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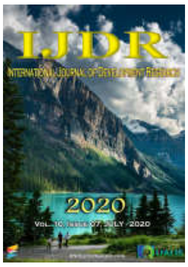

RESEARCH ARTICLE

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# CORROSION STUDY OF BIODIESEL WITH DIFFERENT ACIDITY LEVELS ON A MICROALLOYED STEEL

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## ABSTRACT

The production of biodiesel through the transesterification of vegetable oils and fats using homogeneous basic catalysts requires low acidity and moisture raw materials, which increases the cost of production and compromises the viability of the technology. On the other hand, the feasibility of biodiesel production using higher acidity and lowcost raw materials leads to an increase in the process investment cost due to the need to use equipment built with special steels. The objective of this paper is to evaluate the corrosion resistance of a microalloyed steel, a lower cost material when compared to special alloys, in contact with canola biodiesel. In order to investigate the influence of acidity on steel corrosion resistance, pure biodiesel and biodiesel samples with 1, 3 and 10% oleic acid were added. The corrosion resistance of steels was determined using measures of mass loss, corrosion rate and conductivity. The results suggest that canola biodiesel creates a protective layer called biofilm under the microalloyed steel after a time of contact, causing the corrosion to decrease and a reduction in acidity was also observed. After 30 days of contact, a significant increase in corrosion rates can be observed, probably caused by the rupture of the biofilm.

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## INTRODUCTION

Biodiesel, according to the ANP, consists of a biofuel derived from renewable biomass for use in internal combustion engines with compression ignition or, according to regulations for other types of power generation, that can partially or totally replace fossil fuels. Biodiesel has characteristics that give it advantages over fossil diesel both from the environmental point of view and in terms of functional efficiency. It is free of aromatic and sulfur compounds, contributes less to the greenhouse effect, is biodegradable and obtained from a renewable source. In the economic aspect, it allows oil-importing countries to become less dependent on the foreign market, in addition to stimulating agricultural production and rural development. With respect to performance, it has properties superior to fossil diesel, such as a higher flash point, cetane number and lubricating power. It adapts to the diesel engine without the need for mechanical modifications (Oliveira *et al.*, 2012).

The production and consumption of biodiesel in Brazil was determined through Provisional Measure nº. 214/2004, converted into Law no. 11.097 / 05. This law, contained in the National Biodiesel Production and Use Program (PNPB), can be considered as a milestone in the history of biodiesel in Brazil, since it is from there that biodiesel finds legal support in Brazilian legislation (Tapanes *et al.*, 2013). CNPE Resolution nº16 / 2018, based on Law 13263 of March 2016, established a new schedule for the evolution of the mandatory addition of biodiesel to diesel, with the use of 11% starting in September 2019 and reaching 15% in March 2023. According to statistical data from the ANP, the national production of biodiesel was 5,350,036 m3 or 33,650,712 barrels in 2018. There are 51 plants producing biodiesel authorized by the ANP for operation in the country, corresponding to a total authorized capacity of 25,537, 02 m3 / day. There are also two new biodiesel plants authorized for construction and one biodiesel plant authorized to increase production capacity. The total authorized biodiesel production capacity may be increased by 2,100 m3 / day, which represents a 9% increase in current capacity (ANP, 2018). Biodiesel can be produced by the oil transesterification process, which occurs in the presence of alcohol and a catalyst. Several catalyst options can be used, such as strong base (hydroxides), acids, heterogeneous catalysts and microbiological materials. However, the most used are alkaline catalysts, potassium hydroxide and methoxide, as they have good efficiency and low cost. Transesterification consists the transformation of one ester into another through the exchange of alkoxide groups (Garcia, 2006; Meneghetti *et al.*, 2013). The reaction is basically a triglyceride with alcohol in the presence of a catalyst producing a mixture of monoalkyl esters of fatty acids and glycerol. The transesterification reaction is influenced by the following factors: alcohol / oil ratio, type of alcohol, type of catalyst, catalyst content, reaction temperature, pressure, reaction time and purity of the reagents. In Brazil, about 80% of the factories producing biodiesel use transesterification technology, which requires raw materials with low acidity (<1mg KOH / g) and low water content (<1%), which makes them more expensive, increasing operating costs and compromising the production viability. The use of raw materials with high acidity, on the other hand, increases the investment cost due to the need to use equipment built with special imported steel due to the highly corrosive environment.

The chemical properties of biodiesel and consequently its corrosivity depends on the composition of the ester, the water content that can be absorbed from the humidity of the air, the presence of light and heat, the oxidation and the purity of the raw materials used. During the storage or transport period, the contact of biodiesel with metallic materials combined with the factors mentioned above, can cause corrosion of the components. Metal ions generated by corrosive processes catalyze other undesirable reactions, further degrading the quality of biodiesel (Knothe & Krajl, 2009; Fernandes *et al.,* 2013; Kovácс*et al.,* 2015; Borsato *et al.,* 2012; Jin*et al.,*2015). In Brazil, there is no legislation containing specific and mandatory rules on where and how biodiesel should be stored. In practice, the concern with ensuring product stability, during storage, lies with the distributors themselves, since the fuel characteristics must meet standards regulated by law throughout the national territory. In the storage stage, biodiesel is very vulnerable to variations - the way in which the product is stored has a direct influence on its quality - so some precautions are essential, such as: the tanks must be in good condition, clean, free from water, protected of extreme light and temperature. After washing tanks, pipes, pumps and filters, biodiesel must be circulated throughout the system, in an adequate volume to carry the remaining residues; this entire volume must be drained in order to prepare the tank for receiving the product. Biodiesel is incompatible with copper, lead, titanium, zinc, coated steels, bronze and brass, so it is suggested to store it in carbon steel, stainless steel and aluminum, and two-layer tanks on its internal walls are recommended. Some of these are stainless steels, carbon steel and ARBL steel (high strength and low alloy) (Gallina*et al.,* 2010; Batista *et al.*, 2019). This paper consists of investigating the corrosivity of microalloyed steel, a national material and of lower cost when compared to imported steel, in contact with samples of canola biodiesel. In the work it was also evaluated the influence of acidity in the corrosion process, using samples of biodiesel with different levels of acidity through the addition of oleic acid. The results obtained in this work may contribute significantly to the reduction of the costs of the biodiesel production process in Brazil.

## MATERIALS AND METHODS

The microalloy steel, without being passed to the rolling mill, was used in the tests with biodiesel. The absence of the lamination does not interfere in the evaluation of the corrosion resistance, because this process aims to give the material mechanical properties. The reagents used were commercial refined canola oil, methanol 99.8% and as a catalyst Potassium hydroxide 85% in the form of lentils.

**Synthesis of biodiesel by transesterification:** Canola biodiesel was obtained from the transesterification reaction. for the transesterification reactions, 1000 ml of canola oil were added in a flask, which was placed in a thermostatic bath (30-70 °c) and kept under mechanical stirring (200-1000 rpm). The catalyst potassium hydroxide, previously dissolved in methanol, was added (mass ratio catalyst/oil = 1% and molar ratio alcohol/oil= 6). After 1 hour, the reaction products were separated and cooled. After cooling, the mixture was transferred to a separating funnel and kept at rest for 24 hours. Two phases were formed during decanting: the upper phase (approximately 90% of the total volume) that contains mainly biodiesel, and the lower phase (approximately 10% of the total volume) formed by glycerol. The formed glycerol phase, also called crude glycerin, can contain between 30-50% glycerin, the rest being composed of impurities such as: unreacted alcohol, catalyst and soap. The crude glycerin was separated and stored. The biodiesel phase was purified by washing, decanting and drying. The washing was carried out with the use of a separating funnel with 0.015% citric acid solution at 60ºC. The drying was carried out with the use of a 1000 mL beaker at a temperature of 130ºC and agitation of 500 rpm.

### Biodiesel characterization

**Acid value:** The acidity of vegetable oils is due to the presence of free fatty acids in its composition. The recommended method (EN 14104) uses an alcoholic solution of potassium hydroxide (KOH) as the titrant and phenolphthalein as an indicator, the result being expressed in mg KOH / g of oil. The standard establishes a maximum acidity limit of 0.5 mg KOH per g oil or 3% oleic acid.

**Gas chromatography:** Chromatography is a technique that can be used to assess if the conversion to esters was complete and, consequently, whether there was biodiesel production.The procedure was performed according to the standard EN14103. The levels of fatty acid methyl esters were determined using the gas chromatograph, Shimadzu model GC2014, coupled to a flame ionization detector (FID), split / splitless injector and a capillary column (Carbowax 20M). Stationary phase of polyethylene glycol 30m long, 0.25mm internal diameter and 0.25μm film thickness, Agilent brand.

### Corrosion tests

**Preparation of biodiesel blends:** In addition to pure biodiesel, mixtures of biodiesel with oleic acid were prepared in order to study the influence of biodiesel acidity on the strength of the steel evaluated. four mixtures of canola biodiesel with different levels of oleic acid were prepared, namely: 1, 3 and 10% in relation to the volume of pure biodiesel. the acidity of all samples was determined using standard en 14104.

**Table 1. Areas of test coupons ofmicroalloyed steel**

| Test coupons | A1 | A2 | A3 | B1 | B2 | B3 | C1 | C2 | C3 | D1 | D2 | D3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| OleicAcid*, % | 0 | 0 | 0 | 1 | 1 | 1 | 3 | 3 | 3 | 10 | 10 | 10 |
| Area, cm² | 6,892 | 6,832 | 6,738 | 7,054 | 6,968 | 6,858 | 6,967 | 6,961 | 6,601 | 7,063 | 6,846 | 7,191 |

*Amount of oleic acid added to canola biodiesel,%

**Table 2. Chemical composition of microalloyed steel (% weight)**

| C | Si | Mn | P | S | Al-t | Cr | Ni | Mo | Cu | V |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0600 | 0.2570 | 15.790 | 0.0151 | 0.0021 | 0.0340 | 0.2170 | 0.0110 | 0.1110 | 0.0050 | 0.0010 |
| Nb | Ti | B | N | Ca | Sn | Co | Pb | As | Zr | Zn |
| 0.0620 | 0.0170 | 0.0005 | 0.0050 | 0.0028 | 0.0011 | 0.0033 | 0.0001 | 0.0023 | 0.0030 | 0.0005 |

* Fe – Balance

**Table 3. Factors and its values**

| Factors | Values | | | | | | |
|---|---|---|---|---|---|---|---|
| OL (%) | 0 | 1 | 3 | 10 | | | |
| TI (h) | 24 | 96 | 168 | 336 | 504 | 672 | 1344 |

**Figure 1. Steel test coupons immersed in biodiesel: a) upper image of the sample, b) frontal image of the sample**

**Preparation of test coupons of steel:** The test coupons were sanded using sandpaper of particle sizes 80, 100, 200, 300, 400 and 600, respectively. After the polishing process, were cleaning process, similar to that performed by Kovács et al. (2015). Cleaning started with immersing the coupons in 10% HCl solution for 10 seconds. Then, the coupons were washed with running water and neutral soap, immersed in alcohol for degreasing and washed with running water. The drying step was carried out with a jet of cold air. Table 1 shows the areas of the test coupons, data necessary for calculating the loss of mass of steel in corrosion tests. Table 2 shows the chemical composition of the microalloyed steel.

**Immersion testing:** To assess the corrosivity of biodiesel on microalloyed steel, an immersion test was carried out, through which it was possible to calculate the mass loss and the corrosion rate of the steel test coupons. The test was performed according to the ASTM G1-03 and ASTM G31 Standards. After the treatment described in item 2.3.2, the steel samples were immersed in canola biodiesel, and the mixtures of canola biodiesel with 1, 3 and 10% oleic acid addition. Figure 1shows a sample of immersion test. The tests were carried out following a factorial design in blocks, the factors being the time of immersion of the microalloyed steel in biodiesel (TI) and the content of added oleic acid (OL), the latter being the blocking factor. The response variables were the Corrosion Rate (TC) and the Acidity Index (IA). Table 3 shows the values that each factor adopts when designing experiments. As shown in Table 3, the behavior of the steels during immersion was monitored during specific time intervals. At each withdrawal, the steels were washed, defatted and weighed. The mass loss tests were performed in triplicate. The mass loss for each material was obtained through the differences between the masses before and after immersion. From the results of the mass loss, the corrosion rates of the samples were calculated according to Equation 1. The amount of biodiesel used in each test was quantified respecting the request of the standard that indicates a fluid quantity of 0.20 mL / mm² of sample.

$$\text{Corrosion rate} = (k.w)/(A.t.d) \quad (1)$$

Being:

K = 87600 mm / year (according to ASTM G31);
W = loss of mass, g;
A = steel test coupon area, cm²;
t = time of exposure, h;
d = sample density, g/cm³.

**Statistical analysis of the results of the factorial design in blocks:** Statistical analysis was performed using the Statitica'12 software, obtaining the regression models for each response variable. These models relate the response variable to the factors (Equation 2).

$$\text{Response Variable} = \beta 1 * (\text{Factor } 1) + ... + \beta n * (\text{Factor } n) \pm \text{error} \quad (2)$$

Being $\beta 1 ... \beta n$ the coefficients of the regression model

In addition to the regression model, other outputs were obtained by the software:

- The coefficient of determination ($R^2$) that represents the measure of how much the factors explain the variation of the response variable. A perfect fit results in $R^2 = 1$.
- The adjusted determination coefficient (adjusted $R^2$) is the multiple determination coefficient $R^2$ modified in order to take into account the number of variables and the sample size, allowing the removal of multicollinearity errors. That is, it is a measure of the degree of adjustment of the multiple regression equation to the sample data.
- The residual variance, $S^2$, measures the degree of dispersion between the observed and estimated values of the response variable, and the square root of $S^2$ is called the standard error of the estimate.
- F statistics used to test the joint effect of factors on the response variable. Considering a significance level of 0.05; if Significance $F \leq 0.05$, the regression is significant, but if it is> 0.05, the regression is not significant (Montgomery, 2005).
- T statistics represented for each of the coefficients ($\beta 1$ to $\beta n$) aims to test whether the effect of each factor on the response variable is statistically significant or not. The significance of the T-statistic is represented by the p-value. According to Lapponi (2000) for judgment, P value is compared with the tolerated error ($\alpha$) traditionally 0.05 is used.

To validate the regression models obtained, an analysis of the residues was carried out, verifying: normality, the diagnosis of homoscedasticity and independence of standardized residues.

Figure 2. Synthesis of canola biodiesel a) Reaction b) Phase separation: biodiesel and glycerin c) Final Product

## RESULTS AND DISCUSION

**Synthesis of canola biodiesel:** Figure 2A shows the synthesis process of canola biodiesel, as mentioned in item 2.1. The transesterification method was carried out by reacting the triglyceride with methanol with the aid of the catalyst, producing alkyl esters and glycerol. Figure 2B shows the final decantation phase (24 hours) after the transesterification reaction, canola biodiesel at the top and glycerol at the bottom. Figure 2C shows canola biodiesel after the washing and drying process.

### Characterization of canola biodiesel

**Acidity index:** The analyzes were carried out in triplicate and the average values are shown in Table 4. It is observed that only the sample of canola biodiesel is in accordance with the ANP standards that allow only 3% oleic acid or 0.80mg of KOH for each biodiesel sample. For samples with the addition of oleic acid, a percentage of acidity above that permitted by current legislation is observed.

**Gas chromatography of canola biodiesel:** The average composition of fatty acid ethyl esters of the biodiesel produced is shown in Table 5. There is a predominance of ethyl esters of unsaturated fatty acids, with greater amount of oleic acid, and a total content of approximately 6% of esters ethyl of saturated fatty acids present in the biodiesel sample produced from canola oil. Depending on the raw material, the unsaturated fatty acids composition of biodiesel may vary, high levels of unsaturated fatty acids cause to oxidation reactions accelerated by exposure to oxygen and high temperatures. Figure 3 shows the gas chromatography of canola biodiesel produced. Chromatography revealed the conversion to esters of 94.69% for the canola biodiesel produced.

## Corrosion tests

**Gravimetric tests and corrosion rate in biodiesel:** From the mass loss results, corrosion rates were calculated for samples of steel immersed in biodiesel containing different concentrations of oleic acid.

Figure 4 shows the corrosion rate as a function of the immersion time for the steel sample in different biodiesel conditions. It is observed that the corrosion is more accentuated in the first hours of immersion. The corrosion rate tends to decrease with the immersion time for all samples analyzed during the period between 24 and 720 hours (30 days) of testing. However, after the period between 720 hours (30 days) and 1440 hours (60 days), there is a significant

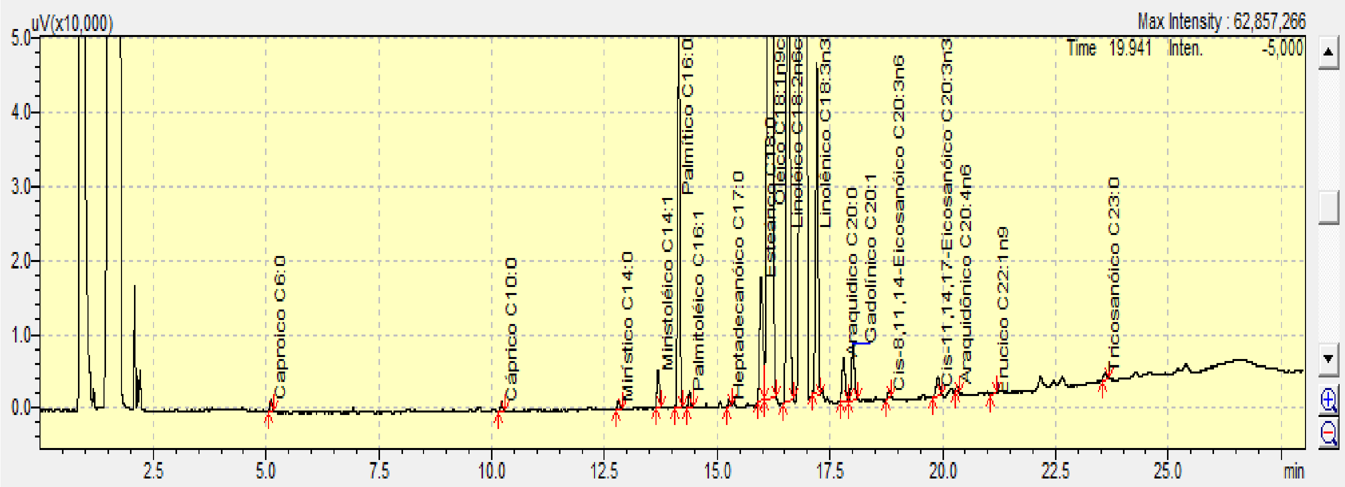

Figure 3. Representative graph of gas chromatography for canola biodiesel

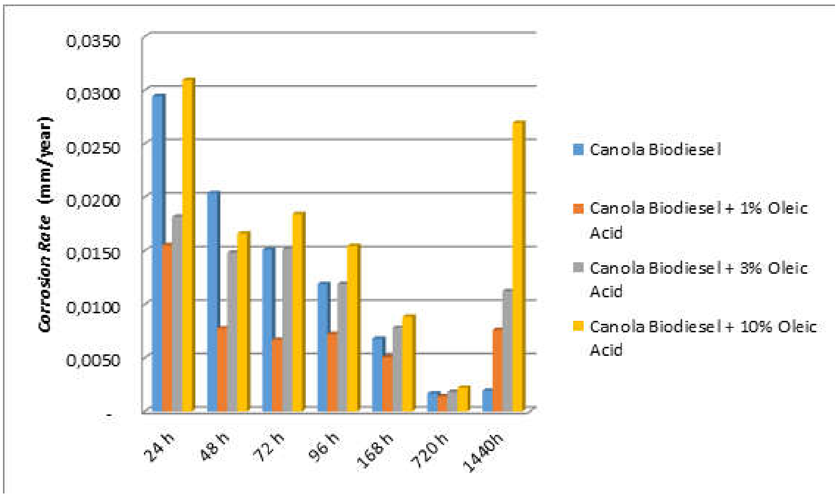

Figure 4. Corrosion rate of microalloyed steel immersed in canola biodiesel

increase in the corrosion rate of the samples, especially those that are immersed in biodiesel with the addition of oleic acid. A possible explanation for this fact can be related to the formation of a biofilm, a protective film against corrosion produced by biodiesel on the surface of the steel samples, during the first thirty days of immersion. After that period, this film may have broken, which caused a significant increase in the corrosion rate of samples immersed with the addition of oleic acid.

## Characterization tests of biodiesel and steel after the corrosion test

**Biodiesel acidity index:** As observed by the data in Table 6 and Figure 5, the acidity index for all samples analyzed showed a reduction over the time of immersion. The lowest acidity indices were observed in the period between 504 (21 days) and 672 hours (28 days) for all samples. After this period, a significant increase in the acidity of all samples was observed. These results corroborate with what was observed for the corrosion rate, which showed a reduction in the first thirty days of testing. Figure 6 shows the color of the biodiesel before immersing the steel samples. The color change of biodiesel is due to the interaction of steel with biodiesel, with precipitated particles being observed at the bottom of the container. Samples with greater acidity have a darker color. The color change and the presence of a bottom body after 1440 hours of immersion is clear evidence of biodiesel degradation. Fazal et al., (2010) found a similar behavior during 1200 hours of copper immersion in palm biodiesel. The color change is more intense for the media to which oleic acid has been added, showing that the presence of acid and ions from the oxidation of steel promote biodiesel degradation.

**Steel micrograph:** The micrographs in Figure 7 show corrosion on the steel surface for all samples analyzed after the sixty-day immersion period. The probable rupture of the biofilm after thirty days of testing caused the appearance of corrosion spots on the analyzed surfaces. Steel immersed in canola biodiesel showed a surface with a lower incidence of corrosion spots when compared to samples with the addition of oleic acid. For samples immersed in biodiesel with the addition of oleic acid of up to 3%, the corrosion observed on the metallic surface is of the uniform type. The steel sample immersed in biodiesel with 10% oleic acid showed higher corrosion rates, including the visualization of pitting corrosion, shown by the arrows in Figure 7d. Table 7 show the result of the phase analysis of the microalloyed steel samples. The results revealed the highest corrosion rates for the samples with the addition of 1 and 3% oleic acid. This analysis did not include the sample with a 10% oleic acid addition.

**Steel micrograph:** The micrographs in Figure 7 show corrosion on the steel surface for all samples analyzed after the sixty-day immersion period.

Table 4. Acidity index of samples before contact with microalloyed steel

| Fuel samples | Acidity index (% oleic acid) |
|---|---|
| Canola Biodiesel | 2,351 |
| Canola Biodiesel + 1% Oleic Acid | 5,889 |
| Canola Biodiesel + 3% Oleic Acid | 15,287 |
| Canola Biodiesel + 10% Oleic Acid | 41,941 |

Table 5. Average composition of fatty acid ethyl esters from canola biodiesel

| FattyAcid | Palmitic Acid C16:0 | Stearic Acid C18:0 | Oleic Acid C18:1 | Linoleic Acid C18:2 | Linolenic Acid C18:3 |
|---|---|---|---|---|---|
| % m/m | 4,57 | 2,15 | 70,13 | 15,54 | 4,14 |

Table 6. Values of the acidity index

| TI (h) | 24 h | 96 h | 168 h | 336 h | 504 h | 672 h | 1344 h |
|---|---|---|---|---|---|---|---|
| Biodiesel | 1,175 | 1,175 | 1,019 | 0,979 | 0,980 | 0,783 | 1,567 |
| Biodiesel + 1% Oleic Acid | 5,487 | 5,095 | 5,095 | 5,291 | 3,723 | 3,919 | 4,899 |
| Biodiesel + 3% Oleic Acid | 14,111 | 13,719 | 13,954 | 13,719 | 10,387 | 10,583 | 12,347 |
| Biodiesel + 10% Oleic Acid | 41,941 | 42,333 | 41,549 | 41,941 | 30,770 | 29,790 | 32,534 |

Table 7. Phase analysis of microalloyed steel after 60 days of immersion (%)

| Fuel samples | Corrosion | Microalloyed steel |
|---|---|---|
| Canola Biodiesel | 64,41% | 35,59% |
| Canola Biodiesel + 1% Oleic Acid | 81,92% | 18,08% |
| Canola Biodiesel + 3% Oleic Acid | 83,23% | 16,77% |

Table 8. Regression Statistics and ANOVA

| Título | For factor IA | For factor TC |
|---|---|---|
| R-Square | 0,9801 | 0,5073 |
| Adjusted R-squared | 0,9777 | 0,4499 |
| Standard Error | 2,1853 | 0,0106 |
| Regression: Significance F | 1,45E-20 | 0,0001 |

Table 9. Effects and coefficients of the regression model for the response variable Acidity Index

| | Coefficients | Standard Error | Stat. t | P value | Effects | Effects errors |
|---|---|---|---|---|---|---|
| Intersection | 1.0946 | 0.8092 | 1.3527 | 0.1888 | -0.5755 | 2.7648 |
| OL | 4.0474 | 0.1543 | 26.2284 | 0.0000 | 3.7289 | 4.3659 |
| TI | 0.0005 | 0.0013 | 0.4032 | 0.6904 | -0.0022 | 0.0032 |
| OLxTI | -0.0010 | 0.0003 | -3.9120 | 0.0007 | -0.0015 | -0.0005 |

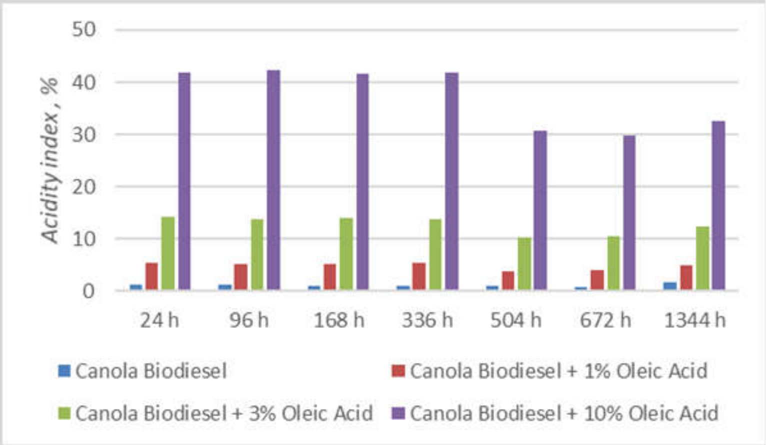

Figure 5. Biodiesel samples acidity index with time of immersion

The probable rupture of the biofilm after thirty days of testing caused the appearance of corrosion spots on the analyzed surfaces. Steel immersed in canola biodiesel showed a surface with a lower incidence of corrosion spots when compared to samples with the addition of oleic acid. For samples immersed in biodiesel with the addition of oleic acid of up to 3%, the corrosion observed on the metallic surface is of the uniform type.

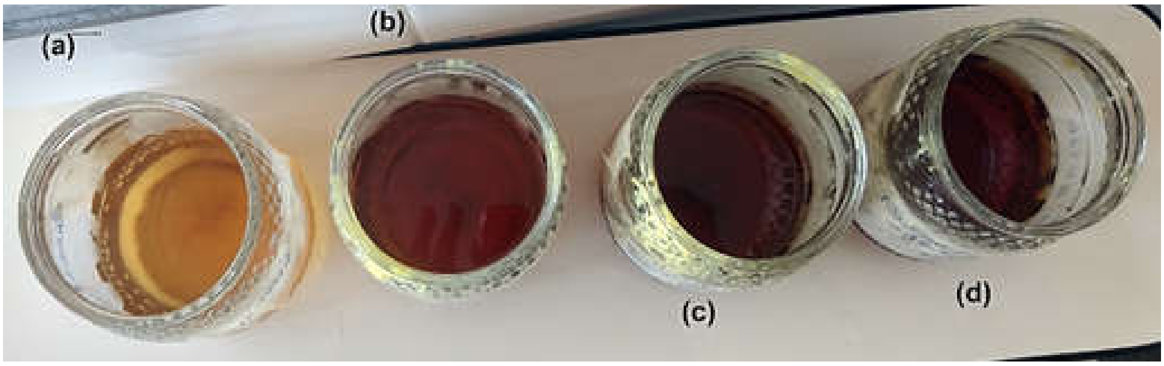

**Figure 6. Biodiesel color changes after 60 days of steel immersion. (a) Canola biodiesel, (b) Canola biodiesel + 1% Oleic acid, (c) Canola biodiesel + 3% Oleic acid and (d) Canola biodiesel + 10 % Oleic acid**

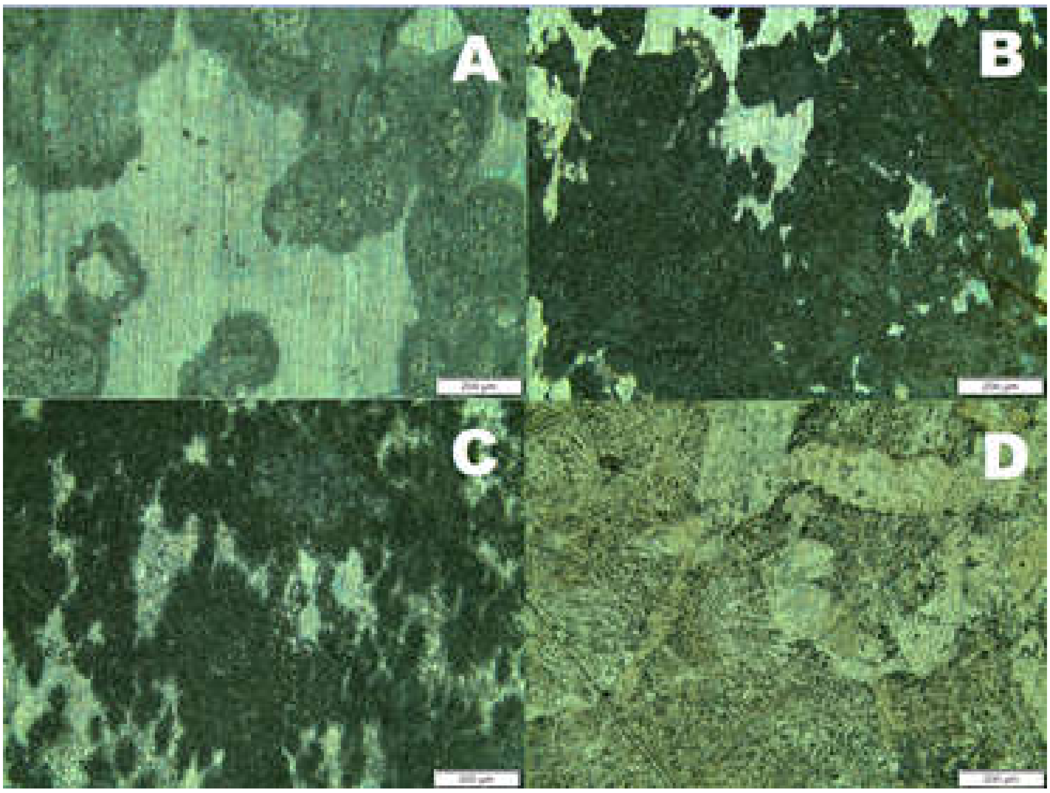

**Figure 7. Microscopy of microalloyed steels after 60 days of immersion 10x:(a) Canola biodiesel, (b) Canola biodiesel + 1% Oleic acid, (c) Canola biodiesel + 3% Oleic acid and (d) Canola biodiesel + 10 % Oleic acid**

The steel sample immersed in biodiesel with 10% oleic acid showed higher corrosion rates, including the visualization of pitting corrosion, shown by the arrows in Figure 7d. Table 7 show the result of the phase analysis of the microalloyed steel samples. The results revealed the highest corrosion rates for the samples with the addition of 1 and 3% oleic acid. This analysis did not include the sample with a 10% oleic acid addition.

## RESULTS OF DESIGN OF EXPERIMENTS

The matrix of factorial design in blocks has as factors the immersion time (TI, days) and the added oleic acid content (OL,%). The latter being the blocking variable, which divides the matrix into 4 blocks, adding up to a total of 28 experiments. The response variables of the statistical analysis were the Acidity Index (IA) and the Corrosion Rate (TC). The following are the statistical results obtained from the application of the design of experiments. The significance of the effects of each factor was assessed with analysis of variance (ANOVA). ANOVA was performed in the 95% confidence interval to assess the importance of the results of the statistical tests shown in Tables 8 and 9. The ANOVA results show that the regression model for the acidity index has a good fit. This result was verified with Adjusted R-squared and the significance F. The Adjusted R-squared is close to 1 demonstrating that there is adherence of the regression equation to the sample data (Table 8), the significance F is practically zero which shows that the regression obtained is significant. The regression analysis for the corrosion rate was not satisfactory, and it is not possible to validate a statistical model from the results obtained for this response variable. Analyzing the P-values of Table 9 it is possible to verify that the content of added oleic acid (OL) is a significant factor ($\alpha \leq 0.05$). Unlike the immersion time factor (TI), which has a P-value of 0. 69 ($>\alpha= 0.05$) which means that there is a 69.04% probability that the TI variable does not adequately represent the model. This result corroborates with the effect of TI on the Acidity Index, which is 0.0005 ± 0.0013, note that the error is greater than the effect itself. The OLxTI interaction proved to be significant, from which we can deduce that the time of immersion only affects the acidity index of the fuel if one considers the synergistic effect with the initial fatty acid content of the sample. Considering the coefficients shown in Table 9, the regression model of the IA can be written as Equation 3.

$IA = 1.095 + 4.047*OL - 0.001\ OL\ TI \pm 0.9$ being *Adjusted* $R^2 = 97.77\%$ (3)

## Conclusions

Was verify a tendency to reduce the corrosion rate of samples of microalloyed steel with the time of immersion in canola biodiesel in the period between 72 hours and 720 hours (30 days). It can be suggested that in this period the formation of a biofilm occurs on the surface of the samples, which causes a reduction in corrosive processes. A reduction in the acidity of biodiesel was observed for all samples analyzed in the period between 360 hours (15 days) and 1344 hours (60 days) of immersion. After the period of 30 days (720 hours) of immersion there is a significant increase in the corrosion rate for all samples of biodiesel with the addition of oleic acid. The variation in the total acidity index corroborates what was observed through the corrosion rate, the higher the rate, the more marked the acidity. The micrographs of steel samples after immersion tests showed that samples immersed in biodiesel with the addition of oleic acid have more corroded surfaces than those immersed in pure biodiesel. The biodiesel sample with the addition of 10% oleic acid showed pitting corrosion points. These results indicate an increase in steel corrosion with an increase in the acidity of biodiesel. The steel phase analysis showed higher corrosion rates for samples with addition of 1 and 3% of oleic acid after 60 days of immersion. The statistical analysis of the results, according to a block factorial design, made it possible to obtain a second order regression model for the acidity index, exposing that the immersion time of the test coupons affects the acidity of the combustible samples if the content is considered of initial oleic acid. It is possible to affirm that the corrosiveness of canola biodiesel increases with the addition of oleic acid and with the contact with the evaluated steel.

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