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Effect of Chemical Conversion Treatment with Oxalic Acid Solution in the Corrosion Resistance of Galvanized Steel in Soybean Biodiesel with Natural Additives

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In many applications, such as fuel storage tanks and fuel lines, galvanized steel is used as a construction material which comes into contact with biodiesel. Considering that biodiesel is more corrosive than petroleum diesel, studies that aim to increase the corrosion resistance of galvanized steel in this environment are required. The present work investigates how the chemical conversion treatment in the oxalic acid solution affects the corrosion resistance of galvanized steel in soybean biodiesel (B100) in the absence and presence of the natural additives the extract the turmeric, clove, ginger, stone breaker, and rosemary. The results obtained indicate that the conversion treatment reduces the corrosion rate of the zinc coating in soybean biodiesel in the absence and presence of additives, and in this condition the effect of the conversion treatment depends on the additive used.

Keywords: *Biodiesel, zinc, oxalic acid, corrosion, oxidative stability, natural additives.*

1. Introduction

The corrosion of metals in contact with biodiesel has aroused the interest of several researchers in recent years because it causes the degradation of diesel engine fuel system materials resulting in a decrease in the useful life of the components[1-4]. In addition to this effect, the metallic sediments resulting from corrosion adversely affect biodiesel oxidation stability[5-9] and when depositing on the various components of the engine this causes problems such as engine choking and filter plugging[10].

Biodiesel is more corrosive than petroleum diesel, which makes research on the corrosive action of biodiesel and on procedures aimed at mitigating this corrosive action important. The greater corrosivity of biodiesel is mainly attributed to the presence of free fatty acids (FFA) that have corrosive characteristics[11,12] and a higher electrical conductivity that favors the oxide-reduction reaction. Biodiesel has a strong tendency to absorb moisture from the atmosphere which, after long storage, can hydrolyze the ester bond causing the formation of FFA[11].

The metal components of the engine fuel system that come into contact with biodiesel are made of various materials including carbon steel, cast iron, copper alloys, stainless steel and galvanized steel. Galvanized steel is used in fuel lines[13] and in fuel tanks, including biodiesel transport and storage tanks[14]. This means that it is important to carry out research aimed at increasing the corrosion resistance of these materials in biodiesel. Studies[14,15] on the corrosion resistance of zinc in biodiesel have found that the corrosion rate of zinc in this medium is lower than that of copper in biofuels from different sources, but it is higher than that of aluminum and stainless steel. It has also been reported that galvanized steel can be used in a blend storage tank containing up to 20% v / v biodiesel (B20), for a long period of time. However, for a higher percentage of biodiesel the amount of Zn dissolved from the Zn coating causes biodiesel to deteriorate and the storage equipment must be made of stainless steel[14].

The use of corrosion inhibitors and chemical conversion treatment can make zinc surfaces more resistant to corrosion and can significantly increase the corrosion resistance of galvanized steel in contact with biodiesel. Additives used as corrosion inhibitors in biodiesel are generally synthetic organic compounds, such as tertiary butyl alcohol (TBA), tert-butylhydroquinone (TBHQ), Butylated hydroxytoluene (BHT), and propyl gallate[16-18]. These additives are generally used to protect steel and cast iron containing hydroxyl groups, whose free electrons form a bond with the surface of the metal. Some corrosion inhibiting additives, such as TBHQ and BHT, also act as antioxidants, increasing the oxidative stability of biodiesel.

It has been found[18] that the addition of TBHQ to soybean biodiesel inhibits the dissolution of zinc, indicating that this additive acts as a corrosion inhibitor for galvanized steel.

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It has also been observed that this additive acts as an antioxidant increasing the oxidation stability (induction period) of neat biodiesel. The effect of the addition of TBHQ in increasing the corrosion resistance of zinc is attributed to the possible formation of a protective film layer on the zinc surface. This effect is also attributed to the reaction of the additive with the oxidation products of biodiesel with the consequent reduction in the corrosive character of the biodiesel. However, it is not clear how zinc corrosion products can be affected by the possible interaction with additives.

An alternative to TBHQ as well as other synthetic organic additives is the use of natural organic additives as corrosion inhibitors. In addition to being less expensive, these additives are more readily biodegradable and non-toxic in biodiesel. It has been found that cardenal, a natural compound extracted from cashew nutshell liquid (CNSL), and rosemary extract act as corrosion inhibitors for aluminum alloy 5052 H32 and commercially available pure aluminum (Al (99.89%)), respectively, in biodiesel. The effect of cardenol is attributed to the adsorption of the molecules of this compound in the active sites on the metallic surface, acting as a protective film against corrosion[19]. The explanation for the effect of the rosemary extract[20] is based on the adsorption of the organic components of this compound on the metallic surface resulting in the inhibition of anodic and cathodic reactions. Furthermore, it has been suggested that both cardenol molecules and components in the rosemary extracts reduce the corrosive behavior of biodiesel by delaying the biodiesel oxidation[21,22]. In a prior study[23] it was found that extracts of curcumin, rosemary, ginger, clove, thyme and stone breaker act as corrosion inhibitors for steel and as antioxidants in soybean biodiesel. Regarding zinc, it was found[24] that tropical almond leaf extract acts as a corrosion inhibitor in soybean biodiesel, and this effect is attributed to adsorption by physisorption of antioxidant compounds on the zinc surface.

Chemical conversion treatment consists of immersing the metal in a conversion solution for a certain period before exposing the metal to the corrosive medium to enable the formation of corrosion products that are more resistant to corrosion. The best known conversion treatment is the chromate conversion layer but this method has been gradually abandoned due to its high-toxicity Cr (VI) content[25]. However, it has been reported[26] that converting the Zn deposit to a 0.1 M oxalic acid solution (immersion for 5 minutes), which is a non-toxic solution, increases the corrosion resistance of the coating in NaCl solution. This effect is mainly attributed to the formation of a layer of zinc oxalate that acts as an anchor base for a layer of simonkolleite or hydrated zinc chloride hydroxide ($Zn_5(OH)_8Cl_2H_2O$), which acts as a protective film. On the other hand, it is necessary that the zinc be subjected to a long exposure time in the chloride solution (around 120 hours of immersion in the 0.1 M NaCl solution) so that the presence of simonkolleite can be effective in protecting against corrosion.

Biodiesel generally does not contain chloride, which implies that simonkolleite would not be formed on the surface of the zinc coating in contact with biodiesel. However, there are other corrosion products that can act as corrosion protectors. It is interesting to analyze whether the presence of a zinc oxalate layer could favor an increase in corrosion resistance in biodiesel because it acts as an anchor base for corrosion products including products resulting from the dissolution of this layer.

The present study analyzed how the chemical conversion treatment in an oxalic acid solution affects the corrosion resistance of galvanized steel in soybean biodiesel in the absence and presence of the natural additives the extract the turmeric, clove, ginger, stone breaker, and rosemary.

2. Experimental Procedure

2.1. Electrodeposition process and zinc coating conversion treatment

Zinc coatings were deposited from an acid bath (pH 4.7) at room temperature without stirring. A deposition bath with the following composition was used[27]: 0.10 mol/L $ZnCl_2$, 2.80 mol/L KCl, and 0.32 mol/L H_3BO_3. The coatings were deposited on an AISI 1020 carbon steel substrate at a current density of 10 $mA.cm^{-2}$ for 34 min; 5 µm thick coating.The conversion treatment involved the immersion of the zinc coating in a 0.1 M solution of oxalic acid for 5 minutes.

2.2. Production of soybean biodiesel and natural additives

The soybean biodiesel, B100, used in the present work as a corrosive medium was obtained in the laboratory by a transesterification reaction[23].

In the present work, the effect of the additions of 1000 ppm on B100[23] of the following natural additives were analyzed: methanol extract of turmeric, clove, ginger and stone breaker leaves. Their scientific names can be found in Table 1. Figure 1 shows the structural formula of the principal components of these extracts. Methanol extracts were obtained by soxhlet method[33].

2.3. Gravimetric test

The gravimetric test involved measurements of mass loss, using samples with dimensions of 2.0 x 2.0 x 0.2 cm. The tests were carried out at an ambient temperature of 25°C. The untreated and treated zinc coatings were immersed in B100, for 30 days. After immersion, the samples were immersed in a 1.36 M solution of amino acetic acid to eliminate the corrosion products. Next, the samples were dried and weighed. To weigh the samples before and after immersion in B100, an analytical balance, BEL ENGINEERING-Italy, M214Ai model, was used.

Table 1. Analyzed compounds and the respective sources from which they were obtained, in addition to the scientific name of the compounds.

Vegetable	Additive (main active compound)	Scientific name
Turmeric	Curcumin	Curcuma longa L
Clove	Eugenol	Dianthus caryophyllus
Ginger	Gingerol	Zingiber of icinalis
Stone breaker	Quercetin	Phyllanthus niruri
Rosemary	Rosmarinic acid	Rosmarinus officinalis

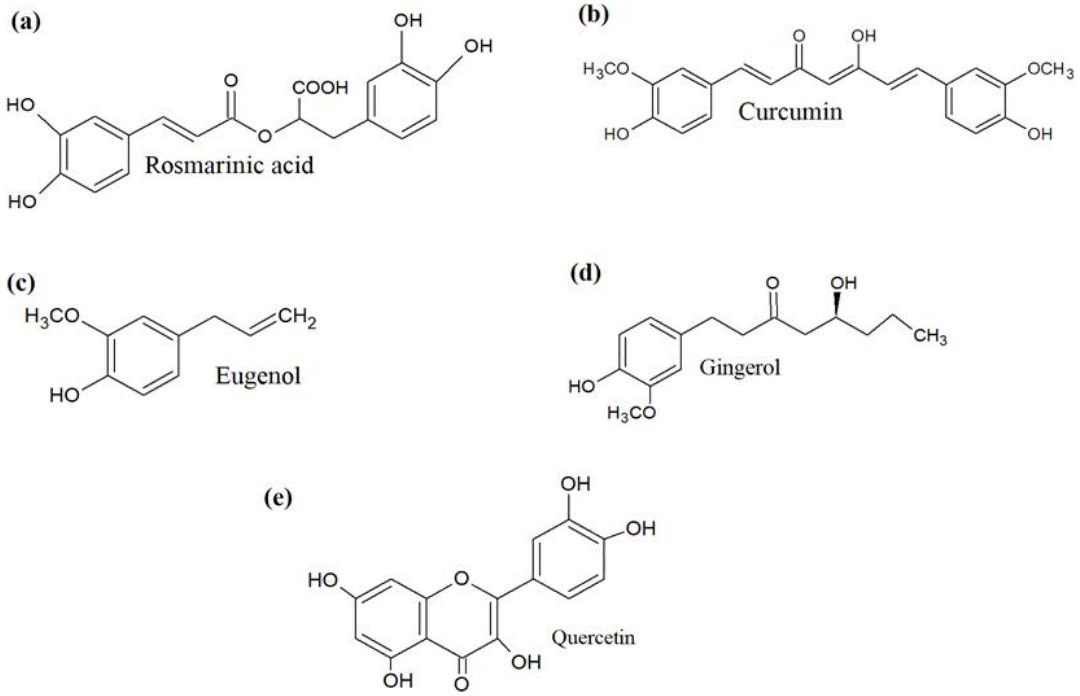

Figure 1. Structural formulas of principal components of methanol extracts used as additives added to the biodiesel: rosemaric acid (a)[28], curcumin (b)[29], eugenol (c)[30], gingerol (d)[31], quercetin (e)[32].

From the mass loss measurements, the corrosion rate and inhibition efficiency of the analyzed additives were obtained using Equation 1 and 2 according to NACE Standard RP0775-2005[34].

$$CR = \frac{K \times W}{A \times t \times \rho} \tag{1}$$

where: C_R is the corrosion rate (μm/y), K is a constant ($K = 8.76 \, x \, 10^4$); W is the mass loss (g); A is the immersed area (cm^2); t is the immersion time (h), ρ is the density of zinc.

$$\eta = \left[\left(C_R - C_{RA} \right) / \, C_R \right] \times 100 \tag{2}$$

Where: η is the inhibition efficiency, C_R is the corrosion rate in the absence of the additive, C_{RA} is the corrosion rate in the presence of the additive. The measurements were performed in triplicate and the minimum, maximum, and average values of corrosion rate and inhibition efficiency were reported in each case.

2.4. Electrochemical measurements

The electrochemical measurements involved obtaining potentiodynamic polarization curves through which the polarization resistance was obtained. These measurements were performed using a potentiostat/galvanostat Gamry Instruments – USA, 1010ETM model coupled to a computer equipped with the Gamry Framework™ version 7 software. The measurements were carried out using Ag/AgCl as a reference electrode and a platinum wire as a counter electrode.

The potentiodynamic polarization curves were obtained at a sweep rate of 10 mV/s[35] between potential ranges from – 3 to 1 V (SSC). The polarization was started after the sample was immersed in the biodiesel B100 for 30 minutes. In order to increase the conductivity of biodiesel, 0.10 mol/L lithium perchlorate was added to this solution[20].

2.5. Surface analysis

The surface of Zn coatings before and after immersion in B100 biodiesel was analyzed by scanning electron microscope (SEM) and X-ray diffraction (XRD).

Micrographs of the surface were obtained using a TESCAN VEGA-Czech Republic, 3LMU model scanning electron microscope. X-ray diffraction (XRD) analysis was performed with a SHIMADZU-Japan, XRD-6000 model.

3. Results

3.1. Evaluation of the effect of the conversion treatment on the corrosion resistance of zinc coating in soybean biodiesel

3.1.1. Potentiodyamic polarization and polarization resistance measurements

Figure 2 shows the potentiodynamic polarization curves in soybean biodiesel of Zn coating subject and not subject to the conversion treatment. From the potentiodynamic curves it can be seen that the conversion treatment causes a slight decrease in anodic current density, in addition to an increase in corrosion potential, E_{corr} (from – 0.877.V vs. Ag/AgCl to – 0.701V vs.Ag /AgCl).

The increase in E_{corr} indicates an increase in corrosion resistance, however, the use of this parameter to assess corrosion resistance is limited as E_{corr} is a dynamic value and therefore does not necessarily reflect the corrosion rate which is a kinetic value[36]. As an example of the limitation of E_{corr}, the fact that it does not reflect the actual effect of the presence of the corrosion product on the corrosion rate can be cited. Therefore, the evaluation of corrosion resistance should not be based only on obtaining the E_{corr}.

3.2. Corrosion rate obtained through weight loss measurements

Figure 3 shows the corrosion rate obtained through mass loss tests of zinc coating samples not subject (Zn) and subject to the conversion treatment (ZnOx). The corrosion rate corresponds to the immersion of the samples in soybean biodiesel, B100, for 30 days in the absence and presence of 1000 ppm of different additives. The purpose of this figure is to determine how the conversion treatment affects the corrosion rate of zinc coating on B100 in the absence and presence of different additives.

The results in Figure 3 show that the conversion treatment in the oxalic acid solution increases the corrosion resistance of the zinc in the soybean biodiesel when subjected to 30 days of immersion. The results also show that in the presence of the additives analyzed, the corrosion rate of both the Zn and ZnOx coating decreases, showing that they act as corrosion inhibitors. However, in the presence of the additive, the effect of the conversion treatment on the corrosion resistance of the zinc coating depends on the nature of the additive. Thus, with the addition of extracts of ginger, stone breaker, and especially rosemary and turmeric, however, with the addition of clove extract, the conversion treatment practically did not affect the corrosion rate.

The corrosion inhibition efficiencies of the additives are illustrated in Figure 4. Curcumin, ginger and quercetin extracts with an average inhibition efficiency between 94.6% and 95.6% for ZnOx samples are the best performing additives. In a previous work[23], in which the performance of natural additives in inhibiting the corrosion of carbon steel in soybean biodiesel was evaluated, it was found that the extracts of rosemary and curcumin show better performance, the addition of 1000ppm of these additives resulted in average inhibition efficiencies between 60.5% to 61.8%, while the ginger and the stone breaker extracts show a lower performance with an average inhibition efficiency of 55.5% and 50.5%, respectively. These results therefore show that the metallic surface affects the behavior of the additive as a corrosion inhibitor and that in a zinc coating with the analyzed additives it is possible to achieve inhibition efficiencies higher than that of carbon steel. Figure 4 shows that the classification of additives in relation to corrosion inhibition efficiencies changes with the coating conversion treatment. This indicates that the presence of the zinc oxalate layer due to the conversion treatment affects the corrosion inhibition mechanism of the additive.

Ginger extract is the additive that provides the lowest corrosion rate for zinc coating treated (ZnOx) and the corrosion rate of this coating in the presence of this additive was compared with the corrosion rate of carbon steel in the absence of the additive, and with the corrosion rate of the zinc coating not subjected to the conversion treatment. Figure 5 shows these corrosion rates, which were obtained after 30 days of immersion in B100 in the absence and presence of 1000 ppm of ginger extract.

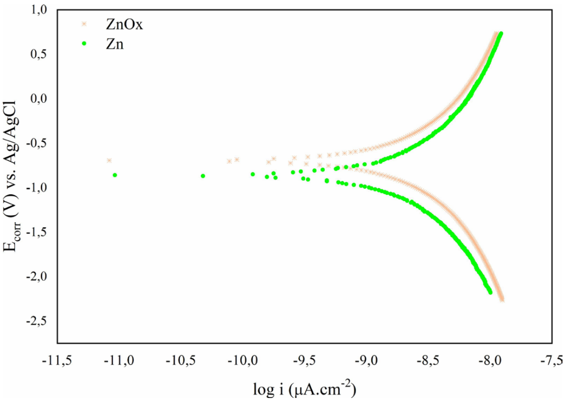

Figure 2. Potentiodynamic polarization curves in soybean biodiesel of Zn coating not subject (Zn) and subject to the conversion treatment (ZnOx). The curves were obtained at a temperature of 25 °C, at a sweep rate of 10 mV/s.

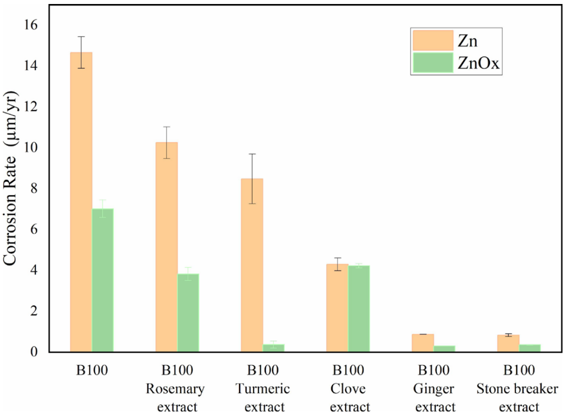

Figure 3. Corrosion rate of zinc coatings not subject (Zn) and subject to the conversion treatment (ZnOx). The corrosion rate was determined after 30 days of immersion in B100 biodiesel in the absence and presence of 1000 ppm of different additives.

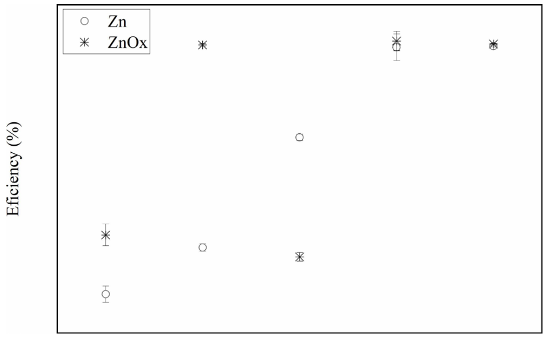

Figure 4. Corrosion inhibition efficiency in B100 solution of additives on zinc coating not subject (Zn) and subject to the conversion treatment (ZnOx).

As can be seen in Figure 5, the results show that even with the conversion treatment and with the addition of the additive, the corrosion rate of steel is lower than that of Zn coating, which indicates that this coating continues to exercise cathodic protection of the steel substrate. Due to the presence of discontinuities in the Zn coating, it is essential that this coating acts as an anode in relation to the steel substrate. Therefore, the optimum condition of galvanized steel in relation to corrosion is a corrosion resistance immediately below the steel substrate.

The present work shows that the conversion treatment in oxalic acid and the addition of 1000 ppm in the biodiesel of ginger extract allows the galvanized steel to present a corrosion resistance in the soybean biodiesel close to the optimum condition. The conversion treatment and addition of ginger extract results in a minimum corrosion rate of $2.42.10^{-8}$µm / yr against a maximum corrosion rate of $2.35.10^{-8}$ µm / yr of steel)

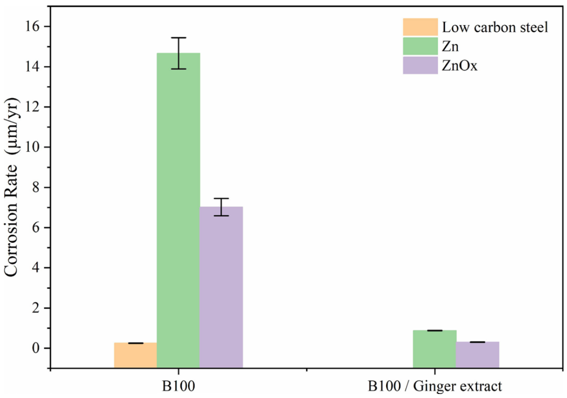

Figure 5. Corrosion rate after 30 days of immersion in B100 in the absence and presence of 1000 ppm of extract ginger as an additive. Corrosion rate corresponds to the following samples: low carbon steel; zinc coating subject to the conversion treatment; and Zn coating not subjected to this treatment.

3.3. Structural characterization

Figure 6 shows the XRD diffractograms of the untreated (6-A, 6-B) and treated (6-C, 6-D) zinc coatings before (6-A, 6-C) and after (6-B, 6-D) exposure for 30 days in B100 biodiesel. Peaks of zinc (phase I) are present in all diffractograms, related to the metallic zinc coating (Zn). The presence of Fe peaks (phase II) corresponding to the carbon steel substrate can also be observed, which is related to the presence of discontinuities in the zinc coating.

Figure 6 shows that the immersion of the Zn coating in the B100 biodiesel did not alter the phases present in the sample not subject to the treatment in oxalic acid (Figures 5A and 5B). In the samples subject to oxalic acid treatment, the peaks of hydrated zinc oxalate ($ZnC_2O_4.2H_2O$) (phase III) (2θ angles at 18.5 °, 22.6 ° and 30.2 °) are present (Figures 6C and 6D). This indicates that this treatment caused the deposition of the zinc oxalate layer on the zinc surface, and that this layer remains after the sample has been exposed for 30 days in B100.

In the diffractogram corresponding to zinc coatings after exposure in the B100 (Figure 6D), zinc hydroxide carbonate ($Zn_5(CO_3)_2(OH)_6$) or hydrozincite (phase IV) (2θ angles 40.95 ° and 58.15°) and of zinc carbide ($ZnCO_3$) (phase V) (2θ angles 25°, 37° and 51°) can also be seen. The presence of these phases was also found in a sample of zinc after being immersed in Pongamia pinnatta biodiesel[37]. In the diffractograms corresponding to zinc coating treated in oxalic acid and before immersion in B100 (Figure 6D) the presence of a peak at 2θ angle 40.95° can be seen, which corresponds to phase III, and a peak at 2θ angle 32°, which indicates the presence of zinc oxide (ZnO) (phase VI), respectively. XPS results show that before immersion in the corrosive solution, the oxalate layer is bonded to the zinc oxide[26].

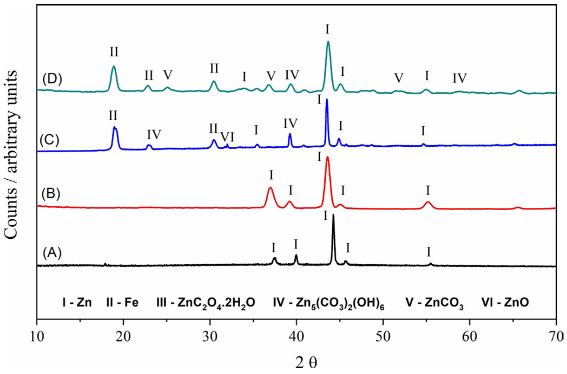

Figure 6. XRD diffractograms of the zinc coating untreated and treated by in oxalic acid solution, before and after exposure for 30 days in B100 biodiesel: (A) Coating untreated before exposure; (B) Coating untreated after exposure; (C) Coating treated before exposure; (D) Coating treated after exposure.

The reactions leading to the corrosion products identified on the surface by X-ray diffractograms (Figure 6) are indicated in Equations 1-6. Studies on corrosion behavior of zinc generally refer to NaCl and NaOH solutions, and it has been proposed that for a slightly acidic NaCl solution (pH 6.5) the cathodic oxygen reduction reaction occurs in the presence of water[26,38,39]. Therefore, it is plausible that in the biodiesel analyzed in the present work with neutral pH the corrosion of zinc proceeds via oxygen reduction in aqueous medium and via the oxidation of zinc.

$$O_2 + 2H_2O + 4e^- \rightarrow \mathbf{4OH^-} \quad (1)$$

$$\mathbf{Zn \rightarrow Zn^{2+} + 2e^-} \quad (2)$$

$$\mathbf{Zn^{2+} + 1/2O_2 \rightarrow ZnO} \quad (3)$$

$$\mathbf{Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2} \quad (4)$$

The formation of zinc hydroxide carbonate and zinc carbonate initially involves the absorption of atmospheric carbon dioxide into the surface electrolyte as shown in Equation 5.

In later stages the carbonate ions react with the zinc cations forming the zinc carbonate (Equation 6) and the hydrogen carbonate ions (formed in Equation 7) react with the zinc hydroxide resulting in the formation of the zinc hydroxide carbonate as shown in Equation 8[38,40].

$$CO_2 + 2OH^- \rightarrow \mathbf{CO_3}^{2-} + \mathbf{H_2O} \tag{5}$$

$$\mathbf{Zn}^{2+} + \mathbf{CO_3}^{2-} \rightarrow \mathbf{ZnCO_3} \tag{6}$$

$$\mathbf{CO_3}^{2-} + \mathbf{H_2O} \rightarrow \mathbf{HCO_3}^{-} + \mathbf{OH}- \tag{7}$$

$$5Zn(OH)_2 + 2\mathbf{HCO_3}^{-} + 2H+ \rightarrow Zn_5(OH)_6(CO_3)_2 + 4H_2O \tag{8}$$

In order for zinc hydroxide carbonate and zinc carbonate to form, it is necessary to have a minimum CO_2 content in the atmosphere that is in contact with the solution, in which the Zn is immersed. It has been reported[41] that zinc hydroxide carbonate is not formed on the Zn electrode immersed in NaCl solution when the CO_2 concentration in the atmosphere is less than 5 ppm.

In the sample not treated with oxalic acid, no peaks corresponding to zinc hydroxide carbonate and zinc carbonate are observed after this sample was immersed in B100 (Figure 6B). The absence of these peaks indicates that the amount of CO_2 absorbed by B100 biodiesel during the 30 day immersion was not sufficient to enable the formation of zinc hydroxide carbonate. The presence of zinc hydroxide carbonate and zinc carbonate in the samples treated in the oxalic acid solution indicates that contact with the oxalic acid introduced carbon in the Zn coating allowing the formation of these compounds. Zinc carbonate was only observed after immersion in B100, which indicates that the immersion of the zinc coating for a certain time in B100 was necessary for the formation of this compound.

Although the qualitative evaluation of the potentiodynamic polarization curves indicates a greater corrosion resistance of the coating subject to the conversion treatment, it must be considered that the difference between these curves is very small. This observation contrasts with the fact that the mass loss tests indicate a significant difference in the corrosion resistance between the samples not subject and subject to the conversion treatment. This apparent contradiction may be related to the immersion time of the samples. It is possible that in the samples subject to the polarization test there was not enough time for the formation of zinc compounds to provide a significant increase in the corrosion resistance of the samples subject to the conversion treatment. Therefore, the potentiodynamic polarization curves and the mass loss tests indicate that the effect of the conversion treatment on the corrosion resistance of the zinc coating depends on the immersion time of the sample in the biodiesel. This effect should be better analyzed in a future work.

3.4. Morphology

SEM micrographs of zinc coatings, untreated and treatment in oxalic solution before and after immersion for 30 days in B100 biodiesel in the absence of additive, are shown in Figure 7 (7-A a 7-D). The untreated zinc coating (Figure 7A) is composed of hexagonal particles, which is typical of coatings obtained from deposition baths with zinc chloride and without additives[42]. The morphology of the zinc coating treated in the oxalic solution (Figure 7B) consists mainly of prismatic particles, which is typical of the zinc coating containing porous zinc oxalate[26]. With the immersion of the samples in the B100, the zinc dissolves with the consequent formation of corrosion products, which alters the morphology of the coatings Figures 7C and 7D show that the oxalic-treated coating has a smoother and more regular surface in relation to the untreated coating. This morphology of treated coating indicates a smaller surface area in contact with the corrosive environment, which favors the corrosion resistance of the coating.

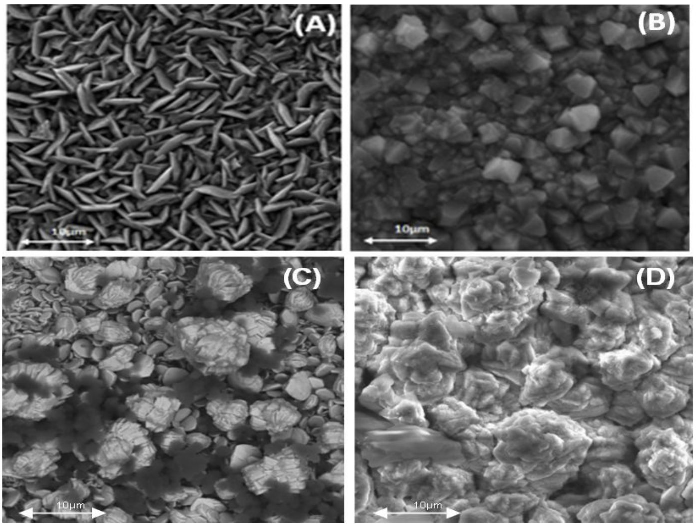

Figure 7. SEM micrographs of zinc coatings, untreated and treatment in oxalic solution before and after immersion for 30 days in B100 biodiesel in the absence of additive: (A) untreated before immersion; (B) treated before immersion; (C) untreated after immersion; (D) treated after immersion.

Figure 8 shows the SEM micrographs of ZnOx after immersion for 30 days in B100 in the absence (Figure 8A) and in the presence (8-B, 8-C, 8-D, 8-E, 8-F) of 1000 ppm of different additives. In the presence of additives, the images show a more uniform surface in relation to the surface immersed in biodiesel without additives. This indicates a lower presence of corrosion products as a consequence of higher corrosion resistance caused by the additives presence.

4. Discussion

As previously seen in the introduction, the increased corrosion resistance of zinc in the 0.1 M NaCl solution due to the treatment with oxalic acid is attributed to the effect of the zinc oxalate layer in promoting the formation of a more protective zinc chloride hydroxide film [26]. With the dissolution of zinc oxalate in the NaCl solution, this layer is replaced by the simonkolleite layer, which has a higher corrosion protection capacity than the simonkolleite layer formed in the absence of treatment with oxalic acid. It has been reported[43,44] that the zinc hydroxide chloride layer and zinc hydroxide carbonate formed in NaCl solution in the absence of zinc oxalate are porous and therefore do not act as a passive protective film. However, zinc chloride hydroxide acts as a protective layer against corrosion in the presence of zinc oxalate. Therefore, it is possible that zinc hydroxide carbonate, as well as zinc carbonate, also acts as a protective layer in the presence of zinc oxalate.

Unlike the 0.5 M NaCl solution, in which the presence of zinc oxalate is no longer observed after 5 days of immersion in the solution[26], in the B100 biodiesel the presence of zinc oxalate is identified after 30 days of immersion (Figure 6), indicating a greater resistance to the dissolution of zinc oxalate in B100. In the present work, it is likely that the zinc oxalate layer acts as an anchor for corrosion products formed from the dissolution of the zinc base during immersion in the B100. It is possible that the zinc hydroxide carbonate and zinc carbonate identified in the sample treated with oxalic acid (Figure 6) are formed from the dissolution of the zinc base and fill the pores of the zinc oxalate layer forming a barrier against corrosion. In the absence of Zn oxalate, the presence of these compounds should occur with less intensity due to the absence of anchoring caused by Zn oxalate.

The results obtained in the present work show that the immersion time of 30 days during which the sample was exposed to B100 was sufficient for the presence of corrosion products to be effective in protecting against corrosion. However, in a future work, XPS measurements will be carried out to detect the presence of possible corrosion products in the zinc oxalate layer that may favor the increase in corrosion resistance.

The effect of corrosion inhibitors on biodiesel is attributed both to the formation of a protective monolayer or multilayer on the metal surface[16-18,45] and to the reaction of the additive with the oxidation products of biodiesel resulting in a reduction in the corrosivity of biodiesel[18,46].

The protective layer, which is formed through the adsorption of the inhibitor components on the metal surface, covers the active sites on metal surfaces and thereby suppresses the corrosion attack of biodiesel[16,17]. However, in addition to the chemical structure of the inhibitor, the adsorption of inhibitor molecules on metal surface also depends on the surface charge of metal, and the nature of biodiesel[19].

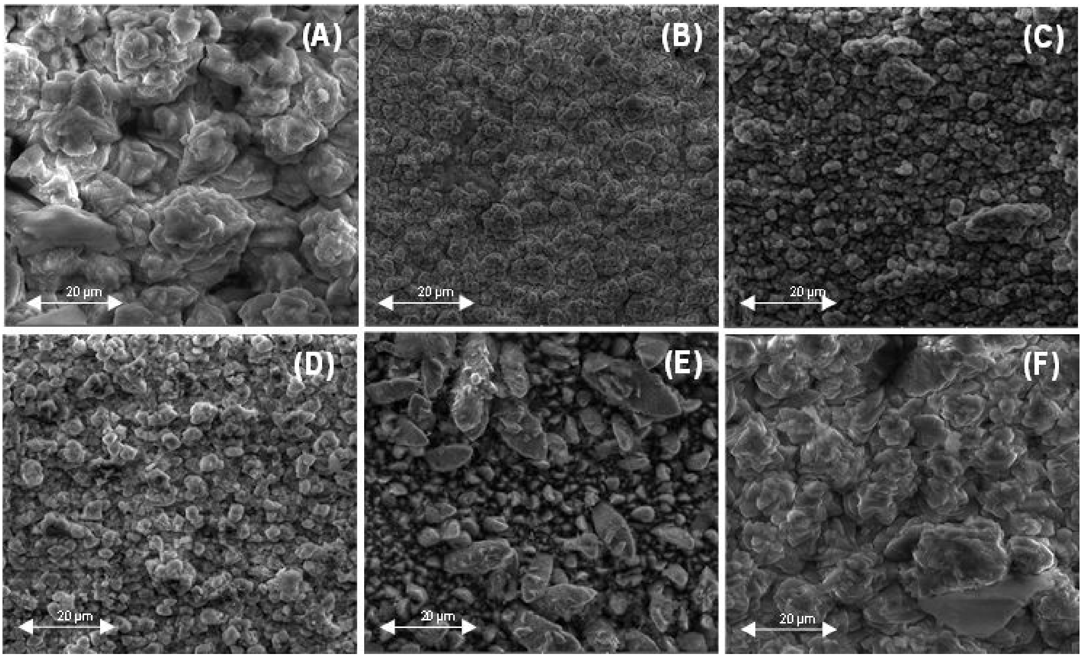

Figure 8. SEM micrographs of zinc coatings treatment in oxalic solution and immersion for 30 days in B100 in the absence and presence of 1000 ppm of different additives: (A) absence of additive; (B) presence of turmeric extract; (C) presence of ginger extract; (D) presence of stone breaker extract; (E) clove extract; (F) rosemary extract.

The corrosion inhibitor molecules in biodiesel are adsorbed to the active sites of the metal through the transfer of electrons from the atom of the inhibitor to the vacant orbital electron of low energy in the metal surface to form a co-ordinate type link[47,48].

In the present work, the presence of the OH group contained in the analyzed additives (Figure 1) may have been sufficient to form a corrosion-protective adsorbed layer on metal surface in soybean biodiesel[16,38], which made it possible to decrease the corrosion rate of the zinc coating. In extracts of turmeric, ginger, and stone break that exhibit the highest corrosion inhibition efficiency (η), the formation of the protective layer can also occur through the electrons present in the oxygen which implies a greater donating electron and consequently in a more protective adsorbed layer[19,20]. On the other hand, the clove extract that contain only the hydroxyl group attached to its aromatic ring exhibit a lower η.

As seen in item 3.2, the fact that the effect of the conversion treatment on the corrosion resistance of the zinc coating depends on the presence of the additive indicates that the alteration of the zinc coating surface due to the presence of zinc oxalate affects the performance of the additive as an inhibitor. This dependence of the inhibitor effect on the metal surface was also found in other studies[45,48], which indicate that the performance of the additive as a corrosion inhibitor depends on the surface of the metal in contact with biodiesel. It has been found[48] that in biodiesel palm PY and BHT exhibit greater inhibition efficiency of copper corrosion compared to mild steel, and that PY exhibits greater inhibitor efficiency in Cu while BHT exhibits greater η in mild steel. However, it is not clear how the metal surface is related to the performance of the corrosion inhibitor in biodiesel.

The adsorption of the inhibitor on the metal surface can occur through the transfer of electrons from the inhibitor atom to the vacant orbital electron of low energy in the metal surface. Therefore it is possible that in a metal that exhibits a low energy orbital with a greater electron vacancy, the adsorption of inhibitor may be favored. However, the mechanism through which the interaction between the inhibitor and the metal surface occurs is complex and several factors can affect this. In the present work, this interaction is particularly complex because the zinc surface is covered by the zinc oxalate layer containing corrosion products.

It has been proposed[47] that in the active region a chemisorption is the dominant adsorption effective for corrosion protection and a good inhibitor must have strong affinity for the bare metal atoms. However, in passive region where the metal surface is extensively oxidized, the inhibitor's performance is related to its ability to form hydrogen bonds with the oxide or hydroxide species on the metal surface. It is possible that the zinc oxalate layer with the pores blocked with the corrosion products acts as a passive film with an extensively oxidized surface, occurring the formation of hydrogen bonds between the hydroxyl of the inhibitor and the oxygen of the surface metal. However, it is necessary to carry out additional studies in future work to clarify the interaction mechanism between the additives and the surface of the zinc coating analyzed in the present work.

Based on the results obtained in the present work, it is possible that the conversion treatment in oxalic acid solution can improve the corrosion resistance of zinc-based coatings containing elements such as Ni and compounds such as $CaCO_3$ – ESP that increase the corrosion resistance of the zinc coating on biodiesel. It has been found[49] that coating consisting of Zn-10%$CaCO_3$-ESP double layer, using $CaCO_3$ derived from eggshell waste (ESP), exhibits a corrosion resistance in biodiesel superior to that of Zn coating. Therefore, in a future work we plan to analyse how the conversion treatment in the oxalic acid solution affects the corrosion resistance of deposits such as Zn-Ni and Zn-10%$CaCO_3$-ESP double layer.

5. Conclusion

The conversion treatment in the oxalic acid solution increases the corrosion resistance of a zinc coating in soybean biodiesel. This behavior is associated with the presence of zinc hydroxide carbonate and zinc carbonate in the zinc coating after 30 days of immersion in biodiesel. It was proposed that these compounds are formed from the dissolution of the zinc base and fill the pores of the zinc oxalate layer forming a barrier against corrosion. It is suggested that the zinc oxalate layer acts as an anchor for of zinc hydroxide carbonate and zinc carbonate and in the absence of Zn oxalate, the presence of these compounds should occur with less intensity due to the absence of anchoring caused by Zn oxalate.

The addition of 1000 ppm of rosemary extract, turmeric extract, ginger extract, clove extract, and stone breaker extract natural additives decrease the corrosion rate of a zinc coating on soybean biodiesel, which indicates that these additives act as corrosion inhibitors under these conditions. This effect is related to the formation of a protective monolayer or multilayer on the metal surface. In extracts of turmeric, ginger, and stone break that exhibit the highest corrosion inhibition efficiency (η), the formation of the protective layer can also occur through the electrons present in the oxygen e no hydroxyl group. On the other hand, the clove extracts that contain only the hydroxyl group attached to its aromatic ring exhibit a lower η.

Regarding additives in biodiesel, the effect of the conversion treatment on the corrosion rate of zinc coating depends on the nature of the additive. With the addition of ginger extract, turmeric extract, stone breaker extract, and especially turmeric extract and rosemary extract, the conversion treatment results in a decrease in the corrosion rate, but when eugenol is added it does not affect the corrosion rate. The lowest corrosion rate of the zinc coating subject to the conversion treatment was obtained with the addition of ginger extract and stone breaker to B100.

The Zn coating, in addition to exerting a barrier effect between the substrate and the aggressive medium, also exerts cathodic protection for the carbon steel substrate. The increase in corrosion resistance due to the conversion treatment and the addition of additives indicates a greater efficiency of the barrier effect. On the other hand, although the conversion treatment and the addition of additives result in a significant decrease in the corrosion rate, this rate remains higher than that of the carbon steel substrate. This behavior is the necessary condition for the Zn coating to cause the reduction of the steel substrate and consequently exert the cathodic protection mechanism in the coating failure sites.

An important contribution of the present work was to show that the procedure that includes the conversion treatment in oxalic acid and the addition of 1000 ppm in the biodiesel of ginger extract allows the galvanized steel to present a corrosion resistance in the soybean biodiesel close to the optimum condition. According to the results obtained the conversion treatment and addition of ginger extract results in a minimum corrosion rate of 2.42.10-8µm / y against a maximum corrosion rate of 2.35.10-8 µm / y of steel. However, an important disadvantage of using the proposed procedure is that a small variation in experimental conditions such as inhibitor concentration can result in a Zn coating with superior corrosion resistance than the carbon steel substrate. In this situation, the coating starts to undergo reduction resulting in galvanic corrosion of the regions of the substrate in the locations of coating failures.

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7. References

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