Research Article

The Use of a Time-Frequency Transform for the Analysis of Electrochemical Noise for Corrosion Estimation


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This work shows the results of evaluating the corrosion type and rate (CR) in the 6061-T6 aluminum alloy exposed to ethanol-gasoline blends (E0, E10, E20, E30, E40, E60, E80, and E100) by analyzing electrochemical noise (EN) signals using the Shannon energy (SSE) and the synchrosqueezing transform (SST). The obtained results are compared against the obtained with the statistical method (Location Index, LI). The results obtained with the SSE method showed that the corrosion type in the 6061-T6 aluminum alloy is classified better than using the statistical method. Moreover, the SST results showed that the corrosion rate increased with the increment of the ethanol content in the ethanol-gasoline blends from values in the order of $10^{-4}$ to $10^{-3}$ mm/year.

1. Introduction

Since the nineteenth century, gasoline and diesel began to be used in internal combustion engines (ICE) as fuels. These fuels are noncorrosive because they have low water content and are also not miscible with water. Corrosion problems appear due to the addition of water and other substances to fuels or their existence in crude oil before refining [1–3]. Nowadays, it is possible to use different fuels to feed an ICE, for example, bioethanol, biodiesel, and anhydrous ethanol mixed with gasoline, among others [4, 5]. Due to the corrosion effects or mechanical problems that biofuels or anhydrous ethanol can cause in an ICE, researchers Reddy et al. and Kaul et al. [6, 7] presented investigations on the mechanical and corrosion effects of using biofuels in an ICE, respectively. An advantage of using ethanol to fuel internal combustion engines lies in the possibility of producing it from biomass (bioethanol) [8].

The corrosion caused by ethanol (even blended with other fuel, such as gasoline) depends mainly on the amount of azeotropic water, acetic acid, and chloride ions that may contain [9, 10]. One of the leading damages caused by ethanol is stress corrosion cracking (SCC), especially in containers for storage and transportation [11]. This is due to the ethanol moisture content that can increase after exposure to humid environments (due to its high hygroscopicity). In some cases,
damage caused by corrosion may occur within one year of equipment use [12].

Using ethanol-gasoline blends, such as E10 or E20, does not cause considerable corrosion in metals. However, higher ethanol content, for example, E80 and E100, may cause corrosive effects that could be serious in metallic parts (especially in steel) and light alloys. Therefore, it is necessary to use metallic coatings or protection processes in fuel tanks, such as nickel plating [9, 13].

In the literature, several works have focused on analyzing the effects of exposing metallic materials to ethanol-gasoline blends under different conditions, such as increasing the ethanol content, adding water, or determining which of its components can aggravate the metal corrosion [14]. The corrosion study of metallic materials in alcoholic solutions, such as ethanol, is a difficult task to perform due to the high resistance of the alcoholic solutions. Sometimes, an electrolyte is necessary to perform the analysis [15].

In the study by Jafari et al. [15], the authors investigated the corrosion caused by water-free and water-contaminated gasoline containing ethanol (0, 5, 10, and 15%) in metallic components (low carbon steel, medium-carbon steel, copper (Cu), aluminum (Al6061), stainless steel 304 (SS), and brazing alloy) of a fuel delivery system. The authors used electrochemical impedance spectroscopy (EIS) for performing the corrosion analysis without adding any supporting electrolytes.

In the study by Lou et al. [16], the authors conducted a study to understand the effect of the chemical composition of fuels (chloride, water, pH, and oxygen level), as well as other control parameters on the behavior of Stress Corrosion Cracking (SCC) of an X-65 carbon steel pipe in simulated ethanol fuel. The authors used the slow strain rate test (SSRT) and open circuit potential (OCP) measurements for the analysis. The authors evaluated the surface and the cracks with a light microscope and SEM. The authors concluded that chlorides strongly affect SCC initiation and growth. The higher concentration of chloride leads to a higher crack density and velocity. The addition of water to the ethanol influences the surface passivation in simulated fuel-grade ethanol (SFGE). SCC to pitting corrosion transition was above 2.5% water concentration in SFGE. Moreover, the authors demonstrated that pH is a critical factor influencing the SCC susceptibility with alkaline SFGE inhibiting SCC initiation in carbon steel. Also, strain rate affects the SCC behavior of carbon steel, showing that a slower strain rate causes an increased crack length and a higher crack density but lower crack velocity. Finally, inclusions of alumina and silicate in X-65 steel acted as early crack initiation sites due to the higher local plastic deformation beginning near the inclusions.

In the study by Ferreira et al. [17], the authors studied the effects of ethanol, sulfuric acid ($\text{H}_2\text{SO}_4$), and chlorides on the corrosion resistance of AISI 316L SS using potentiodynamic polarization and EIS to perform the analysis. In the solution containing 65 wt.% ethanol and 35 wt.% water, the corrosion potentials were higher than those obtained in an aqueous solution. Moreover, the steel corrosion potentials were affected due to the sulfuric acid ($\text{H}_2\text{SO}_4$) and sodium chloride (NaCl) addition. In solutions with and without ethanol, plus 0.35 wt.% NaCl, the presence of 1 wt.% H2SO4 inhibits the pitting corrosion. In the study by Bhola et al. [18], the authors studied the corrosion effects in the A36 steel exposed to ethanolic solutions of 1%, 3%, 5%, 7%, and 10% water volume. The authors used electrochemical tests, such as OCP, EIS, and potentiodynamic polarization. For evaluating, pitting in the metal was used the SEM analysis. The authors concluded that the water content in ethanol with values from 3 to 10% promotes corrosion.

Research works related to Al alloys exposure in ethanol-gasoline blends were conducted [19, 20]. Peña-Ballesteros et al. [19] evaluated the corrosion of duralumin in gasoline and bioethanol blends. The authors performed tests using the EIS, Tafel polarization, and gravimetry (for 28 days) techniques. Duralumin showed susceptibility to intergranular corrosion. The corrosion rate resulted inversely proportional to the concentration of bioethanol and the exposure time. The corrosive process of duralumin tends to passivate. The weight loss curves and electrochemical tests demonstrated this fact. The analyses showed that the current intensity was relatively small. The maximum corrosion rate calculated was $2.28 \times 10^{-2} \text{mpy}$, classifying the mixtures as a low corrosive medium. The same corrosion type was estimated by analyzing the current densities. The maximum limit was $5.1383 \times 10^{-2} \mu\text{A/cm}^2$. The predominant factor of the corrosion existence is the presence of impurities from bioethanol, such as acetic acid, and the aging of the blend that generates organic acids, accelerating the duralumin corrosion. Baena et al. [20] evaluated the aggressiveness of an ethanol-gasoline blend (E20) on metallic materials commonly used in auto parts: Al of silicon 4032, chromed steel DIN 93 X 45 CSR1, SS DIN X 50 CrNnNiN 229, carbon steel 1005, electrolytic copper (Cu) (99%), Al, and pure tin (99%). According to the mass loss, only the carbon steel is prone to corrosion of the E20 blend. From the EIS tests, the carbon steel and Cu presented corrosion. However, it must be taken into account that, in addition to possible corrosion damage, materials such as aluminum and its alloys are also prone to wear or deformation caused by high temperatures or the vibrations and shocks to which they are exposed [21, 22]. Therefore, it is necessary to develop analyses additional to those of corrosion in materials.

On the other hand, Matějovský et al. [23] tested the laboratory-prepared ethanol-gasoline blends E10, E25, E40, E60, and E85, which were artificially oxidized independently during their induction period. The authors used the oxidized fuels for evaluating their corrosion aggressiveness after their thermal load in the presence of oxygen or after the expiry of their shelf life. The authors used steel, copper, aluminum, and brass to analyze corrosion properties by EIS and Tafel curve analysis. The highest corrosion rate was present in mild steel, copper, and brass exposed to the E60 oxidized blend. Moreover, for ferrous metals, acidic substances act as corrosion agents. Concerning steel and aluminum, the authors observed an increase in the corrosion rates as the total acid number of fuels increased. Furthermore, for copper and its alloys, acidic substances were weaker corrosion agents than the peroxides due to a low amount of peroxides causing
significant corrosion effects. The oxidation products can influence the fuels’ conductivity and the corrosion course. Both electrochemical methods (polarization and EIS) proved to be complementary and adequate to measure the properties of the metal-fuel systems based on ethanol. The EIS is a method applicable even in low-conductive environments such as petrol and fuels with lower contents of ethanol that do not exhibit properties of an electrolyte.

Whereas, the authors in [24], evaluated the corrosion in metals used for auto parts manufacturing. The stainless steel, tin, carbon steel, and copper, were exposed to pure bioethanol (E100) and bioethanol-gasoline blends (E30, E50, and E85). The authors presented EIS curves under static conditions at 45 °C. According to the EIS results, the most susceptible metals to corrosion were copper and carbon steel in all blends. The stainless steel and tin showed high values of Rt (transfer resistance obtained from the second arc of the EIS measurements) in all media. Thus, these metals can be considered compatible with ethanol-gasoline blends, even at high ethanol concentrations.

Recently, Ramos-Negrón et al. [25, 26] introduced the use of the Stockwell Transform (ST) and the Shannon energy for analyzing electrochemical noise signals to identify the corrosion type in 6061-T6 Al in different solutions (H2SO4, at 15% v/v, NaCl at 3.5% v/v, and demineralized water) at two different temperatures (NaCl 3.5% v/v at 22 °C and 75 °C). The authors concluded that the combination of the ST and SSE techniques provides excellent results for identifying the corrosion type. Whereas, Rocabruno-Valdés et al. [27] performed a corrosion analysis to identify the corrosion type. The authors analyzed the 6061-T6 Al alloy in bioethanol obtained from sugarcane (E100), regular gasoline (E0), and bioethanol-gasoline blends (E5, E10, E20, and E85 (85% v/v bioethanol). The authors applied three mathematical tools to perform the corrosion analysis, the statistical method, Fast Fourier transform, and ST. The results showed that ST is a powerful tool capable of determining the corrosion resistance, corrosion type, and kinetics of the process.

As shown in the literature review, there are different investigations about the corrosion effects caused by using ethanol. Most of the researchers performed optical analysis or mass loss analysis, and those who use electrochemical techniques do not fully include the electrochemical noise (EN).

As shown in the literature review, the corrosion effects caused by using ethanol have been studied widely by several authors. Most of the researchers performed optical analysis or mass loss analysis, and those who use electrochemical techniques do not fully include the electrochemical noise (EN). Therefore, in this work, a corrosion analysis in an aluminum alloy exposed to ethanol-gasoline blends through the synchrosqueezing transform (SST) and the Shannon Energy (SSE) is presented and evaluated. The synchrosqueezing transform and the Shannon Energy methods are new proposals used to identify the corrosion type and rate in the study by Arelano-Pérez et al. [28]. These methods have proven to be effective in establishing the corrosion type and rate in solutions with high resistance and with slight variations in ethanol content.

2. Methods and Materials

This section describes the methods and materials used to develop this research.

2.1. Electrochemical Noise. The electrochemical noise (EN) technique studies the spontaneous fluctuations of electrochemical potential noise and electrochemical current noise (EPN, ECN) in an electrode exposed to a corrosive media. This technique works under open circuit potential conditions without needing an external polarization that can influence the electrochemical reaction. Therefore, this technique is considered a noninvasive online technique used for monitoring corrosion in different fields [29–31].

It is possible to apply the EN technique in two-phase environments: organic and aqueous phase, as in the case of the water-oil blend because it is a sensitive technique. The EPN and ECN signals can be measured simultaneously by three nominally identical working electrodes (WE), or it is possible to use a configuration of two working electrodes and one reference electrode (RE) of a different material. The first pair of electrodes measure the EPN, and the second pair measures the ECN, having a common electrode. Measuring or recording the EN is a simple task (in appearance), but analyzing the signals is not an easy task [32–34].

2.2. Materials and Experimental Procedure. Probes of 6061-T6 Al alloy in E0, E10, E20, E30, E40, E60, E80, and E100 ethanol-gasoline blends are analyzed to perform the corrosion analysis. The reasons for selecting the 6061-T6 Al alloy to perform this work are due to the 6061-T6 Al alloy being the most common and widely used, among its applications are the aerospace and automotive manufacturing parts. Moreover, the 6061-T6 Al alloy has high corrosion resistance. On the other hand, the 6061-T6 Al alloy has been studied previously by different authors [15, 35, 36], allowing to use of the previously published research to validate the present investigation. The chemical composition of the 6061-T6 Al alloy used to make the working electrodes was determined by Energy Dispersive Spectroscopy, Table 1.

A block diagram of the procedure for estimating the corrosion type, as well as the corrosion rate, is shown in Figure 1, consisting of the following steps (1) Carry out the preparation of the working electrodes (WE) and the reference electrode (RE). The WE are two Al electrodes, and RE is an electrode of silver/silver chloride (Ag/AgCl) in potassium chloride (KCl) 3.5 M. (2) After the WE and RE preparation, they are encapsulated in epoxy resin, sanded, cleaned, and dried. (3) Each probe is immersed in a different solution of ethanol-gasoline blends (E0, E10, E20, E30, E40, E60, E80, and E100). (4) The data acquisition system is configured and started. The sample rate is set up to one data per second, measuring the first 1024 samples of each hour (17.0667 minutes) for 24 hours. (5) Analyze the electrochemical signals with the statistical method and SST-SSE for estimating the corrosion type and rate. Finally, (6) the results are analyzed to carry out the conclusion.
2.3. Synchrosqueezing Transform. The synchrosqueezing transform (SST) is a time-frequency algorithm proposed by Daubechies and Maes [37]. This algorithm was introduced in the context of signal analysis because it reallocates the coefficients resulting from a continuous wavelet transformation based on frequency information for obtaining a concentrated image on the time-frequency plane, for extracting the instantaneous frequencies [38]. Therefore, the SST can decompose a time-variant signal $h(t)$ into its fundamental components, with stability under noise disturbances. The SST presents a good time-frequency resolution and a good decomposition analysis [39].

Consider that $h(t)$ has the form

$$h(t) = \sum_{j=1}^{N} A_j \cos \omega_j(t) + \epsilon(t), \quad (1)$$

where $A_j(t)$ is the time-variant amplitude, $\omega_j(t)$ is the instantaneous frequency, and $\epsilon(t)$ is the measurement error. Recovering the amplitude and the instantaneous frequency for $j = 1, \ldots, N$ [40].

The first step is to calculate the continuous wavelet transform (CWT) coefficients $W_h(\alpha, \beta)$ of the signal $h(t)$ for estimating the instantaneous frequencies. Defining the CWT of a signal $h(t)$ as follows:

$$W_h(\alpha, \beta) = \frac{1}{\sqrt{\alpha}} \int h(t) \psi^\ast \left( \frac{t-\beta}{\alpha} \right) dt, \quad (2)$$

where $\alpha$ is the scale, $\beta$ is the time offset applied to the mother wavelet $\psi$, and $\ast$ is the complex conjugation.

According to Daubechies et al. [39], the instantaneous frequency $\omega_h(\alpha, \beta)$ is obtained by differentiating $W_h(\alpha, \beta)$ at each point $(\alpha, \beta)$:

$$\omega_h(\alpha, \beta) = \begin{cases} \frac{-j}{W_h(\alpha, \beta)} \frac{\delta}{\delta \beta} [W_h(\alpha, \beta)], & |W_h(\alpha, \beta)| < 0, \\ \infty, & |W_h(\alpha, \beta)| = 0. \end{cases} \quad (3)$$

Next, using the procedure known as "synchrosqueezing," the CWT coefficients are reassigned to the time-frequency domain transferring the CWT from the time domain to the time-frequency plane, converting every point $(\beta, \alpha)$ into $(\beta, \omega_h(\alpha, \beta))$ [39].

$$T_h(\omega, \beta) = \frac{1}{\Delta \omega} \sum_{\alpha_k} W_h(\alpha_k, \beta) \alpha_k^{-3/2} \Delta \alpha_k, \quad (4)$$

Table 1: Chemical composition (wt.%) of the 6061-T6 Al.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.15</td>
<td>2.03</td>
<td>0.28</td>
<td>0.79</td>
<td>0.01</td>
<td>0.31</td>
<td>0.03</td>
<td>Rest</td>
</tr>
</tbody>
</table>

Figure 1: Diagram of the experimental procedure for estimating the corrosion type and corrosion rate.
where $\Delta \omega = \omega_i - \omega_{i-1}$ and $\Delta \alpha_k = \alpha_{k-1} - \alpha_k$. Finally, the SST can be inverted to obtain the original signal $h(t)$ [41].

2.4. Shannon Energy. The SSE estimates the energy of the local spectrum for each sample, emphasizing the energy located at medium amplitudes [42]. One of the main application areas of the SSE is the analysis of heart signals [43, 44]. However, in earlier studies [25, 26, 28], it was applied to perform corrosion analysis with excellent results. To calculate the SSE, (5) is applied [45].

$$SSE(i) = -\sum_{j=1}^{N} \sum_{n=f_{\text{min}}}^{f_{\text{max}}} ||S(j, n)||^2 \log ||S(j, n)||^2,$$

where $i$ is the number of frequencies ranges, $f_{\text{min}}$ is the initial value, and $f_{\text{max}}$ is the final value of each frequency range, respectively.

2.5. Corrosion Rate Calculation. The noise resistance ($R_n$) is defined as the relation between the standard deviation of EPN ($\sigma_r$) and the standard deviation of ECN ($\sigma_t$) and therefore, $R_n = \sigma_r/\sigma_t$. Because $R_n$ is equivalent to the polarization resistance ($R_p$), $R_p$ can be replaced in (6) by $R_n$, resulting in (7) [46–49]:

$$R_p = \frac{B}{i_{\text{corr}}},$$

$$i_{\text{corr}} = \frac{B}{R_n},$$

where $i_{\text{corr}}$ represents the current corrosion density and $B$ is related to the cathodic ($\beta_{\text{c}}$) and anodic ($\beta_{\text{a}}$) Tafel slopes of the system.

Therefore, the corrosion rate can be obtained by applying (8) [50]:

$$CR = k \left( \frac{W_{\text{eq}}}{\rho} \right),$$

where $k$ is a constant (see Table 2); $\rho$ and $W_{\text{eq}}$ are the density and the equivalent weight of the alloy, respectively.

3. Results and Discussion

This section presents the results of the electrochemical noise signals analyses performed with the statistical method, the synchrosqueezing transform, and the Shannon energy to estimate the corrosion type and rate. The experimental tests were repeated three times for each blend for ensuring repetitively.

3.1. Corrosion Analysis Using the Statistical Method. Figure 2 presents the results of the localization index (LI) calculus from the EN records. The LI is the quotient of the standard deviation of the ECN signals and the root mean square (RMS) of the ECN signals [51, 52]. The LI results showed that almost all the blends cause localized corrosion in the material. The E30, E60, and E80 blends in the first four hours of the test caused mixed corrosion, but only the material in the E80 until time 18 h approximately had mixed corrosion. The results obtained with the statistical method are not conclusive because according to Jafari et al. and Baena et al. [15, 20], pure gasoline and ethanol-gasoline blends with low ethanol content cause passivation or uniform corrosion in the 6061-T6 Al alloy. Therefore, this research presents the SST and the SSE methods to calculate the corrosion type in 6061-T6 Al alloy.

To estimate the corrosion rate (CR), $R_n$ is calculated from the records of EPN and ECN signals. The EPN and ECN signals are filtered using the least-squares approximation to remove the DC drift because the statistical method applies only to stationary signals [32, 53]. For calculating $i_{\text{corr}}$, $B$ is taken equal to 0.026 V. Finally, (8) is used to calculate CR.

Figure 3 shows the CR results. The CR values obtained from the Al alloy exposed to pure gasoline (E0) are the lowest, in order of $10^{-5}$. Also, the figure shows that the CR values increase gradually as the ethanol content increase in the blends. As shown in the figure, the CR values in the Al exposed to E0 decrease as time increases. On the other hand, the CR values in the Al exposed to E80 and E100 increase as time increases, highlighting that the E100 blend causes the highest CR values.

3.2. Corrosion Analysis Using the Synchrosqueezing Transform and Shannon Energy. According to Arellano-Pérez et al. [28], the ECN signals give information related to corrosion type. Therefore, each ECN record (of each blend) was analyzed using the SST and the SSE in different frequency ranges. The SST toolbox developed by Eugene Brevdo [39, 54] was used with a Morlet type of wavelet and 64 voices. Table 3 shows the frequency ranges used for the SSE analysis.

Figure 4 shows the results of the SST-SSE analysis using the ECN signals obtained from analyzing the 6061-T6 Al alloy exposed to each ethanol-gasoline blend. Each box plot in the figure represents 72 records associated with each analysis performed. The figure shows how the ethanol content increases the SSE levels (energy). Note that E0 showed the lowest energy levels. On the other hand, E80 and E100 presented the highest energy levels. The SSE of the samples exposed to the blends with the lowest and highest ethanol content decreased and increased, respectively, at frequency ranges from 3.9–7.8, 1.9–3.9, and 0.9–1.9 mHz.

Arellano-Pérez et al. [28] established the thresholds to define each corrosion type in the 6061-T6 Al alloy exposed to standard solutions using the SSE analysis. In the present analysis, the thresholds previously established are considered as references to compare the effects of the ethanol-gasoline blends in the 6061-T6 Al alloy. Figure 5 shows the results of this comparison. The blue, black, and red thickest lines represent the SSE values obtained in the study by Arellano-Pérez et al. [28], continuous lines represent the maximum values, and the dashed lines represent the minimum values of SSE. Between the blue, black, and red dashed and continuous lines are the areas of localized, mixed, and generalized corrosion, respectively. The figure shows in thin
Table 2: Values of $k$ for the CR calculus.

<table>
<thead>
<tr>
<th>CR</th>
<th>$i_{corr}$</th>
<th>$\rho$</th>
<th>$k$</th>
<th>Values of $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mpy</td>
<td>$\mu A/ \text{cm}^2$</td>
<td>g/ cm$^3$</td>
<td>Mpy $g/ \mu \text{a cm}$</td>
<td>0.1288</td>
</tr>
<tr>
<td>mm/year</td>
<td>$\mu A/ \text{m}^2$</td>
<td>kg/ m$^3$</td>
<td>mm kg/ a m year</td>
<td>327.20</td>
</tr>
<tr>
<td>mm/year</td>
<td>$\mu A/ \text{cm}^2$</td>
<td>g/ cm$^3$</td>
<td>mm g/ $\mu \text{a cm year}$</td>
<td>$3.27 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Figure 2: Results from the LI analysis carried out on the 6061-T6 Al alloy exposed to ethanol-gasoline blends.

Figure 3: Results of the Corrosion Rate (CR) carried out by the calculation of the noise resistance $R_n$.

Table 3: Frequency ranges used for evaluating the ECN signals.

<table>
<thead>
<tr>
<th>Number of range ($i$)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{\text{min}}$ and $f_{\text{max}}$ (mHz)</td>
<td>250 to 500</td>
<td>125 to 250</td>
<td>62.5 to 125</td>
<td>31.3 to 62.5</td>
<td>15.6 to 31.3</td>
<td>7.8 to 15.6</td>
<td>3.9 to 7.8</td>
<td>1.9 to 3.9</td>
<td>0.9 to 1.9</td>
</tr>
</tbody>
</table>
continuous and dashed lines the maximum and minimum SSE values, respectively, corresponding to the analysis of the 6061-T6 Al alloy exposed to the ethanol-gasoline blends by each one of the frequency ranges. The results showed that the values of the SSE at frequencies from 3.9–7.8, 1.9–3.9, and 0.9–1.9 mHz, the E20, E30, E60, E80, and E100 blends tend to mixed corrosion and the SSE values tend to passivation or generalized corrosion at higher frequencies.

Now, applying the SST method, the corrosion rate is calculated. This analysis was developed by considering an equivalence between the noise resistance $R_n$ and the spectral noise resistance $Z_n$ defined in (9), where $\Psi_V$ and $\Psi_I$ are the power spectral density of potential and current, respectively [55, 56]. For calculating the $Z_n$, the EPN and ECN signals are analyzed directly with the SST without filtering the signals because the SST can work with nonstationary signals [57–59]. Two matrices by each record are obtained by analyzing EPN and ECN with the SST. The matrix columns represent the results in the time domain and the matrix rows in the frequency domain. Next, the standard deviations of the values in the last column of each matrix are calculated. These data sets correspond to the highest time instant (1024 s), knowing that $f = 1/t_m$, where $t_m$ is the sample time and the frequency value will be the minimum. Therefore, $Z_n$ is calculated with equation (9). Then, $R_n$ is substituted by $Z_n$ in equation (6) to calculate the corrosion rate.
Figure 6 shows that the CR values calculated with $Z_n$ are in the same order as those calculated with $R_n$. The lowest CR values belong to the Al samples exposed to E0. However, adding low ethanol contents (E10 and E20), the CR values increment in two decades, and at higher ethanol contents (E80 and E100), the CR values increased three decades.
The corrosion type was calculated using the minimum and maximum values of ECN. The results from analyzing the minimum values of ECN showed that the corrosion type in the 6061-T6 Al alloy exposed to the E0, E10, E20, E30, E40, E60, E80, and E100 was generalized corrosion. Whilst the probes of Al exposed to E0 (pure gasoline) and E100 (pure ethanol) had the lowest and highest energy levels (SSE) in all frequencies, respectively. These results are consistent with those obtained from the literature (see Table 5). Moreover, the results obtained from analyzing the maximum values of ECN showed that the corrosion type in the 6061-T6 Al alloy was uniform at the highest and medium frequencies. Whilst the samples in ethanol-gasoline blends E20, E30, E40, E60, E80, and E100 at the frequencies ranges 3.9–7.8, 1.9–3.9, and 0.9–1.9 presented mixed corrosion, highlighting that there was no detected localized corrosion.

On the other hand, two methods were evaluated for calculating the CR. The first method uses \( Rn \), and the second one consists of applying the SST method and using \( Zn \). The results from analyzing the Al alloys in E0 were \( 7.278 \times 10^{-7} \text{mm/year} \) and \( 9.257 \times 10^{-7} \text{mm/year} \), for the first and second methods, respectively. Jafarian et al. [36] calculated a corrosion rate in aluminum exposed to E0 of \( 8.20 \times 10^{-6} \text{mpy} \) (2.082 \( \times 10^{-7} \text{mm/year} \)). This result is similar to the one obtained in the present work. However, further analysis is required to validate the SST method.

4. Novelty and Application

The main novelty of this work lies in the application of the SST and SSE to estimate the corrosion type and rate, analyzing the electrochemical noise signals from a probe of 6061-T6 Al alloy exposed to ethanol-gasoline blends. These methods showed to be effective for establishing both the corrosion type and the corrosion rate in solutions with high resistance and with slight variations in the ethanol content. As a potential application, the SST and SSE can be integrated into embedded systems for estimating the corrosion type and rate in metallic materials exposed to different fuels, especially those obtained from biomass, such as oils, bioethanol, or biodiesel. These because the SST allows analyzing time-varying signals without removing the DC trend.

5. Conclusions

The conclusions of the analysis of the corrosion type and rate in an 6061-T6 Al alloy exposed to ethanol-gasoline using the SST and SSE methods are presented below.

1. From the comparison between the SSE results against the localization index, the conclusion was that the SSE method provides better corrosion type identification because this method gives localized corrosion in the probes exposed to E0 (pure gasoline).
2. The corrosion rate was calculated by the statistical method and the SST method. Both results were similar, reaching the same order of magnitude. However, further analysis with other materials is required to validate the SST method.
3. The analysis of the EN signals using the SST and SSE allowed verifying how the ethanol content increases the corrosion effects in the 6061-T6 Al alloy. The results showed material passivation using pure gasoline and mixed corrosion using ethanol-gasoline blends.

Data Availability

The electrochemical signal data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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