Síntese e caracterização de biodiesel de soja utilizando técnicas quimiométricas [Monography]. Caraúbas – RN: Universidade Federal Rural do Semi-Árido, 2016.
- [10] American Society for Testing and Materials. Standard Test Methods for Flash by Pensky Martens Closed Cup Tester: ASTM D93, 2008.
- [11] American Society for Testing and Materials. Standard Test Methods for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity): ASTM D 445, 2004.
- [12] American Society for Testing and Materials. Official and Tentative Methods (AOCS). 3. Ed. Chicago: 1985. V1.
- [13] ASTM D792 08. Standard test method for density and specific gravity (Relative Density) of plastics by displacement, ASTM International, West Conshohocken, PA, 2008.
- [14] Singh, D. K.; Ebenso, E. E.; Singh, D. B.; Udayabhanu, G.; John, R. P. J. Mol. Liq. 2018, 250, 88. [Crossref]
- [15] Domingos, D. V.; Tozzi, F. C.; Barros, E. V.; Pinto, F. E.; Sad, C. M. S.; Filgueiras, P. R.; Lacerda-Jr, V.; Dias, H. P.; Aquije, G. M. F. V.; Romão, W. J. Braz. Chem. Soc. 2018, 29, 2244. [Crossref]
- [16] Kazimierczak, H.; Morgiel, J.; Swiatek, Z.; Vega, J. M.; Garcia-Lecina, E. Corros. Sci. 2018, 135, 107. [Crossref]
- [17] Freitas, S.; Malacarne, M. M.; Romão, W.; Dalmaschio, G. P.; Castro, E. V. R.; Celante, V. G. Fuel 2013, 104, 656. [Crossref]
- [18] Dias, H. P.; Barros, E. V.; Sad, C. M. S.; Yapuchura, E. R.; Gomes, A. O.; Moura, R.; Pinto, F. E.; Domingos, D. V.; Aquije, G. M. F. V.; Lacerda-Jr, V.; Romão, W. J. Braz. Chem. Soc. 2018, 29, 1690. [Crossref]
- [19] Candeia, R.A. Biodiesel de Soja: Síntese, Degradação e Misturas Binárias. Tese [Doutorado em Química]. João Pessoa: Universidade Federal da Paraíba, 2008.

- [20] Farias, A. F. F. Avaliação da estabilidade do biodiesel de soja obtido da mistura de óleos e gorduras em diferentes formulações. Dissertação [Mestre em Química]. João Pessoa: Universidade Federal da Paraíba, 2011.
- [21] Silva, C. L. M. Obtenção de Ésteres Etílicos a partir da Transesterificação do Óleo de Andiroba em Etanol. Dissertação [Mestrado em Química]. Campinas – SP: Universidade Estadual de Campinas, 2005.
- [22] Cunha, Michele Espinosa. Caracterização de biodiesel produzido com misturas de sebo bovino, óleo de frango e óleo de soja. Dissertação [Mestrado em Química]. Porto Alegre: Universidade Federal do Rio Grande do Sul, 2008.
- [23] Fagundes, C. A. M. Síntese e caracterização de biodiesel metílico e etílico a partir de blendas dos óleos de tungue e de soja. Dissertação [Mestre em Química Tecnológica e Ambiental]. Rio Grande: Universidade Federal Do Rio Grande, 2011.
- [24] Galvão, L. P. F. C Avaliação termoanalítica da eficiência de antioxidantes na estabilidade oxidativa do biodiesel de mamona. Dissertação [Mestrado em Química]. Natal – RN: Universidade Federal do Rio Grande do Norte, 2007.
- [25] Zheng, S. et al. Biom. Bioen. 2006, 30, 267. [Crossref]
- [26] Kaul, S.; Saxena, R. C.; Kumar, A.; Negi, M. S.; Bhatnagar, A. K.; Goyal, H. B. Fuel Process. Technol. 2007, 88, 303. [Crossref]
- [27] Singh, B.; Korstad, J.; Sharma, Y.C. Renewable Sustainable Energy Rev. 2012, 16, 3401. [Crossref]
- [28] Ashraful, A. M.; Masjuki, H. H.; Kalam, M. A.; Rashedul, H. K.; Sajjad, H.; Abedin, M. J. Energy Convers. Manage. 2014, 87, 48. [Crossref]
- [29] Szklarska-Smialowska, Z. Corros. Sci. 1999, 41, 1743. [Crossref]
- [30] Li, Z.; Lv, S.; Gao, X.; Srivatsan, T. S. Emerging Mater. Res. 2019, 8, 206. [Crossref]
- [31] Frankel, G. S. *J. Electrochem. Soc.* **1998**, *145*, 2186. [Crossref]