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EVALUATION OF CORROSIVE PROCESSES, OF 304 STEEL IN BIODIESEL ENVIRONMENT, BY ELECTROCHEMICAL NOISE TECHNIQUE

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Abstract. *The concern with the emission of greenhouse gases in the atmosphere led to the development of biofuels, as a way to reduce the use of fossil fuels. Despite its promising use, the apparent corrosion of metal parts in contact with the biofuel makes a better understanding of its oxidative behavior necessary. The analysis of its behavior is of interest, for example, in storage before distribution to the market and also during regular use, avoiding the utilization of corrupted biofuel. Thus, this work aims to evaluate the effectiveness of using the electrochemical noise technique to monitor the corrosion of AISI 304 stainless steel in a system that emulates a biodiesel storage tank and its use at 60ºC. This technique is relatively new and promising, providing real-time monitoring of the phenomenon by detecting the spontaneous and potential current fluctuations that the electrochemical interaction presents. In this study, a hermetically insulated and temperature-controlled electrochemical cell was built, using commercial biodiesel B10 as an electrolyte and electrodes for capturing the noise data proposed in stainless steel AISI 304. After collecting the experimental data, it could be verified that the electrochemical noise technique, together with the proposed data processing methods, is feasible when evaluating the modification tendency of the corrosive process and its intensity in a material during its exposure to the corrosive environment.*

Keywords: *Biofuel, biodiesel corrosion, corrosion monitoring, electrochemical noise technique*.

1. INTRODUCTION

Due to the increase in greenhouse gas emissions caused by human activity, one of the main research fronts in recent decades has been the development of biofuels. The aviation, naval, and land transport sectors are identified as some of the main actors in this problem, due to the consumption of fossil fuels, such as special kerosene and diesel oil. This situation resulted in the development of alternative fuels from renewable sources such as aviation biokerosene and biodiesel, for example, in addition to providing state and institutional incentive initiatives, with scientific consequences.

The different characteristics of biodiesel compared to diesel oil make it an excellent alternative. In addition to being produced from renewable sources, biodiesel has advantages in terms of pollutant emissions, storage safety, and the absence of sulfur in the fuel, enabling the partial or total replacement of diesel oil by this biofuel (Ajala et al., 2015), with use supported by local law, such as in Brazil. Biodiesel was introduced into the Brazilian energy matrix by law in 2005 as a blend of 2% biodiesel as diesel, then called B2 (Presidency of the Republic Civil House Subchefia for Legal Affairs, 2005).

The logistics of its use became a topic of interest in this context, highlighting its storage and interaction with the different metallic materials present in a compression ignition cycle engine, whether for vehicles or stationary (Singh et al., 2012), thus resulting in concern about its corrosivity.

Biodiesel is not considered a corrosive material, but due to characteristics such as hygroscopicity and low oxidative stability, its corrosion capacity may change over time and result in aggression to the materials that are in contact, leading it to be considered more corrosive than diesel oil in some studies. Note that, as it is hygroscopic, it can accumulate residual water in itself, which in turn favors the development of colonies of microorganisms whose metabolic behavior results in acidification of the environment, that is, acidification of biodiesel.

Fuel from a renewable, biodegradable, sulfur-free source and considered to be of low toxicity, biodiesel is composed of monoalkyl esters of long-chain fatty acids obtained from vegetable oils or animal fat through the transesterification or esterification reaction (Haseeb et al., 2011). It is noteworthy that biodiesel can be used directly in diesel engines and produce less dirty burning when compared to petroleum diesel, as it emits fewer polluting gases such as sulfur oxide (Sundus et al., 2017).

Among the logistical problems that biodiesel inherently brought with its greater use, there is the corrosion of metallic alloys. Corrosion is a destructive attack on a material caused by a reaction to the environment that is involved. Many aqueous environments promote corrosion due to many complex conditions in production and processing systems, for example, pipelines and storage tanks. The corrosion process is made up of four elements: the anode, which is the site of the corrosive metal; the electrolyte, which is the corrosive medium that allows the transfer of electrons from the anode to the cathode; the cathode that forms the electrical conductor in the cell that is not consumed in the corrosion process and the material susceptible to the process and that conducts the reaction electrons; and the metallic circuit that serves as a bridge for the transit of electrons between anode and cathode.

Previous work (Hoang et al., 2019; Alves et al., 2019; Jin et al., 2015) demonstrated that, although biodiesel does not contain sulfur, unlike petroleum diesel, it is more aggressive to alloys. metallic, highlighting the copper-based alloys that present greater degradation and the stainless steels that are referred to as satisfactory due to the low corrosion rate (Haseeb, 2011; Kugelmeier et al., 2021). Some authors point out that aluminum alloys also have satisfactory performance in the application of tanks, but studies have shown that the corrosion rate is above stainless steel – for corrosion at 80 °C the corrosion rate of aluminum is 0.202 and of stainless steel is 0.015 millimeters per year, respectively (Fazal et al., 2011). By analyzing the use of biodiesel blends in petroleum diesel, it was found that the more biodiesel present, the greater the corrosion rate and the greater acidity, amount of free water, and oxidation products in biodiesel (Alves et al., 2019). With an increase in temperature, the aggressiveness of the biofuel rises to a certain point, where above 60 °C the worsening of corrosivity becomes negligible (Fazal et al., 2011).

Punctiform corrosion is pointed out as the most recurrent for ferrous and non-ferrous metals in biodiesel (Singh et al., 2012). According to Hoang et al. (2019), stainless steels are immune to this type of corrosion in this medium. However, Rocabruno-Valdés et al. (2018) and Alves et al. (2019) claim that this class of steel suffers localized pitting and micro-pitting corrosion.

Essential for the integrity of equipment and the most diverse structures, corrosion monitoring is a sensitive step in any type of industrial operation where techniques are used that can provide information of interest for controlling the phenomenon of corrosion, especially the rate and the type of corrosion. A corrosive process can be monitored using several techniques, each of which has intrinsic characteristics that influence its choice as the most appropriate monitoring method. Among these techniques, emphasis is placed on electrical resistance, using metallic coupons, and electrochemical, with the analysis of electrochemical noise.

Regarding the definition of Electrochemical Noise, the literature presents it as spontaneous current and potential oscillations in a time interval as a result of corrosive reactions in the environment. Such oscillations can be monitored using electrodes, thus constituting the Electrochemical Noise Analysis (ENA), and are associated with the reactions of electrochemical phenomena that occur in the system. There is Electrochemical Potential Noise and Electrochemical Current Noise, where the first is the fluctuation of electric potential between a reference electrode and a relative one, also called the working electrode, and the next is the oscillation in the reaction current. According to Baptista (2018), the electrochemical potential is related to the driving force of the reaction and the corrosion current is associated with the reaction rate of the reaction,

Another important point is that for reading the electrochemical noise of a given reaction system, it is not necessary to use external signals, that is, the entire analysis process takes place in a sensitive way, where the outputs come from purely natural phenomena of corrosion. in the middle (Jambo and Fófano, 2008). This characteristic is considered the greatest advantage of ENA compared to other electrochemical techniques for monitoring and studying corrosion. With everything arranged, it can be stated that the measurement of Electrochemical Noise is relatively simple and that the processing of the data obtained plays a fundamental role in understanding the monitored phenomena. Such data can be worked in such a way that one has the corrosion rate and knowledge of the corrosive species of the process.

According to Mansfeld et al. (1994), the main works on the study of Electrochemical Noise were published in the 1970s and 1980s, coinciding with the greater availability and better technology in electronic equipment necessary for the study of this phenomenon. Because it is relatively recent, the methodology on Electrochemical Noise is still in the development and improvement phase for the most diverse applications, among them the use in monitoring and controlling corrosion. There is already its use in control techniques in a complementary way, but there is still no mass use of this phenomenon as the main source of data for analysis (Mansfeld et al., 1994).

It is expected at the end of this study obtain data that validate the application of the electrochemical noise technique as a tool for monitoring corrosion in stainless steel 304, indicating the behavior of the system at 20 ºC and 60 ºC.

2. MATERIALS AND METHODS

2.1 Electrolyte

Biodiesel B10 was used as an electrolyte in this study, being a mixture of 10% biodiesel in petrodiesel. B10 has a commercial origin, therefore it must follow the current regulations regarding quality, presence of additives, and antioxidants – according to ANP (National Petroleum Agency) Resolution N° 798 of 08/01/2019 and ANP Resolution N° 30 of 06/23/2016– thus ensuring that the phenomenon studied is more accurate when emulating a real use of these fuels.

2.2 Electrochemical cell

The electrochemical cell, illustrated in Figure 1, was constructed in a commercial borosilicate glass 3.3 reagent bottle with an anti-drip ring and polypropylene screw cap, with a capacity of 250 ml (Laborglas – ref. 91801365). The corrosion probe was inserted into the lid of the flask, along with a sealing ring to ensure that the interior of the electrochemical cell was hermetically isolated. In this way, possible interferences related to the materials used in the assembly of the cell were minimized.

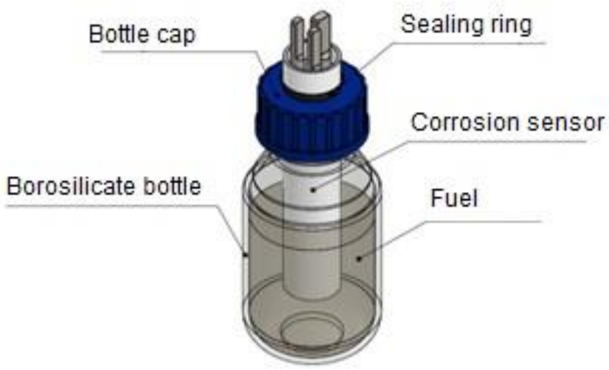

Figure 1. Representation of the electrochemical cell

To capture the electrochemical noise signals of the processes inside the electrochemical cell, a support was created to house the electrodes used, called a corrosion probe, as Figure 2.

In the corrosion probe, a commercial polyvinyl chloride tube, epoxy resin, medium-density fiberboard guide disk, and AISI 304 stainless steel electrodes were used.

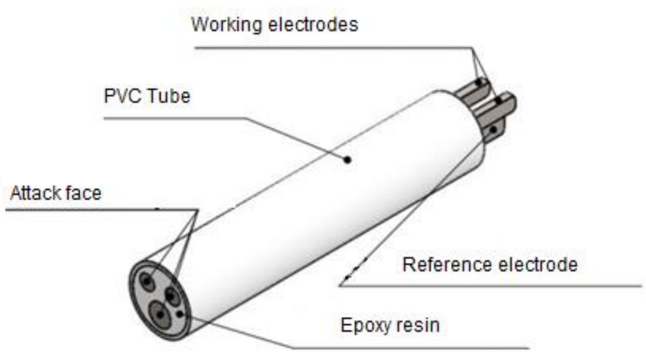

Figure 2. Schematic diagram of the corrosion sensor

AISI 304 stainless steel (diameter = 5/16”; length = 150 mm) was used for the working electrodes and AISI 316 stainless steel was used for the reference electrode (diameter = 3/8”; length = 150 mm). To reduce the presence of contaminants on the surface of the electrodes, they were degreased in an alcoholic solution of potassium hydroxide, followed by washing in distilled water and drying using a hot air blower.

The electrodes were embedded in the epoxy resin in such a way that only the cross-section of one of its ends (attack face) remained exposed to the electrolyte (B10) inside the electrochemical cell, the other end was connected to the electrochemical noise measurement system. After mounting the corrosion probe, the attack face was sanded down to 600-grit sandpaper to even out the surface.

2.3 Test methodology

To evaluate the effect of temperature variation on the corrosion caused by B10 biodiesel on a 304 stainless steel sample, the electrochemical cells were maintained at a constant temperature of 20 °C in the first test and 60 °C in the second test (with the aid of a heating mantle), since after 60 ºC the acceleration in the corrosion rate is minimal (Fazal et al., 2011). Electrochemical noise potential and current data were obtained using a Galvanostat/ Potentiostat/ZRA/Reference 600 (Gamry Instruments), connected to the electrodes of the corrosion probe. Data were acquired with the aid of the ESA 410 software (Gamry Instruments), with the experimental system for collecting electrochemical noise data illustrated in Figure 3.

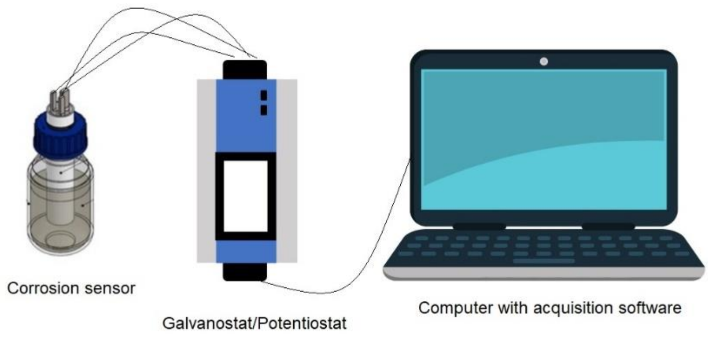

Figure 3. Experimental system for electrochemical noise data collection

Signal acquisitions were performed for periods of 10 min, every 24 hours, for 1752 h (73 days). The electrochemical noise signals of acquired current and potential were treated according to the Reaction Charge methodology. The Reaction Charge of a corrosive process refers to the current fluctuation between two working electrodes, which can be obtained using the integral of the current curve over time (Al-Mazeedi and Cottis, 2004; Abrantes, 2015), according to Eq. (1):

$$Q=\int I\, dt \tag{1}$$

where Q is the reaction load (C cm^{-2}), I is the current noise module (A), and t is the collection time (s). This methodology presents an online and sensitive monitoring and qualitative evaluation of the type of corrosion that occurs on the surface of the electrodes by relating the noise resistance with the frequency of events.

With the information obtained by the electrodes, the Noise Resistance can be arrived at, given by Eq. (2):

$$Rn= \sigma_E/\sigma_I \tag{2}$$

where σ_E is the standard deviation of the potential and σ_I is the standard deviation of the current.

The work of Cottis (2001) proposes that the current should be interpreted as individual charge packets of short duration, where the total charge in a given sampling interval is the sample of a binomial distribution. In case the average of pulses is high enough, this sample can be approximated to a normal distribution making the parameters of average corrosion current (I_{CORR}), average event load (Q_{MED}), and frequency of events (f) possible to be known, these parameters being related by Eq. (3):

$$f=I_{CORR}/Q_{MED}= B^2b/\sigma^2_E \tag{3}$$

Where B is the Stern-Geary coeficiente (26 mV/dec) and b is the equipment operation frequency (500Hz).

3. RESULTS AND DISCUSSION

After collecting potential and current electrochemical noise data, was evaluate the number of corrosion events during the experiments. Figures 4 to 6 show the results of the frequency of events versus noise resistance for the two systems in 216 h (beginning of the experiment and first peak of the corrosion rate at 20 ºC), 1076 h (highest corrosion rate at 60 ºC) and at 1752 h (end of the experiment).

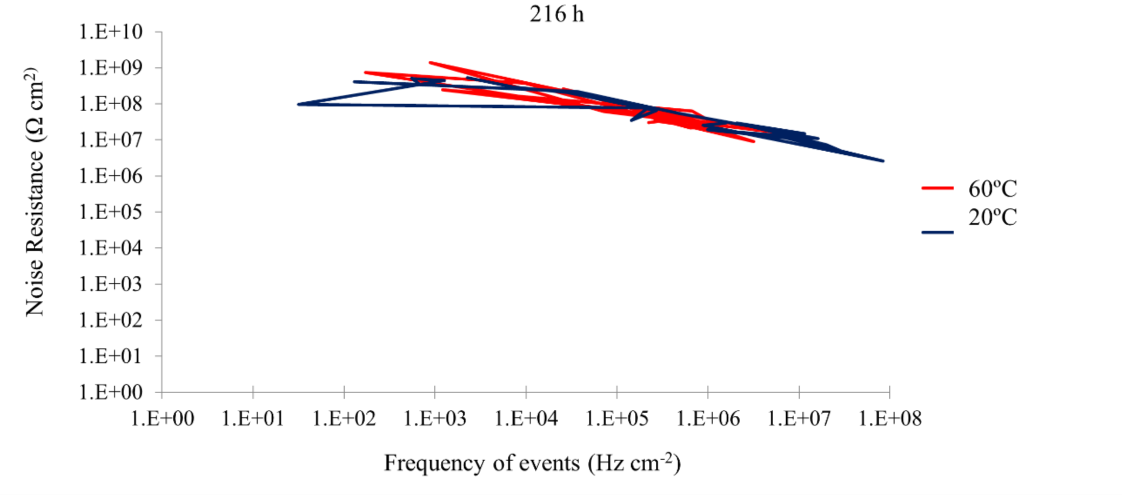

Figure 4. Frequency versus Noise resistance for the system at 20 ºC and 60 ºC after 216 h of experiment, B10 biodiesel, 304 stainless steel electrodes

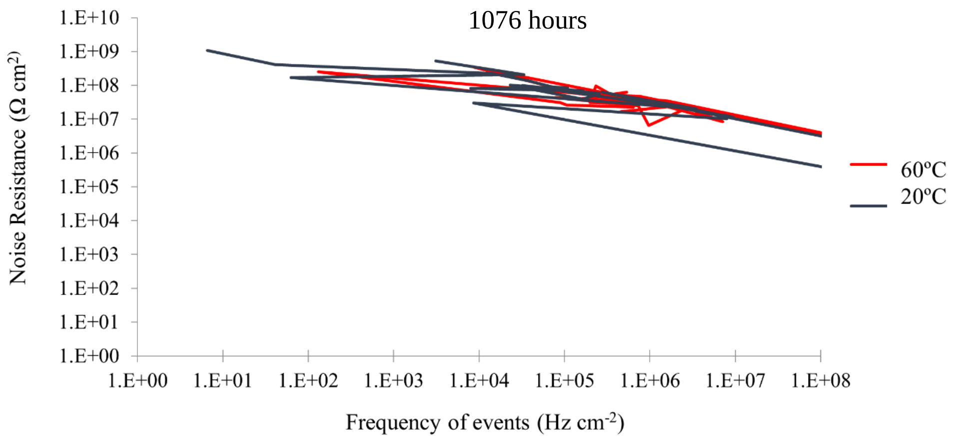

Figure 5. Frequency versus Noise resistance for the system at 20 ºC and 60 ºC after 1076 h of experiment, B10 biodiesel, 304 stainless steel electrodes

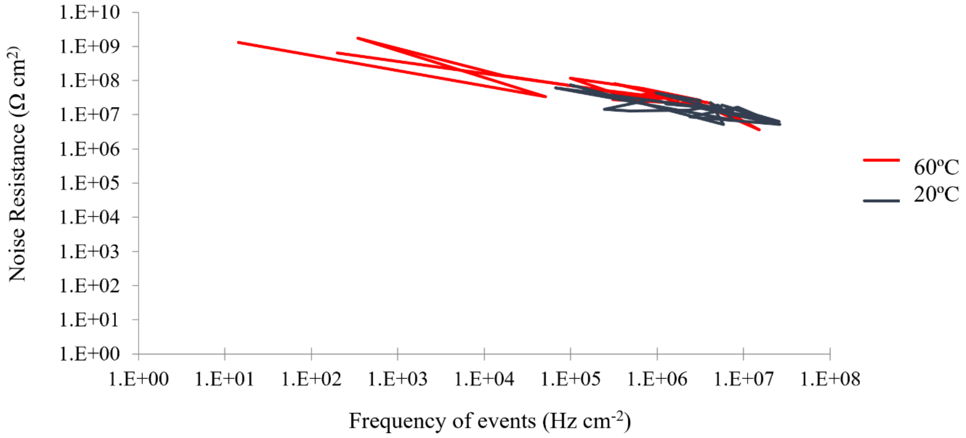

Figure 6. Frequency versus Noise resistance for the system at 20°C and 60°C after 1572 h of experiment, B10 biodiesel, 304 stainless steel electrodes

Figures 4 and 5 show that the frequency of events is more concentrated in the same noise resistance region for the two temperatures studied. Thus, it can be said that the system suffers generalized corrosion. However, with the advancement of the experiment time, a trend of displacement of the frequency of events at the temperature of 60 ºC was observed (Figure 6), which may indicate, in this case, the beginning of localized corrosion, which may have more serious consequences than generalized corrosion, as it is more difficult to detect, prevent, and control.

4. CONCLUSIONS

The experimental system used allowed the evaluation of the influence of temperature increase, from 20 to 60 ºC, on the corrosion process in stainless steel 304 by B10 biodiesel. The electrochemical noise analysis technique was efficient for the determination of the prediction of the corrosive scenario, for static systems. The maid was sensitive to the conditions used, indicating different modes of corrosion of the material – generalized and localized.

5. ACKNOWLEDGMENTS

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