Sustainable Development of Palm Oil: Synthesis and Electrochemical Performance of Corrosion Inhibitors

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ABSTRACT

Palm oil production is among the highest worldwide, and it has been mainly used in the food industry and other commodities. Currently, a lot of palm oil production has been destined for the synthesis of biodiesel; however, its use in applications other than the food industry has been questioned. Thereby for a sustainable development, in this paper the use of palm oil of low quality for corrosion inhibitors synthesis is proposed. The performance of the synthesized inhibitors was evaluated by using electrochemical techniques such as open circuit potential measurements, linear polarization resistance and electrochemical impedance spectroscopy. The results indicate that the fatty amides from palm oil are excellent corrosion inhibitors with protection efficiencies greater than 98%. Fatty amides molecules act as cathodic inhibitors decreasing the anodic dissolution of iron. When fatty amides are added, a rapid decrease in the corrosion rate occurs due to the rapid formation of a molecular film onto carbon steel surface. During the adsorption process of the inhibitor a self-organization of the hydrocarbon chains takes place forming a tightly packed hydrophobic film. These results demonstrate that the use of palm oil for the production of green inhibitors promises to be an excellent alternative for a sustainable use of the palm oil production.

Keywords : Palm oil, Sustainable development, Corrosion inhibitor, Fatty amides, Electrochemical techniques

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1. Introduction

Palm oil tree is one of the oleic sources with the highest oil yield per unit of cultivated area. From the whole fruit, the palm oil can be obtained from both the mesocarp and the seed (nut). The oil obtained from the mesocarp is red due to the presence of carotenoids, and is a rich source of vitamins, co-enzymes and sterols. The higher quality oil is used primarily in the food industry, and the oil of lower quality (inedible) is used for the production of soap, candles, cosmetics, biofuels, and other commodities [1-3]. Palm

oil has unique characteristics; such as a similar content of both saturated and unsaturated fatty acids (50:50), being the palmitic acid the main saturated fatty acid, and the oleic acid the major unsaturated fatty acid [2]. The use of palm oil for applications other than food is of great interest because it has the highest balance of fossil energy and the lowest production cost relative compared to other commodities [4]. In this sense, the use of palm oil of low quality for the synthesis of corrosion inhibitors promises to be a good alternative to diversify its applications.

For economic reasons, the transport of many industrial fluids is done through steel pipes. However, due to the aggressive nature of many industrial fluids, steel pipes are exposed to corrosion processes that

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reduce its useful life. Corrosion affects the structural integrity of materials due to degradation processes occurring between the metallic surface and an aggressive environment. One way to reduce corrosion damage is the dosage of chemicals defined as corrosion inhibitors. Corrosion inhibitors can be organic or inorganic substances. In particular, corrosion inhibitors of organic nature have in its structure two essential components; a polar end (rich in electrons) formed by heteroatoms (such as oxygen, nitrogen, and sulfur), with the ability to be adsorbed (through coordination bonds) onto an electrovalent metal surface (since it has additional external electrons to fill the vacant or share with the *d* orbital of the metal surface), and a hydrophobic end (hydrocarbon tail) which can efficiently repel the contaminants of the aggressive electrolyte [5-13]. These kind of organic corrosion inhibitors are widely used in the oil and gas industry to protect the carbon steel pipelines against internal corrosion. Carbon steel is prone to corrosion in brine environments containing CO₂ dissolved. In the oil industry, this is a concern because the water contained in the hydrocarbons can act as electrolyte, solvent, and even as reagent in combination with dissolved gases such as CO₂, O₂, and SO₂ [14]. The organic corrosion inhibitors inhibit the corrosion because they form a protective film onto steel surface. Inhibitors are able to be absorbed as a monolayer or a multilayer (due to overlapping of monolayers) on the metal surface. When the formed protective film is a monolayer we can speak of molecular organic coatings with thicknesses in the order of Angstroms [11].

Since palm oil is one of those of greater world production, and their uses and applications are very diverse. For a better sustainable development of the palm oil production, it is necessary to diversify its uses and applications [3,15]. Even though one of the most successful applications is the synthesis of biodiesel, its production has been plagued by controversy because of its competition with the food scenario. This has led to an increase in the prices of raw materials, and therefore an increase in the production cost of biodiesel [16,17]. Besides the closure of many production plants or reduction of the biodiesel production [17]. It is possible to increase the profitability of a biodiesel production plant if it is considered the alternative synthesis of other higher value-added products from raw materials used for the

production of biodiesel, or biodiesel itself. Even further, using the low quality oil, which by its high content of free fatty acids (FFA), it is not suitable for food use or for the synthesis of biodiesel. A possible alternative is the production of corrosion inhibitors based on the hydrocarbon chains of vegetable oils, which have found to be successful in the field of oil industry [18,19].

In this particular case, it is possible to use palm oil of low grade for the inhibitor synthesis where a purification process is not required, since the byproducts (mainly glycerol) can act as diluents of the main product (inhibitors). In this sense, the production of biodiesel can be considered a primary biorefining process, and the production of other higher value-added products (such as corrosion inhibitors) can be considered as a secondary biorefining process. Thereby this paper considers the use of palm oil as a source of fatty acids for the synthesis of corrosion inhibitors, useful in the oil industry. It was carried out the synthesis of fatty acid amides derived from palm oil, and the evaluation of its performance by electrochemical techniques

2. Experimental Section

2.1 Characterization of Palm Oil

Fatty acids of palm oil were methylated and analyzed by gas chromatography (GC) (150302-ext-01 STE 4981) with a flame ionization detector (FID). Fatty acid methyl esters were prepared as follows; in a flask, 5 g of palm oil was placed and heated at 70°C, then a KOH-methanol solution (0.076 g in 2 mL) was added drop by drop, stirring for 30 min. One microliter of sample was injected into the equipment operated with a split of 50, and a flow 1.8 mL/min, and the separation was carried out in an AT-FAME capillary column (30 m × 0.25 mm 0.25μm), using helium as the carrier gas. The oven temperature was held at 180°C for 15 min, followed by a temperature gradient of 10°C/min up to 230°C, and held for 3 min. Injector and detector temperatures were both 250°C. Peaks of fatty acid methyl esters were identified by matching their relative times with those of commercial standards of fatty acid methyl esters (FAME).

Table 1, shows the fatty acid profile of palm oil. According to the results, oleic and palmitic acid are the main fatty acids present in the oil. Concentration

of unsaturated fatty acids is slightly higher than the concentration of saturated fatty acids. The fatty acid ratio is close to that reported by other sources [2,20-21].

2.2 Synthesis of Fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide

Fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide, (fatty amide), was prepared through the amidation direct of palm oil and hydroxyethyl ethylendiamine, as shown in Fig. 1.

N-(2-hydroxyethyl) aminoethylamine (10.8 g) and palm oil (30 g) was placed in a 250 ml flask in mole ratio of 3:1. Mixture was stirred for 2 hours at 140°C. The reaction progress was followed using thin layer chromatography (TLC) and Fourier transform infrared spectroscopy (FTIR). For the TLC a silica support and a heptane ethyl acetate solution (9:1) as eluent were used. After 2 hours of reaction; it was observed the complete formation of amide. TLC showed complete conversion of the triglyceride to the amide, obtaining a quantitative yield of 15.6 g. However, in order not to increase the production costs, for

the corrosion tests the product was not purified, i.e., the glycerol formed was not separated from the reaction crude. The product was dissolved in isopropanol in a 5:95 ratio (w:w), and in that condition was used in the electrochemical tests.

2.3 Material

For corrosion tests, cylinders of 1018 carbon steel with dimensions of 25 mm long and 5.0 mm in diameter were used. The chemical composition (wt.%) of carbon steel used was 0.190 C, 0.670 Mn, 0.0003 P, 0.001 S, and balance Fe. Prior to the tests, the carbon steel cylinders were ground with grit abrasive paper of silicon carbide up to 600 grain. Subsequently, they were washed with distilled water, acetone and distilled water. Samples with this surface condition were used as working electrode (WE) in the electrochemical tests.

2.4 Corrosive Electrolyte

The corrosion tests were performed in a 90:10 mixture (v/v) of 3% NaCl solution and diesel, respectively. Before the corrosion tests, the mixture was

Table 1. Fatty acid composition of palm oil.

Fatty acids	Structure	Type of fatty acid	Fatty acids (wt%)
Lauric	C12:0	Saturated	0.39
Myristic	C14:0	Saturated	0.78
Palmitic	C16:0	Saturated	35.11
Palmitoleic	C16:1	Unsaturated	0.35
Stearic	C18:0	Saturated	4.32
Oleic	C18:1 <i>n</i> -9 cis	Unsaturated	45.7
Linoleic	C18:2 <i>n</i> -6 cis	Unsaturated	10.06
Alpha-linolenic	C18:3 <i>n</i> -3 cis	Unsaturated	0.23
Arachidic	C20:0	Saturated	0.41

Fig. 1. Synthesis of fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide. R = alkyl chains of fatty acids of palm oil.

saturated by bubbling CO₂ for 2 hours, and the CO₂ bubbling was maintained throughout the test, at 50 °C, and gentle stirring. Once the mixture was saturated with CO₂, the working electrode was immersed into electrolyte for 1 h before the injection of the inhibitor. The inhibitor concentrations evaluated were; 0, 5, 10, 25, 50 and 100 ppm.

2.5 Electrochemical Measurements

The electrochemical tests performed were the following; measurements of open-circuit potential (OCP), linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). The tests were performed in a three electrode electrochemical cell. As reference electrode was used one saturated calomel with a Luggin capillary bridge and, as counter electrode a graphite rod was used. LPR measurements with a sweep of -20 to 20 mV respect to open circuit potential, and a scan rate of 1 mV/s were performed. LPR and OCP measurements were performed every 60 minutes for 24 hours. Electrochemical impedance spectroscopy (EIS) measurements were performed using AC signals of 10 mV peak to peak amplitude (in the open circuit potential) in a frequency range from 100 kHz to 1 mHz. For the electrochemical measurements a 1000 Gamry Interface Potentiostat/Galvanostat/ZRA analyzer was used.

3. Results and Discussion

3.1 Synthesis of Fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide

Amide synthesis was performed in a single reaction step. The aminolysis reaction was performed directly on the triglyceride, without performing the trans-esterification of palm oil [22]. Dinesh Kumar et al. [23] reported in 2015, the synthesis of fatty acid amides in one step from triglycerides using sodium doped calcium hydroxide as a nanocrystalline heterogeneous catalysis, in their work the total conversion of the amide was a function of the amount of the catalyst and excess amine used at 110°C. Other methodologies have reported the use of catalyst for the reaction of aminolysis of oils [24-25]. However, the methodology proposed in this study reports the total conversion of triglycerides to fatty amides without using an excess of amine and solid catalyst, simply by increasing the temperature to 140°C. The kinetic reaction showed that at 2 hours of reaction, the total

conversion of triglyceride to amides was performed.

The use of IR spectroscopy is ideal for characterizing triglycerides and their reaction products as a whole. Fig. 2 shows the infrared spectra of the fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide derived from palm oil. Four characteristic bands are exhibited for the fatty amide, which are known as amide bands. The sharp and strong band in 3304 cm⁻¹ is assignment to N-H stretch of secondary amide, very sharp band at 1637.5 cm⁻¹ corresponds to C=O stretch of secondary amide, very strong band at 1556.5 cm⁻¹ for N-H deformation, and broad band at 1440 cm⁻¹ for stretching C-N amide. The strong and broad band of 3100 cm⁻¹ to 3650 cm⁻¹ is assignment to O-H stretch. The methyl and methylene group appear at 2920 cm⁻¹ and 2852 cm⁻¹ for C-H stretch and about 1464 cm⁻¹ for CH₂ scissors vibration. For the secondary amine is observed a very weak band at 3415 cm⁻¹ for N-H stretch, and at 1118 cm⁻¹ a medium band for C-C-N bending. At 1053 cm⁻¹ a very strong band for C-O stretch in primary alcohols is observed. Finally, at 719 cm⁻¹ is observed the CH₂ rocking in methylene chains. However the formation of glycerol is not as evident by this technique.

In order to determine the kinetic profile and product yield of the synthesis of the fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide, five samples were taken and analyzed to times: 0 min, 30 min, 60 min, 90 min, and 120 min. Fig. 3 shows the FTIR spectra of the synthesis of fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide a different reaction times. Spectra evolution clearly shows the hidroxyethylethenamide

Fig. 2. Infrared spectra of Fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide.

Fig. 3. Infrared spectra evolution of the aminolysis reaction kinetics of palm oil.

Fig. 4. Comparison of infrared spectra for pure palm oil and fatty amide.

formation (1637 cm^{-1}), and how the characteristic bands of the ester group disappear (1743 and 1159 cm^{-1}) indicating the remaining long chain triglyceride. Fig. 4 shows a comparison of the FTIR spectrum of pure palm oil after completion of the

reaction at 140°C . It can be observed that the broad bands between $3500\text{--}3000\text{ cm}^{-1}$ as the bands at 1556 cm^{-1} y 1444 cm^{-1} appear, and how the bands for methyl and methylene groups at $3000\text{--}2800\text{ cm}^{-1}$ are maintained. For simplicity hereafter the fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide will be referred as fatty amide.

3.2 OCP Measurements

OCP variation versus time for 1018 carbon steel immersed in CO_2 -saturated (3% NaCl + 10% diesel) mixture with and without fatty amide at 50°C , is shown in Fig. 5. It can be seen that, in the absence of inhibitor (0 ppm), the OCP values slowly change to more positive values, this indicates the formation of a protective oxide film onto metal surface which provides some corrosion protection. However, in the presence of inhibitor, in all cases was observed a sharp drop in the OCP values during the first four hours after that the inhibitor was added, later the OCP values showed only slight variations. In presence of inhibitor, the nobler potential value was observed with the addition of 100 ppm, and the more active potential value was obtained with the addition of 5 ppm. It is known that an increase in the OCP values is associated to the formation of a passive film, as well as a decrease in the OCP values may be due either to breakdown, dissolution, or no formation of the passive layer, furthermore, constant values of OCP are associated to the absence of corrosion due to the presence of a protective layer [26]. The observed trends in Fig. 5 indicate that carbon steel continuously tends to form a protective layer, but without actually stabilize. Because the formation of a protective film is associated with the corrosion of a metal surface, then it can be inferred that the carbon steel was continuously corroded. On the other hand, the sharp drop in OCP values, when inhibitor was added, can be associated to a change in the chemical equilibrium of the system due to the presence of an alkaline compound (fatty amides). Subsequent to this, the OCP values indicate the formation of a passive layer due to the inhibitor adsorption onto metallic surface. According to the OCP values, it is probable that the inhibitor concentration of 100 ppm favors greater protection. In all cases, in the presence of inhibitor, the drop in OCP values respect to the blank behavior is greater than 350 mV. This difference indicates that fatty amides act as cathodic inhibitors. It has been

Fig. 5. Change of the OCP values as function of testing time for 1018 carbon steel in CO₂-saturated (3% NaCl + 10% diesel) mixture, with and without fatty-amides of palm oil at 50°C.

reported that if the shift in the OCP value is ± 85 mV, the inhibitors can be classified of type either anodic or cathodic, and otherwise mixed-type [27-29]. Therefore, the fatty amides palm oil act by decreasing the anodic dissolution of iron, and this is possible due to the adsorption of a protective film which acts as a barrier preventing aggressive ions reach the metal surface.

3.3 LPR Measurements

Polarization resistance (R_p) for 1018 carbon steel immersed in CO₂-saturated (3% NaCl + 10% diesel) mixture with and without fatty amide at 50°C is shown in Fig. 6. Polarization resistance was determined by polarizing of the WE ± 20 mV around OCP at a scan rate of 1.0 mVs⁻¹. This small polarization of the working electrode (ΔE) will produce a measurable current flow (ΔI) at the working electrode surface, and the slope of the obtained ratio is the R_p . When the potential perturbation is small (ΔE), the current variation (ΔI) is directly proportional to I_{corr} and hence to the corrosion rate. Polarization resistance is inversely proportional to the corrosion current density, and this relationship together with the values of the Tafel slopes (b_a , b_c) is defined in the Stern-Geary equation.

$$R_p = \frac{b_a b_c}{2.303 I_{corr} (b_a + b_c)} \quad (1)$$

Figure shows that corrosion resistance of carbon steel, in the absence of inhibitor, tends to decrease as the immersion time progresses, indicating that the corrosion products formed not act as a protective bar-

Fig. 6. Change of R_p values as function of immersion time for 1018 carbon steel in CO₂-saturated (3% NaCl + 10% diesel) mixture, with and without fatty-amides of palm oil at 50°C.

rier, and is permeable to the diffusion of aggressive ions. However, when the inhibitor is added, a sudden increase in the corrosion resistance of carbon steel is observed. This behavior is because the inhibitor molecules are adsorbed rapidly onto carbon steel surface by forming a molecular layer that protects it from aggressive ions. It is noted that three or four hours after the inhibitor is added, the corrosion resistance values tend to reach a maximum value depending on the concentration of inhibitor added. With the addition of 5 ppm, it is observed that the corrosion resistance reaches a maximum value and then tends to decrease; this may indicate that the inhibitor concentration added is insufficient to form a continuous protective layer. However, at higher concentrations, corrosion resistance values remain stable or tend to increase slowly. It is noted that by increasing the inhibitor concentration, the corrosion resistance also increase, however, above 50 ppm significant differences are not observed. The presence of oscillations is observed in all curves. These oscillations or instabilities can be interpreted as adsorption-desorption processes of the inhibitor molecules. It is known that when the inhibitor molecules adsorbed exceeds a certain number, the occurrence of electrostatic repulsion forces can cause desorption of the adsorbed molecules, leaving unprotected sites to be subsequently protected again. This can occur due to the interaction with one another of the hydrocarbon chains, change of orientation of the molecules, or to the presence of corrosion processes due to permeation of electrolyte [11,28-32].

Fig. 7 shows the efficiency of inhibition depending

on the concentration of fatty amides. Inhibition efficiencies were calculated from R_p values (Fig. 6) based on the following relation:

$$E(\%) = \frac{R_{p_i} - R_{p_b}}{R_{p_i}} \times 100 \quad (2)$$

Where; R_{p_b} is the LPR without inhibitor and R_{p_i} is the LPR with inhibitor.

From figure it can be seen that although, the corrosion resistance increases by increasing the amount of added inhibitor (Fig. 6), inhibition efficiency achieved is greater than 98% for inhibitor concentrations greater than 5 ppm. In addition, for concentrations above 10 ppm, maximum protection efficiency is achieved 3 hours after the addition of the inhibitor. These values of inhibition efficiency indicate that fatty amides from palm oil have a high affinity for the metal surface; therefore, they are an excellent choice as corrosion inhibitors.

In order to determine the type of interaction between the fatty amide molecules and the metallic surface, adsorption isotherms were determined. It is known that the adsorption of the inhibitor molecules is carried out by a process of substitution with the water molecules adsorbed onto metallic surface. The adsorption isotherms were determined based on the information obtained from the LPR measurements. For this, the experimental data were adapted in agreement with the Langmuir isotherm. This model is the most used and is described by the following equation:

$$\frac{C_i}{\theta} = \frac{1}{K_{ads}} + C_i \quad (3)$$

In this equation C_i is the inhibitor concentration,

Fig. 7. Evolution of inhibition efficiency as determined by LPR measurements.

K_{ads} is the adsorption equilibrium constant and θ is the surface coverage. The degree of surface coverage (θ) was calculated according to:

$$\theta = 1 - \frac{R_{p_i}}{R_{p_u}} \quad (4)$$

Where R_{p_u} are the polarization resistance values without inhibitor, and R_{p_i} the polarization resistance values with inhibitor. The R_p values used for the calculations correspond to the average of the last four hours of the LPR measurements. Fig. 8 shows the graph of the adsorption isotherm. From the plot it is observed that the adsorption process of the inhibitor molecules onto metallic surface obeyed Langmuir adsorption model.

From the value of the ordinate to the origin the adsorption equilibrium constant was obtained, $K_{ads} = 126.58 \times 10^4$, the K_{ads} value imply a high adsorption ability of the fatty amides onto carbon steel surface, and its magnitude reflects a high inhibition efficiency. This agrees with the previously described results. From K_{ads} value the standard free energy of adsorption was calculated according to:

$$K_{ads} = \frac{1}{55.5} e^{\left(\frac{-\Delta G_{ads}^0}{RT}\right)} \quad (5)$$

Where ΔG_{ads}^0 (J mol^{-1}) is the standard free energy of adsorption, R is the gas constant (8.314472 J/K mol), T (K) is the absolute temperature, and 55.5 is the concentration of water in the solution. Generally, the ΔG_{ads}^0 value is associated with the adsorption process of the inhibitor molecule, being that values less than -20 kJ mol^{-1} indicate a physisorption process, and values around or higher than -40 kJ mol^{-1}

Fig. 8. Langmuir adsorption isotherm from LPR data.

indicate that the inhibitor molecule shared or transferred electrons to the metallic surface to form a coordinate bonds, which is characteristic of a chemisorption process. According to the calculations, a value of ΔG_{ads}^0 of $-48.56 \text{ kJ mol}^{-1}$ was obtained, indicating that the adsorption of the fatty amides studied occur spontaneously due to strong interactions between the inhibitor molecule and the steel surface by a chemisorption process. During the chemisorption process the molecular film of inhibitor is formed due to the interaction between iron atoms (d orbital) and atoms of the inhibitor molecule such as N and/or O (sp^2 electron pairs).

3.4 Impedance Measurements

Fig. 9 shows the Bode plots for 1018 carbon steel exposed to CO_2 -saturated (3% NaCl + 10% diesel) mixture at 50°C . The interpretation of the Bode diagram is simpler if performed by frequency regions. From Fig. 9 in the high frequency region ($f > 1000 \text{ Hz}$), the typical response of the solution resistance is observed, i.e., the presence of a plateau ($\log |Z|$ vs $\log f$), and phase angle approaching zero (phase angle vs $\log f$) [33-34]. In the region of intermediate frequency ($1000 > f > 1 \text{ Hz}$), the capacitive behavior of the electrode surface is observed, the phase angle values indicate a constant value (around 55°), but with a shift to low frequencies (50 to 10 Hz), on the other hand, the impedance modulus values show a linear relationship with the frequency but with a slope less than -1, besides, the slope tends to decrease as immersion time elapses. These characteristics (slope lower than -1, and phase angle less than 90°) are typical of non-capacitive surface layers where the corro-

sion process can be under mixed control (diffusion and charge transfer). Moreover, the shift towards lower frequencies of the phase angle, as well as decreasing slope, can be associated with a detachment or thinning of the protective layer [9,11,35]. Finally, in the low frequency region ($f < 1 \text{ Hz}$), the dispersion of experimental data is observed, besides the apparent presence of a plateau. The development of apparent plateau shows a decrease in modulus values impedance over time, the phase angle also shows the presence of a new time constant, with a phase angle value lower 10° (low capacitance). It is known that in the low frequency region are detected processes like; charge transfer, mass transfer, adsorption or other relaxation processes that are carried out into the film-electrolyte interface or within the pores of the surface film. According to the observed characteristics, the corrosion resistance of carbon steel decreases constantly and adsorption-diffusion processes are observed. This may be due to absorption of intermediate species (FeOH) derived from the hydrolysis of iron, or due to adsorption of the water-soluble fractions (WSF's) of the diesel [9,11,36].

Fig. 10 shows the Nyquist and Bode plots for carbon steel exposed in the CO_2 -saturated (3% NaCl + 10% diesel) mixture with and without inhibitor at 50°C after 24 hours. From Nyquist plot can be observed the presence of a depressed capacitive semicircle, where the diameter increases by increasing the concentration of inhibitor. In addition, a dispersion of experimental data is also observed at the end of the semicircles (low frequency region). This analysis only shows that the corrosion resistance of carbon steel increases with increasing the concentra-

Fig. 9. Bode plots for 1018 carbon steel in CO_2 -saturated (3% NaCl + 10% diesel) mixture without inhibitors at 50°C .

tion of the added inhibitor. The only analysis of the Nyquist plots has disadvantages that do not allow a correct interpretation of the superficial processes occurring onto working electrode, for example; suppresses and hides the semicircles formed in the high frequency region, and it is not possible to analyze the evolution of the spectra as a function of frequency. Therefore, and especially when the performance of corrosion organic inhibitors is analyzed, it is recommended the analysis from the point of view of the Bode plots. In this way, it is possible observe if the inhibitor is adsorbed onto metal surface (flat or perpendicular adsorption) and if it acts as a barrier between the electrolyte and the metal surface. Otherwise, it possible that the inhibitor only modify the corrosiveness of the electrolyte (change of pH, reaction with corrosives, etc.). Based on the concepts described above (analysis of Fig. 9), from Fig. 10 is possible to observe the following; in the high frequency region ($f > 1000$ Hz), in the presence of inhibitor, the impedance module ($|Z|$) is frequency dependent (not plateau), and the slope of this relationship increases by increasing the inhibitor concentration, at the same time, the evolution of the phase angle ($0^\circ \rightarrow 75^\circ$) is observed. These changes prove the presence of a new time constant in the corresponding region to the electrolyte resistance, and this is caused by the adsorption of a film of oily nature (inhibitor) onto working electrode surface, which acts as an effective barrier to the diffusion of corrosive agents of the electrolyte. The increase in the phase angle value suggests an increase in the thickness film of inhibitor formed onto carbon steel surface, and therefore an increase in its protective ability. On the other hand, in the intermediate frequency region ($1000 > f > 1$ Hz), it is observed an increase in the slope of the $\log |Z|$ vs $\log f$ relationship, and a change in the phase angle ($55^\circ \rightarrow 64^\circ \rightarrow 50^\circ$), as well as a shift of the maximum phase angle ($10^\circ \rightarrow 40^\circ$). The evolution of both slope and phase angle is associated with the adsorption, thickening and compacting of the inhibitor film onto working electrode surface. In addition, the absorption mode of the inhibitor molecules is flat (change of the phase angle) and perpendicular (new time constant in the high frequency region) to the surface of the working electrode. In the low frequency region, an increase in the impedance module by increasing the inhibitor concentration is observed; the increase is up to three

Fig. 10. Nyquist and Bode plots for 1018 carbon steel in CO_2 -saturated (3% NaCl + 10% diesel) mixture with different additions of inhibitor after 24 hours.

orders of magnitude with the addition of 100 ppm. In addition, it is also noted that by increasing the inhibitor concentration, the plateau region is better defined. Regarding the phase angle, the same characteristics described in the analysis of Fig. 9 are observed, however the main difference observed is an initial increase in the phase angle up to an inhibitor concentration of 10 ppm, and then a decrease by increasing the inhibitor concentration. It has been suggested that the experimental data dispersion at low frequency region is because the existence of diffusion processes known as transmissive finite diffusion due to

the presence of a stagnant layer onto steel surface [37]. These features are due to compaction of the inhibitor film which limits the diffusion of aggressive species to the surface of the working electrode.

Fig. 11 shows the evolution of the impedance spectra in Bode format for carbon steel exposed in the CO₂-saturated (3% NaCl + 10% diesel) mixture with 100 ppm of inhibitor at 50°C. Similar behaviors were obtained with the other concentrations. In the high frequency region ($f > 1000$ Hz) clearly the formation and evolution of a new time constant is observed due to the adsorption of the inhibitor onto working electrode surface. The evolution of the time constant may be associated with the strong bonding of the amide group of the inhibitor molecule onto metal surface, followed by a self-assembly of the amide groups to form a dense overlayer, and a self-organization of the hydrocarbon chains to form a dense tightly packed hydrophobic film which prevent that the corrosive species (water, oxygen, and electrons) reach the metal surface [38-39]. The maximum value of the phase angle increases and shifts to higher frequencies (74° at 40,000 Hz). This may be associated with an increase in the thickness of the inhibitor film which increases its protective ability. In the intermediate frequency region ($1000 > f > 1$ Hz), an increase in the slope value of the linear relationship, $\log |Z|$ vs $\log f$, is observed. This suggests the protective nature of the surface layers formed onto working electrode. On the other hand, from the phase angle-frequency relationship, in the first six hours of immersion, it is observed an initial increase and shift to lower frequencies of the maximum value of the phase angle, after that, decreases and moves toward higher frequencies. This

can be associated to the bonding and self-assembly of the amide groups of the inhibitor molecule onto metal surface. That is, the response observed in the region of intermediate frequency (increase and displacement of the time constant) is associated to the flat adsorption of the amide group of the inhibitor molecule, and the response observed in the high frequency region (formation and evolution of a new time constant) is due to the presence of the hydrophobic group (self-organization of the hydrocarbon chains) of the molecule inhibitor. It is known that the adsorption of an inhibitor molecule is performed by replacing water molecules adsorbed onto alloy, besides, the adsorption process dependent of the molecular structure of the inhibitor, surface charge of the alloy, and nature of the electrolyte [11]. The inhibition efficiency of an inhibitor can increases with the presence of substituents on the functional groups of the inhibitor molecule and the electron donor capacity of the substituents [40]. Such as the double bonds of the hydrocarbon chain [11,22]. According to the discussed, Fig. 12 illustrates the adsorption process suggested for the fatty amides from palm oil. The flat adsorption can be carried out through the amide

Fig. 12. Suggested adsorption mode of the fatty amides of palm oil.

Fig. 11. Bode plots for 1018 carbon steel in CO₂-saturated (3% NaCl + 10% diesel) mixture with 100 ppm of fatty-amides of palm oil at 50°C.

group, and the unsaturations present in the hydrocarbon chains (oleic and linoleic fatty acids), and the saturated hydrocarbon chains (palmitic fatty acid) form the main hydrophobic barrier together with part of the hydrocarbon chains of both oleic and linoleic fatty acids. At low frequency region ($f < 1$ Hz), impedance module ($|Z|$) increases (up to three orders of magnitude) as time elapsed, also, the dispersion of the experimental data is reduced, and the phase angle tends to zero values.

3.5 Analysis of Impedance Data

Based on the discussion of the evolution of EIS spectra, it is possible to establish the equivalent circuits shown in Fig. 13 in order to analyze impedance data. The analysis of impedance data through equivalent circuits is useful in order to model the electrochemical behavior of the surface processes carried out onto working electrode surface. Through this it is possible to determine parameters such as; electrolyte resistance (R_s), charge transfer resistance (R_{ct}), and the double layer capacitance (C_{dl}). However, in the case of the proposed equivalent circuits it has been used the concept of constant phase element (CPE) in place of a capacitor to compensate the inhomogeneity (irregularities of the surface, charge transfer non-uniformly distributed) in the system. The impedance of a CPE is a function of the frequency and it is defined as:

$$Z_{CPE} = \frac{1}{Y_0} (i\omega)^{-n} \quad (6)$$

where Y_0 is a proportional factor related to the surface and electroactive species; i is imaginary number ($\sqrt{-1}$), ω is the angular frequency ($\omega = 2\pi f$, f is the frequency), and n is related to the slope of the $|Z| - f$ relationship, and usually is in the range 0.5 and 1. Some authors consider that n is associated with sur-

face irregularities, which causes the depression in the Nyquist diagram semicircle [5]. If $n = 1$, CPE describes an ideal capacitor and Y_0 is the capacitance, if $0.5 < n < 1$, CPE describes a distribution of dielectric relaxation times in frequency space, and if $n = 0.5$, CPE represents a diffusional process, and its effect is observed in the Zre-Zim spectra (depression of the capacitive semicircle) [41].

Similarly a diffusion element was used because to the adsorption phenomena of intermediate species or to the presence of the WSF's which affect the mass transfer processes:

$$Z_W = \frac{R_W \times \tanh([\sqrt{-1} \times T \times \omega]^P)}{(\sqrt{-1} \times T \times \omega)^P} \quad (7)$$

More details on the meaning of the equivalent circuits are explained elsewhere [11]. In order to verify the validity of the assumptions made in the discussion of the impedance spectra which resulted in the proposed equivalent circuits, simulation of the experimental data was performed. Fig. 14 shows the values of R_{ct} obtained, and it is possible to observe that there is excellent agreement with the values of R_p shown in Fig. 6. This demonstrates and strengthens the validity of the hypothesis discussed previously. Analysis of the impedance spectra through the Bode plots, it is a more consistent and accurate way to define the processes occurring onto working electrode surface, the emergence and evolution of the time constant into domain of the solution resistance, it is due to the presence of the hydrophobic group of the inhibitor molecule, the evolution and displacement of the time constant into intermediate frequency region are due both to the flat-adsorption (hydrophilic group) process of the inhibitor molecule, and the compaction of the protective layer. Corrosion resistance of

Fig. 13. Equivalent circuits; (a) without inhibitor, (b) with inhibitor.

Fig. 14. R_p variation for carbon steel at different concentrations of fatty amides of palm oil.

carbon steel increased by increasing the concentration of inhibitor added, and this is possibly due to the densification process of the protective layer.

Few studies have been reported on the use of palm oil for the synthesis of corrosion inhibitors. More recent studies mention the synthesis of inhibitors such as sulfonatoxy fatty acid-mono and diethanol-amine complexes [42-43]. These studies show that the inhibition efficiency of the proposed compounds is higher than 98%, in doses similar to those reported in this study. However, its synthesis process is more complex. These results are consistent with those obtained in this work, and are similar to inhibition efficiencies reported for inhibitors synthesized from other vegetable oils [9-11,35].

The experimental evidence presented demonstrates that palm oil can be used for synthesis of green inhibitors that contributes to sustainable development of palm oil production.

4. Conclusions

In this study has been proposed the synthesis of corrosion inhibitors based in fatty amides of palm oil, and the evaluation of their performance by electrochemical tests. The results have shown that the use of palm oil for the production of green inhibitors promises to be an excellent alternative for a sustainable development of the palm oil production. The synthesized inhibitors were not purified, and the protective efficacy was higher than 98%. Methodology proposed for the synthesis of inhibitors reports the total conversion of triglycerides to fatty amides in 2 hours of reaction. The OCP measurements show that fatty

amides of palm oil act as cathodic inhibitors forming a passive layer onto metallic surface decreasing the anodic dissolution of iron. Polarization resistance tests showed a sudden increase in the corrosion resistance of carbon steel in presence of inhibitor due to the rapid formation of a molecular film onto carbon steel surface. From electrochemical impedance measurements the protective nature of the surface layers formed onto working electrode was showed. The excellent performance of inhibitors was due to the strong bonding of the amide group of the inhibitor molecule onto metal surface, and the self-assembly of the amide groups which formed a dense overlayer, and a self-organization of the hydrocarbon chains to form a dense tightly packed hydrophobic film. It was shown that the analysis of the Bode diagram is more appropriate to evaluate the performance of organic corrosion inhibitors. Simulation of experimental data using the equivalent circuits demonstrated the validity of the discussed hypothesis.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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