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Corrosion Behavior of Al in Ethanol–Gasoline Blends

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Abstract: The corrosion behavior of pure aluminum (Al) in 20 *v/v*% ethanol–gasoline blends has been studied using electrochemical techniques. Ethanol was obtained from different fruits including sugar cane, oranges, apples, or mangos, whereas other techniques included lineal polarization resistance, electrochemical noise, and electrochemical impedance spectroscopy for 90 days. Results have shown that corrosion rates for Al in all the blends were higher than that obtained in gasoline. In addition, the highest corrosion rate was obtained in the blend containing ethanol obtained from sugar cane. The corrosion process was under charge transfer control in all blends; however, for some exposure times, it was under the adsorption/desorption control of an intermediate compound. Al was susceptible to a localized, plotting type of corrosion in all blends, but they were bigger in size and in number in the blend containing ethanol obtained from sugar cane.

Keywords: Al; ethanol-gasoline blends; corrosion behavior

1. Introduction

Engines that use gasoline and alcohol as renewable energy sources have gained relevance lately and have been the subject of intense research studies all over the world. Due to its high octane number, ethanol has been extensively used either as an additive to gasoline or as another fuel instead of fossil fuel, leading to a number of research works dealing with both engine performance and pollution. However, alcohol absorbs water because it is highly hygroscopic and shows ethanol impurities (i.e., organic acids, esters, and ketones), which makes metallic materials that come in contact with ethanol-gasoline highly susceptible to corrosive attacks [1–3]. Numerous studies have been undertaken to evaluate the corrosion behavior of metallic materials used in components of vehicle fuel systems [4–17]. Bahena et al. [18] evaluated the corrosion behavior of four metals, including pure aluminum, chromium steel carbon steel, and copper in a 20% ethanol-80–gasoline blend using both weight loss and electrochemical impedance spectroscopy. They found that carbon steel and copper exhibited a greatest corrosion rate. Similarly, Yoo et al. studied the corrosion behavior of A384 aluminum alloy in bio-ethanol blended gasoline with 10, 15, and 20% of ethanol at 60, 80, and 100 °C using electrochemical impedance spectroscopy [19]. They found that the corrosion rate increased with an increase in the ethanol contents, and the lowest value was found at 80 °C. The type of corrosion was a plotting type. In a similar work carried out by Park et al. [20] with the same alloy in the same environment, it was found that acetic acid increased the alloy corrosion rate but water enhanced the formation of protective corrosion products, which led to a decreasing corrosion rate of the alloy. Finally, in a similar study [21], Jafari et al. evaluated the

effect of ethanol contents (0, 5, 10, and 15%) and the addition of water with gasoline on the corrosion behavior of 304 type stainless steel, low/high carbon steel, aluminum, copper, and brazing alloy by using electrochemical impedance spectroscopy. They found that the corrosion rate in all tested alloys increased when ethanol contents increase. However, the addition of water increased the corrosion rate in ferrous metals, whereas the opposite behavior was observed for the nonferrous alloys. Metals were susceptible to a uniform type of corrosion, either in the presence or absence of water. No localized types of corrosion were observed in any specimen. Thus, the goal of the present study was to evaluate the effect of the ethanol source on the corrosion behavior of pure Al in a 20% ethanol–gasoline blend by using different electrochemical techniques. Herein, we used different sources of ethanol, such as sugar cane, oranges, apples, or mangos.

2. Experimental Procedure

2.1. Synthesis of Ethanol

Ethanol is most commonly produced by the fermentation of fruits. In this study, we produced ethanol via sugar cane, oranges, apples, or mangos, which were obtained by standard fermentation procedures. All fruits were obtained in a local market. Herein, we used the following substrates: modified Yellow Prussiate of Soda (YPS) with 250 g/L, KH2PO4 (99.3%, Sigma) 1 g/L, MgSO4.7H2O (99%, J.T. Baker) 0.5 g/L, peptone frm Bacto (Becton, Dickinson) 10 g/L, and yeast (Oxoid, Hampshire) 5 g/L. Sugar content was determined using the dinitrosalicylic acid method, whereas saccharose was determined via hydrolysis with 10% HCl al 10% at 95 °C. The ethanol quantification process was performed using gas chromatography (Agilent 300 A). To determine water content, 10 g of ethanol was weighed in glass tubes (in triplicate) that were previously dried in a muffle and weighed. After one hour at 105 °C in a forced convection oven, samples were removed and placed in a desiccator for 20 min at room temperature. Then, the samples were weighed. The procedure was repeated until a constant weight value was obtained. To determine the water content, the following formula was used:

Water Content (%) =
$$\frac{w(g) - w_1(g)}{w_2(g)} * 100\%$$
 (1)

where w is the initial weight (sample + tube), w_1 is the weight after drying (sample + tube), and w_2 is the sample weight.

2.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

A Perkin–Elmer FTIR system was used to study the obtained ethanol by analyzing the attenuated total reflectance (ATR) under a ZnSe crystal in a range 4000 cm⁻¹ to 650 cm⁻¹. Commercial gasoline was used as a reference and was mixed with the different ethanol.

2.3. Electrochemical Measurements

Employed electrochemical techniques had open circuit potential (OCP), specifically electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN). For this purpose, a potentiostat from ACM instruments was used. By using a standard glass cell, a graphite rode was used as the auxiliary electrode, where a saturated calomel electrode (SCE) was the reference electrode and aluminum (Al) bars with a surface area of 0.32 cm^2 were used as working electrodes. Before carrying the experiments, specimens were abraded with 1200 grade emery paper, degreased with acetone, and rinsed with deionized water. For the EN measurements, the current between the working electrode and another nominally identical working electrode were taken. Moreover, the potential noise was taken versus the SCE reference electrode in blocks of 1024 points. EIS measurements were taken with the application of a signal of 30 mV around the free corrosion potential value, E_{corr} , in a frequency range of 0.05-20,000 Hz. Experiments lasted 90 days at room temperature, which was around $25 \,^{\circ}C$.

2.4. Surface Characterization

Specimens that corrode surfaces were investigated using a LEO brand, model 1450 VP scanning electron microscope (SEM) (ZEISS, Jena, Germany).

3. Results and Discussion

3.1. Infrared Results and Chemical Composition

FTIR results of the obtained alcohols are shown in Figure 1, whereas the water content of different obtained ethanols are given in Table 1. This table shows that the water content was higher for the ethanol made from sugar cane than ethanol obtained from oranges, apples, or mangos, which affected corrosion results. Ethanol purity was higher than 99%, according to Table 1. Figure 1 clearly shows that the four alcohols displayed a virtually identical FTIR spectrum to a different intensity for different functional groups. The hydroxyl group was identified by its bending vibration, which was found with an intense and wide signal at 3370 cm⁻¹. There was evidence that a hydroxyl group was found from an alcohol group at 1053 and 594 cm⁻¹. The presence of CH₃- and CH₂-OH groups were evident at 2887 and 2972 cm⁻¹, respectively, whereas those for CH₂- and C-OH are found at 1647 and 1040 cm⁻¹. All signals were more intense in the mango ethanol.



Figure 1. Fourier transform infrared spectroscopy (FTIR) spectra for the different obtained ethanols.

Table 1. Water and oxygen contents for the different obtained ethanols.

Ethanol Source	Water Contents (%)			
Apple	0.3			
Mango	0.4			
Orange	0.4			
Sugar cane	0.8			

3.2. OCP Measurements

The effect of the ethanol source on the variation of the OCP value with time for Al in the different ethanol–gasoline blends are shown in Figure 2. The noblest values were obtained in pure gasoline, due to its high resistivity, as well as its low water and oxygen solubility. On the other hand, the most active OCP value was obtained in the blend made with ethanol obtained from sugar cane, which was

probably due to higher water and oxygen contents. The OCP values obtained in the blends made with ethanol from oranges and mangos were very noble; however, after 30 days of exposure, their values became more active. A similar trend was observed for the OCP values obtained for the blend made with ethanol obtained from apples. The shift towards more active values was probably due to the dissolution of any air formed from the oxide layer, whereas the shift into the noble direction was due to the formation of corrosion product layers after metal dissolution [22].



Figure 2. Variation on the open circuit potential (OCP), value for Al in the different ethanol–gasoline blends.

3.3. LPR Measurements

Time variation for polarization resistance, R_p, in different ethanol–gasoline blends is given in Figure 3. Corrosion current density values, I_{corr}, can be calculated by using following equation:

$$I_{corr} = K/R_{p}$$
⁽²⁾

where K is a constant that involves cathodic and anodic Tafel slopes obtained from polarization curves not obtained in this study due to the high solution resistivity values. Figure 3 shows that the lowest R_p values, and thus the highest I_{corr} values, were obtained for the blend made with the ethanol obtained from sugar cane. The R_p obtained in blends made with ethanols obtained from either oranges, apples, or mangos were higher by at least two orders of magnitude than those obtained in the blend made with sugar cane ethanol. The highest R_p values, and thus the lowest I_{corr} values, were obtained from pure gasoline, due to its low water and oxygen affinity [21]. However, in all cases, regardless of the ethanol source, R_p values had erratic behavior with time, since sometimes it increased and other times it decreased.

The increase in the R_p value was a result of the accumulation of a corrosion product layer on the metal surface, whereas a decrease on its value was a result of the detachment of this corrosion product layer. According to Rawat et al. [23], the oxygen contents in pure gasoline was 0, whereas in sugar cane the ethanol was 34.7 wt. %. In a 20% ethanol–gasoline blend, this decreased to 7.0. Similarly, water solubility in pure gasoline was 0, whereas in ethanol it was 100%. Yet in the 20% ethanol–gasoline blend this value was between 0.5 and 0.7%. Thus, the difference in R_p values and, therefore, in the corrosion rates, were a result of a difference in both oxygen content and water solubility value in the different ethanol sources. In the same research work [23], Rawat et al. evaluated the effect of different ethanol–gasoline blends on the corrosion rate of different metals, including carbon steel, copper, and brass. In all cases, regardless of the metal chemical composition, they found that the corrosion rate increased with the ethanol contents due to an increase in both oxygen content and water solubility value.



Figure 3. Variation on the R_p value for Al in the different ethanol–gasoline blends.

3.4. Electrochemical Noise Measurements

The spontaneous fluctuations in both potential and current density values of a metal in an electrolyte (i.e., its electrochemical noise) was a powerful tool to determine the susceptibility of that metal for a localized type of corrosion, such as plotting [24]. As an example of these fluctuations, the time series in both the current density and potential density 84 days after exposure in a blend containing ethanol made from sugar cane are given in Figure 4. For day 1, the time series consisted of a combination of low intensity and high frequency transients, with some other transients with a slightly higher intensity but much lower frequency, indicating a metal undergoing a localized type of corrosion [25,26]. The intensity was around 10^{-8} mA/cm² for the transients in the current density and 0.02 mV for the transients in the potential density, respectively. However, after 84 days of exposure, the frequency of transients with a higher intensity increased, since the intensity for these transients was 10^{-6} mA/cm², which indicated a higher susceptibility to a localized type of corrosion. By dividing the standard deviation in the potential density, δ_V , by the standard deviation in the current density, δ_I , we could calculate the noise resistance, R_n , as stated below:

$$R_n = \delta_V / \delta_I \tag{3}$$

The variation on the R_n value with time in the different ethanol–gasoline blends are given in Figure 5. The lowest R_n value was, once again, for the tests carried out in the blend with the ethanol made from sugar cane, whereas the highest values were obtained in pure gasoline, similar to the results given by R_p in Figure 4. Thus, different techniques give similar results, which was encouraging, as it confirmed that the highest corrosion rates were obtained in the blends made with ethanol obtained from sugar cane.



Figure 4. Noise in current and in potential for Al in the blend containing ethanol obtained from sugar cane after ((**a**) and (**b**)) 1 day and ((**c**) and (**d**)) 84 days of exposure.



Figure 5. Variation on the R_n value for Al in the different ethanol–gasoline blends.

In order to have a quantitative estimation of the metal susceptibility to localized corrosion, a factor called the "localized index", LI, can be calculated by dividing the root mean square value of the current density, I_{rms} , by the standard deviation in the current density, δ_I , according to:

$$R_n = I_{rms} / \delta_I \tag{4}$$

Obtained results are given in Figure 6. Metal had a high propensity to suffer from the localized type of corrosion when the LI value were between 0.1 and 1, where it would suffer from a uniform mixture and localized corrosion type if its value were between 0.01 and 0.1. Results shown in Figure 6 indicate that Al was highly susceptible to a localized type of corrosion, such as plotting, in all the ethanol–gasoline blends regardless of the ethanol source. For the blend containing ethanol made from sugar cane, these results indicated that Al could develop a mixture of localized and uniform type of corrosion.



Figure 6. Variation on the LI value for Al in the different ethanol–gasoline blends.

3.5. Electrochemical Impedance Spectroscopy (EIS) Measurements

EIS data in both the Nyquist and Bode formats for Al corroding in the ethanol–gasoline blend that contained ethanol made from mango during 90 days of exposure are given in Figure 7.





Figure 7. Electrochemical impedance spectroscopy (EIS) data in the (**a**) Nyquist and (**b**) Bode formats for Al in the blend containing ethanol obtained from mangos.

Data plotted in the Nyquist diagram shows a charge-transfer control since it observed one capacitive semicircle at all frequency values (Figure 7a). However, in some cases such as at 28, 42, and 77 days of exposure, an inductive loop at low frequency values appeared, which showed that

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The Bode diagram, shown in Figure 7b, indicated that the impedance modulus sometimes increased or decreased with time, which was indicative of the formation of the corrosion product layer and its detachment. The presence of two different slopes in this plot was also evident, thus indicating the presence of two time constants. Thus, in Nyquist plots, there were two different semicircle: one, at high and intermediate frequency values, due to the redox reactions that took place at the metal/corrosion products layer, and a second semicircle at lower frequency values, due to the redox reactions that took place at the metal/corrosion took place at the metal/electrolyte interface (the double electrochemical layer). According to the Bode plot, the highest impedance modules were within the order of 10^{10} ohm cm², which was similar to the R_p and R_n values reported above in Figures 4 and 5.

Figure 8 shows EIS data in the Nyquist and Bode formats for Al that corroded in the ethanol–gasoline blend containing ethanol made from sugar cane 90 days after exposure. Nyquist diagrams (Figure 8a) display one capacitive semicircle at high and intermediate frequency values, whereas at lower frequencies an unfinished capacitive semicircle was observed, indicating a charge transfer controlling corrosion process. The observed loop at the high frequency semicircle represented the redox reactions that took place at the metal/corrosion product layer, whereas the low frequency loop represented the electrochemical reactions that took place at the metal/electrolyte (double electrochemical layer) interface. This time, the presence of inductive loops was not observed as in the ethanol–gasoline blend containing ethanol made from mangos (Figure 7a). Bode plots (Figure 8b) show that the impedance modulus decreased with an increase in exposure time and presence of two different slopes, suggesting two different time constants: one for the electrochemical reactions that took place at the double electrochemical layer, and a second one for the electrochemical reactions that took place through the corrosion product layer. It is important to note that the impedance values were within the order of 10^6 ohm cm², which was much lower than those obtained for Al in the blend containing ethanol made from mangos, similar to the R_p and R_n values given in Figures 4 and 5.



Figure 8. Cont.



Figure 8. EIS data in the (**a**) Nyquist and (**b**) Bode formats for Al in the blend containing ethanol obtained from sugar cane.

For Al corroding in the ethanol–gasoline blend containing ethanol made from apples, Nyquist data (Figure 9a) shows the presence of one capacitive semicircle at high and intermediate frequency values, overlapped with a second capacitive loop at the lowest frequency values; the high frequency loop was associated with the redox reactions that took place at the metal/corrosion product film, whereas the lowest frequency loop was related to the redox reactions that took place at the metal/electrolyte interphase or double electrochemical layer, indicating that the corrosion process was under charge transfer control. On the other hand, Bode plots (Figure 9b) show that the impedance modulus sometimes increased or decreased with time, indicating the formation of a corrosion products film detached from the corrosion product film. Two different slopes were observed in the modulus-frequency plots, which was indicative of two different time constants. The impedance values were within the order of 10^{10} ohm cm², which was similar to the R_p and R_n values given in Figures 4 and 5.

Finally, Figure 10 presents the Nyquist and Bode plots for Al corroding in the ethanol–gasoline blend containing ethanol made from oranges. The Nyquist diagrams (Figure 10a) show a single capacitive semicircle in the whole frequency interval, i.e., a corrosion process controlled by the charge transfer reaction; however, the presence of two slopes were observed in the Bode plots (Figure 10b). Thus, the two time constants indicated that there were two different capacitive loops: one at high and intermediate frequency values, which was associated with the electrochemical reaction that took place at the metal/corrosion product film, and a second capacitive low frequency loop, which was associated with the electrochemical reaction that took place at the metal/electrolyte interface or double electrochemical layer. However, after 35, 42, and 77 days of exposure, an inductive loop at the lowest frequency values following the high frequency loop was observed, indicating that the corrosion process was controlled by the adsorption/distortion of some intermediate species. Bode plots also showed that the impedance modulus values, in general terms, increased as time increased due to the formation of corrosion product films, and the existence of two different time constants: one corresponding to the electrochemical reactions that took place at the metal/corrosion products film, and a second one representing the electrochemical reactions that took place at the metal/electrolyte interphase or double electrochemical layer.





Figure 9. EIS data in the (**a**) Nyquist and (**b**) Bode formats for Al in the blend containing ethanol obtained from apples.

Electric circuits are commonly used to simulate EIS results and. in this case, the ones that had the best fit are shown in Figure 11, As such, their elements had a solution resistance, R_s , and charge transfer resistance, R_{ct} , associated with the double electrochemical layer. Moreover, C_{dl} was the double layer capacitance that was inversely proportional; R_f had corrosion product film resistance and C_f was its capacitance; L was the inductor and R_L its resistance. Polarization resistance, R_p , was the sum of all of these resistances, i.e., $R_s + R_{ct} + R_f$. The double layer and corrosion products film capacitance value, C_{dl} and C_f , were affected by surface imperfections, such as roughness, which were made instead of a pure double layer capacitor, C_{dl} , when a constant phase element, CPE, was used [27]. The impedance of CPE, Z_{CPE} , is given by [28]:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \tag{5}$$

where Y_0 is the admitance, j is $(-1)^{1/2}$, ω is the angular frequency, and n is the CPE exponent that gives information on the metal surface such as metal roughness (Figure 11). Obtained parameters that best fit the Nyquist and Bode results of Al after 7 days of exposure to the different ethanol–gasoline blends by using electric circuits are shown in Figure 11 and Table 2.



Figure 10. EIS data in the (**a**) Nyquist and (**b**) Bode formats for Al in the blend containing ethanol obtained from oranges.



Figure 11. Electric circuits used to simulate EIS data for Al in ethanol–gasoline blends when the corrosion process is under (**a**) cage transfer and (**b**) adsorption/desorption control.

Table 2. Parameters used to fit the EIS data for Al corroding in the different ethanol–gasoline blends after 7 days of exposure.

Ethanol Source	R _S (ohm cm ⁻²)	CPE _{dl} (ohm ⁻¹ m ⁻² s ⁿ)	n _{ct}	R _{ct} (ohm cm ⁻²)	CPE _f (ohm ⁻¹ m ⁻² s ⁿ)	n _f	$ m R_{f}$ (ohm cm ⁻²)
Apple	$2.8 imes 10^4$	4.1×10^{-11}	0.9	2.2×10^{9}	1.1×10^{-9}	0.8	4.4×10^9
Orange	3.6×10^4	3.1×10^{-11}	0.9	1.7×10^{9}	2.3×10^{-9}	0.8	6.6×10^{9}
Mango	1.1×10^4	2.3×10^{-11}	0.9	2.2×10^{9}	1.3×10^{-10}	0.8	4.7×10^{9}
Sugar cane	$4.6 imes 10^4$	6.6×10^{-10}	0.6	$2.6 imes 10^6$	$1.6 imes 10^{-6}$	0.7	$5.9 imes 10^6$

The first important thing to note is the high solution resistance values, R_s , within the order of 10^4 ohm cm² regardless of the ethanol source. The second thing to note is that the values for R_f are always higher than those for R_{ct}, indicating that the corrosion resistance of Al in the different blends is given by the protectiveness of the corrosion product film. The lowest values for R_f and R_{ct} were obtained in the blend containing ethanol made from sugar cane, indicating that, in this blend, Al exhibited the highest corrosion rate as given by Equation (1) above, in agreement with the results obtained in the LPR and electrochemical noise measurements (Figures 4 and 5). Since the capacitance was inversely proportional to the resistance value, an increase in the resistance value corresponded to a decrease in its capacitance. When the values for n were close to 1.0, a low metal surface roughness had a low dissolution rate. On the contrary, when it was close to 0.5, it was because of a high surface roughness due to a high dissolution rate. According to data given in Table 1, values for both n_{ct} and n_f were within 0.8 and 0.9 for the tests carried out in blends containing ethanol obtained from oranges, apples, or mangos, due to a low surface roughness because the corrosion rate of Al in these blends was low. On the contrary, the values for both n_{ct} and n_f were 0.6 and 0.7 for the tests carried out in the blend containing ethanol obtained from sugar cane due to a high surface roughness because the corrosion rate of Al in this blends was high. Thus, all the test suggest that the blend containing ethanol obtained from sugar cane was more aggressive for Al than the blends containing ethanol obtained from oranges, apples, or mangos, which may be a result of higher water and oxygen content.

3.6. Surface Characterization

Figure 12 shows micrographs of Al corroded surfaces after 90 days of exposure to different ethanol blends. For the test done in pure gasoline, specimens did not show any type of attack, as can be seen in Figure 12a; however, for the tests carried out in blends containing ethanol made from oranges, apples, or mangos, some shallow plots with a size smaller than 10 μ m could be seen. Even more, for the test carried out in the blend containing ethanol made from sugar cane (Figure 12d), the plot size was larger than 40 μ m and deeper than those observed in other blends. Nonetheless, it was very likely that it was a coalescence of several smaller plots. Thus, these micrographs were in agreement with all the electrochemical tests results, i.e., that Al did not suffer from any type of corrosion attack in pure gasoline; that the ethanol made form sugar cane was the most aggressive among the different ethanol tested in this research work, perhaps because of its higher oxygen and water contents than those in the rest of the ethanol obtained from oranges, apples, or mangos.



Figure 12. Micrograph of Al corroded in (**a**) gasoline and in ethanol–gasoline blends containing ethanol made from (**b**) apples, (**c**) mangos, (**d**) oranges, and (**e**) sugar cane.

4. Discussion

The most widely used form to explain Al corrosion in ethanol–gasoline blends was the electrochemical process produced by water and dissolved oxygen, which enhanced cathodic reactions due to phase separation [28]. Oxygen was introduced as an automotive fuel that could produce better

engine performance, whereas ethanol was oxidized by this dissolved oxygen to form water plus acetic acid [29].

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O \tag{6}$$

Acetic acid corroded Al not in an electrochemical way, but in a chemical way that produced hydrogen gas and aluminum acetate [30]:

$$Al + CH_3COOH \rightarrow 3/2H_2 + Al(CO_3COO)_3$$
(7)

Water either facilitates aqueous conditions that enhance corrosion processes, or forms protective layers of corrosion products, such as bayerite (Al(OH)₃) or boehmite (AlOOH) [30]. This film can be disrupted in some localized places or, due to the amount of water and oxygen present in the blend, it does not cover the whole Al surface, inducing a localized type of corrosion, such as the observed plots. The protective nature of these films depends upon the presence of impurities such as chlorides, sulfates, and other organic compounds that depend on the source of the ethanol, among other factors. Due to the different nature of the obtained ethanol, the presence of these impurities must be different to explain the diverse effects they have on Al corrosion behavior.

5. Conclusions

In this study, we conducted an investigation on the corrosion behavior of pure Al in 20% ethanol–gasoline blends using electrochemical techniques that contained ethanol obtained from sugar cane, oranges, apples, or mangos. Each technique showed that corrosion rates obtained in the blends were higher than that obtained in gasoline. However, corrosion rates were highest in the blend containing ethanol obtained from sugar cane. The corrosion process was controlled by the charge transfer in all the blends regardless of the ethanol source; however, for some exposure times, it was under the adsorption/desorption of an intermediate compound. Although Al was susceptible to the localized type of corrosion in all blends, plots were much bigger and deeper in the blend containing ethanol obtained from sugar cane.

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