

Electrochemical Evaluation of the Corrosion Rate Inhibition Capacity of Eugenol, *o*-Eugenol and Diphenol, on AISI 1020 Steel Exposed to 1M HCl Medium

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Due to corrosion damages, petrochemical industry invests millions of dollars in the mitigation of this problem, which is presented basically in equipment and metal pipes, both externally and internally. A possible solution to the different consequences caused by corrosion is the use of green corrosion inhibitors. In the present research project, the inhibition capacity of the eugenol, *o*-eugenol and diphenol, on AISI 1020 carbon steel exposed to a 1M HCl acid medium is evaluated. Hence, the corrosion rate of the material in solutions with and without green corrosion inhibitor was calculated under the influence of two operating variables: temperature and immersion time; applying techniques such as Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization. In addition, the surface of AISI-1020 carbon steel was characterized by Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-ray Spectroscopy (EDS). Experimental tests show that the diphenol-based inhibitor obtained a corrosion rate inhibition efficiency of 96.24 % for AISI 1020 steel, compared to 76.87 % for Eugenol and 71.01 % for *o*-eugenol. The experimental results have shown that the percentage of inhibition increases as the temperature and immersion time of the electrochemical cell increase in the system, achieving a maximum percentage of inhibition in the corrosion rate of AISI 1020 steel of 92.23 % for a temperature of 80 °C and 6 h of immersion time.

1. Introduction

In the top system of the atmospheric distillation towers inherent to the refining of crudes occur several corrosion phenomena, such as acid corrosion, under-deposit corrosion and/or fouling. Acid corrosion and under-deposit is a problem of complex corrosion that is presented by the conditions of high temperature, pressure, and concentration of different impurities contained in the crudes that are subjected to the current refining processes (Castellanos, 2012). These impurities are mostly highly corrosive and deteriorate the equipment and the process lines by generating incrustations, corrosion products or steel wear. The deterioration degree in the equipment or line depends on the material of manufacture (Castellanos, 2012). The acid corrosion in the top system is caused by the presence of hydrochloric acid (HCl), which in the vapor phase considerably deteriorates steels that have low carbon content, and can generate a considerable damage when it is condensed on the materials of the atmospheric distillation towers. Formation of HCl in the top system results from the hydrolysis of inorganic salts such as calcium and magnesium chlorides (Castellanos, 2012), (Peña et al., 2014), which are then condensed in cold areas and generate HCl on contact with water (Peña et al., 2014). Once formed, HCl dissolves in water and attacks the metal surface, producing pitting corrosion (Peña et al., 2014). An alternative used in the petrochemical industry to mitigate this type of damage is the use of corrosion inhibitors, which are added in high concentrations (Ramezanzabeh et al.,

2015). Depending on the nature of the inhibitor, it can be classified as inorganic or organic (Sastri, 2011). Inorganic corrosion inhibitors act on the steel surface either cathodically or anodically (Sastri, 2011). However, some of these inhibitors are no longer currently used in the petrochemical industry because they have high toxicity and greatly affect the environment (Merchán, 2016). Otherwise, organic type inhibitors can form by physisorption or chemisorption phenomena a layer on the material surface, which can act as a physical barrier and provide some protection degree to the material exposed to acidic systems (Quraishi M et al., 2015), (Joseph et al., 2015), (Bentiss F et al., 2015). For this reason, the present research proposes the use of organic molecules that have more environmentally friendly characteristics, which are known as green corrosion inhibitors (GCIs) (Merchán, 2016), (Sastri, 2011). Most GCIs are non-toxic, biodegradable and abundant in nature. Currently, the GCIs from extracts of seeds, fruits, leaves and flowers, among others have been used; and it is proven that these greatly reduce the corrosion rate of ferritic materials exposed to acid systems (Merchán, 2016). This is because plant extracts contain a large number of chemical compounds, especially heterocyclic compounds, which can efficiently inhibit the corrosion of ferritic alloys exposed to HCl systems (Merchán, 2016). The inhibitory effect is attributed to the adsorption of these organic substances on the metal surface, which causes the displacement of the water molecules, blocking the active sites and forming a layer that acts as a barrier between the acid medium and the material (Quraishi M et al., 2015), (Joseph et al., 2015), (Bentiss F et al., 2015). Physisorption can be influenced by variables such as: the surface charge of the metal, the type of electrolyte, temperature and chemical structure of the inhibitor. In fact, the specific interaction between the organic functional groups, the metal surface and the nitrogen, oxygen, sulfur and phosphorus heteroatoms play a key role in inhibiting corrosion due to the free electron pairs they possess (Merchán, 2016), this is the reason why a great interest has been aroused in the petrochemical industry for the study of organic type molecules of green origin that can reduce the corrosion of the ferritic alloys in acidic systems (Solmaz et al., 2016), (Zakaria et al., 2016), (Sastri, 2011). Hence, in the present investigation work, the inhibition capacity to acid corrosion of eugenol, *o*-eugenol was determined. In addition, the effect of temperature and exposure time on the corrosion rate of AISI 1020 carbon steel exposed in a 1M HCl medium was evaluated, applying electrochemical techniques such as Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization. The surface of AISI1020 steel was characterized by Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray Spectroscopy (EDS).

2. Methodology

Coupons for the electrochemical tests were machined from a piece of AISI 1020 carbon steel, obtaining a rectangular shape with the following dimensions: 30 mm long, 10 mm wide and 2 mm thick, which were characterized according to ASTM E-415 standard. A metallographic preparation was performed following the guidelines of ASTM G1-03 for each coupon, which consists of a mechanical roughing using silicon carbide sandpaper No. 220, 400, 600 and 1000. To ensure that the exposure area of the coupons was equal to 1.8 cm², an inorganic type coating was made on one side of each of them to be used in the electrochemical tests. MERCK analytical grade hydrochloric acid (37 % wt) was used for each of the electrochemical tests, using 60 mL of a solution with 1M concentration. The assembly for the development of electrochemical tests consists of a Gamry 3000 Potentiostat, a thermostatic bath and an electrochemical cell of three electrodes, which is composed of an Ag/AgCl electrode as the reference electrode, a graphite bar as a counter electrode and an AISI 1020 carbon steel as the working electrode. The electrochemical tests performed to determine the behavior of the corrosion rate of AISI 1020 carbon steel exposed to the 1M HCl solution were: Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization, and were performed following the guidelines of ASTM G59-97, ASTM G102-89 and ASTM G3-89. The OCP test was performed for 1 hour to define the stability of the system. In the EIS technique, a scanning frequency range from 10⁻³ to 10⁵ Hz was used. The amplitude of the sinusoidal AC wave was 10 mV. For the Potentiodynamic Polarization, measurements were started from the cathodic direction to the anodic (-0.5 to +1.5 V) with a scanning speed of 1.0 mV/s. The corrosion rate calculations for AISI 1020 carbon steel were made according to ASTM G59-97 and ASTM G102-89. The inhibition efficiency of the GCI was calculated from Eq (1):

$$E(\%) = \frac{(CR_o - CR_i)}{CR_o} \times 100 \quad (1)$$

Where E (%) is the inhibition efficiency, CR_o is the corrosion rate of the target and CR_i is the corrosion rate of the test. The morphological characterization of the AISI 1020 carbon steel surface was determined by applying Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-ray Spectroscopy (EDS).

3. Results and discussion

Initially, electrochemical tests were carried out using the eugenol, *o*-eugenol and diphenol organic compounds to determine the GCI with the highest percentage of corrosion rate inhibition of AISI 1020 steel exposed to a 1 M HCl acid medium. The electrochemical tests were carried out at room temperature for 6 h of exposure, using a concentration of 200 ppm for each of the GCIs. The open-circuit potentials for the target (without inhibitor) and for the GCI are presented in Figure 1, where it is observed that all four systems reach steady state. Moreover, it is inferred that all the GCI present a behavior that tends to an anodic direction increasing their values compared with the target. The corrosion potentials of the GCIs are larger compared to the target, which may indicate the possible formation of a layer on the AISI 1020 steel surface due to the interaction of the GCI molecules with the metal surface.

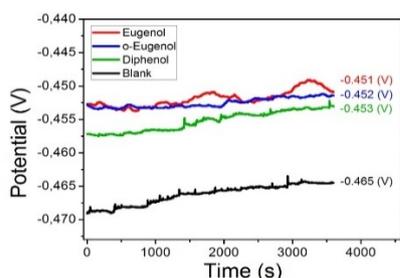


Figure 1. Open circuit potential

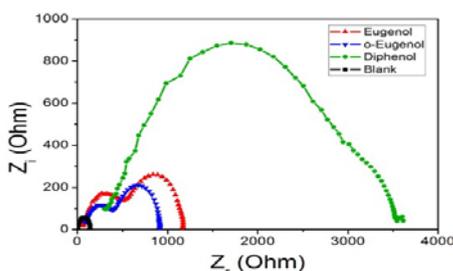


Figure 2. Nyquist diagrams

The Nyquist diagrams of Figure 2 allow the analysis of the effect of GCIs on the corrosion rate of AISI 1020 steel in a 1M HCl acid medium at constant temperature and exposure time. The domes observed in Nyquist diagrams for all GCIs are larger in size than the target, which represents the decrease in the corrosion rate of AISI 1020 steel for all developed electrochemical tests. The Nyquist diagram obtained for the diphenol-based inhibitor exhibits a larger dome compared to those obtained for eugenol and *o*-eugenol-based inhibitors, from which it is determined that the inhibitor with greater capacity to inhibit the corrosion rate of AISI 1020 steel exposed to a 1 M HCl system is the inhibitor based on diphenol. For the Nyquist diagrams of the eugenol and *o*-eugenol-based inhibitors, a double dome is present, which is attributed to the formation of corrosion products (CP) on the AISI 1020 steel surface formed by the chemisorption phenomenon. In addition, these domes do not behave as ideal semicircles, indicating that the formed CPs are not completely homogeneous and stable on the surface of AISI 1020 steel, giving the possibility of a greater localized attack of the chloride ions and, therefore, accelerating the deterioration of the metal in the 1 M HCl system. In Table 1, results of the electrochemical tests for the GCIs are presented applying Tafel Potentiodynamic Polarization at constant temperature and exposure time, where it is detailed that the values of the current density (i_{corr}) decrease with respect to the target. Moreover, it is observed that for the Diphenol-based inhibitor, the corrosion rate of AISI 1020 steel is 0.916 mpy, reaching a corrosion rate inhibition efficiency of more than 96 %, compared to the efficiencies of eugenol and *o*-eugenol-based GCIs equivalent to 77 and 71 %, respectively. Based on these results, the diphenol-based inhibitor is selected to evaluate its efficiency to inhibit the corrosion rate of AISI 1020 steel as a function of temperature and exposure time in the 1 M HCl system.

Table 1. Interpolation of Tafel curves.

Test	Slopes		E_{corr} [V]	i_{corr} [$\mu A/cm^2$]	Corrosion Rate [mpy]	Efficiency [%]
	Cathodic	Anodic				
Blank	-0.111	0.048	-0.431	52.883	24.389	-
<i>o</i> -Eugenol	-0.151	0.123	-0.441	15.286	7.050	71.09
Eugenol	-0.156	0.124	-0.431	12.228	5.640	76.88
Diphenol	-0.129	0.140	-0.450	1.986	0.916	96.24

In Figure 3, Nyquist diagrams of the diphenol-based inhibitor with a concentration of 200 ppm at 40, 60 and 80 °C operating temperatures and exposure times of 2, 4 and 6 h in a 1 M HCl system, are detailed. For all EIS tests, the influence of the Diphenol-based inhibitor in the increase of the domes size in the Nyquist diagrams is observed to the temperature and time conditions of the developed electrochemical tests, which implies a decrease in the corrosion rate of the exposed AISI 1020 steel. This is due to the fact that this type of organic molecules are normally constituted by two essential parts: an electron-rich polar part, capable of adhering to a metallic surface through coordination bonds or other ions via electrostatic bonds, and a hydrophobic part that can efficiently repel the corrosive substances present in the acid medium (Jovancicevic et al., 1999).

Therefore, the complexes formed during the inhibition process covered large areas of the metal surface of AISI 1020 steel, whereby the Diphenol-based inhibitor controls the anodic reaction of hydrochloric acid on the steel surface, blocking the active sites where the material would rapidly degrade.

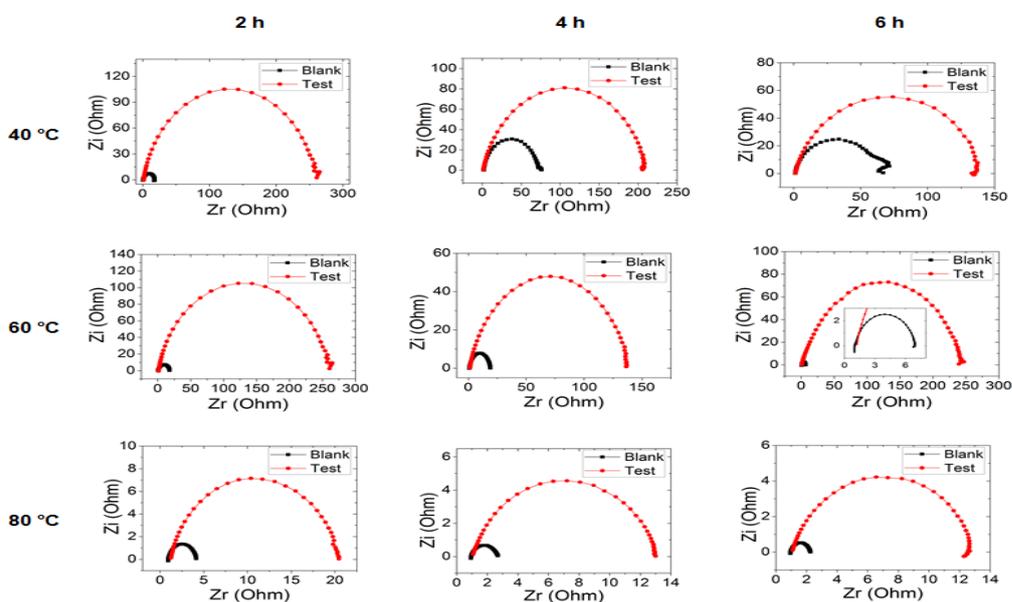


Figure 3. Nyquist diagrams at 2, 4 and 6 hours of exposure and 40, 60 and 80 °C.

In Table 2, the values of the corrosion rates of AISI 1020 steel are related, which exhibit a decreasing behavior as the temperature and the exposure time increase with respect to its target in all the electrochemical tests carried out in the 1 M HCl system. In addition, the values of the inhibition efficiency of the Diphenol-based inhibitor corrosion rate are related, which increased with the increase of temperature and immersion times, as a consequence of the action of the GCI on the material surface by the formation by physisorption of an interfacial layer, which prevents the attack of the material blocking the action of chloride ions on the AISI 1020 steel surface.

Table 2. Interpolation of Tafel curves.

Temperature [°C]	Time [h]	Blank			Test			Efficiency [%]
		E_{corr} [V]	I_{corr} [$\mu\text{A}/\text{cm}^2$]	Corrosion Rate [mpy]	E_{corr} [V]	I_{corr} [$\mu\text{A}/\text{cm}^2$]	Corrosion Rate [mpy]	
40	2	-0,447	64,591	29,789	-0,304	51,370	23,692	20,468
	4	-0,417	43,986	20,286	-0,471	30,527	14,079	30,598
	6	-0,446	110,608	51,012	-0,472	73,367	33,837	33,669
60	2	-0,460	184,588	85,131	-0,447	92,328	42,581	49,982
	4	-0,379	150,059	69,206	-0,464	59,227	27,315	60,531
	6	-0,446	230,271	106,200	-0,465	48,914	22,559	78,758
80	2	-0,415	823,913	379,984	-0,453	97,663	45,042	88,146
	4	-0,428	2253,519	1039,311	-0,449	212,450	97,981	90,573
	6	-0,446	2819,894	1300,519	-0,43	219,102	101,049	92,230

In Figure 4, the Tafel Potenciodynamic Polarization curves show that all the AISI 1020 steel coupons exhibit good electrochemical behavior in the working zone for all tests performed. The current density decreases and the potential is shifted to less active zones with respect to its target, thus, benefiting the protection of the metal. This is attributed to the formation of an interfacial layer on the metal surface by the action of the Diphenol-based inhibitor, which influences the decrease of the corrosion rate of AISI 1020 steel exposed in the 1 M HCl system.

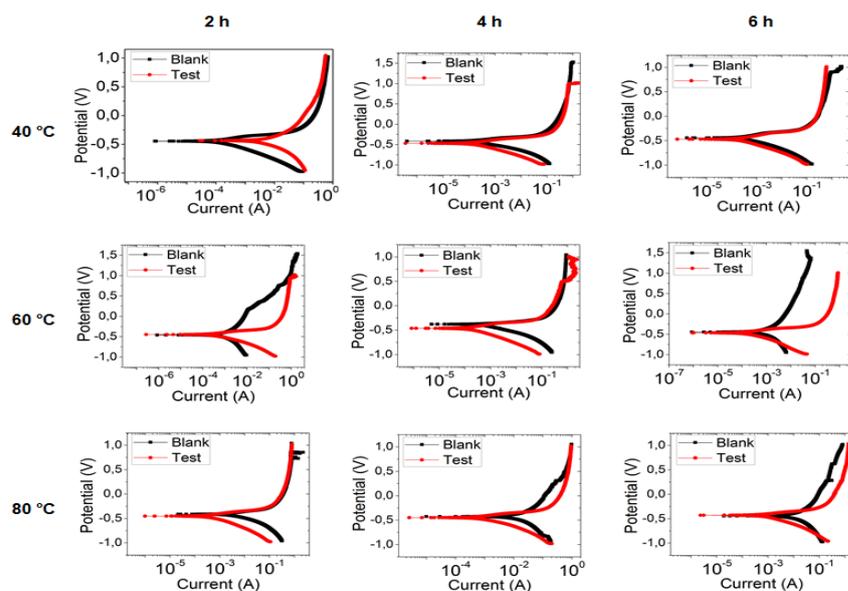


Figure 4. Tafel Polarization curves at 2, 4 and 6 h of exposure and 40, 60 and 80 °C.

In Table 3, results of the EDS analysis performed on the coupons surface are related, where it is inferred that the surface of AISI 1020 steel shows a decrease in its iron percentage from 96.53 to 48.34 Wt % for the target exposed to the 1 M HCl system, and from 96.53 to 69.50 Wt % for the diphenol-based GCI system.

Table 3. EDS of 1020 steel, target and electrochemical test at 80 °C and 6 hours of exposure.

Sample	CK	OK	AlK	SiK	SK	CK	FeK
AISI 1020 steel	03.47	-	-	-	-	-	96.53
Blank	14.34	-	-	-	-	-	85.66
Test	16.37	12.02	0.42	0.79	0.41	0.49	69.50

Sample	CK	OK	AlK	SiK	SK	CK	FeK
AISI 1020 steel	03.47	-	-	-	-	-	96.53
Blank	20.30	27.70	0.72	1.62	0.36	0.97	48.34
Test	39.74	21.91	0.46	0.82	0.38	0.40	36.29

Figure 5. SEM-EDS of the AISI 1020 steel surface, target in 1M HCl acid medium, and with Diphenol-based GCI at 80 °C and 6 hours of exposure.

Figure 5 shows the analysis of SEM performed on the surface of three AISI 1020 carbon steel samples used in the electrochemical tests. The choice of the coupons was made considering the results of the electrochemical tests developed, in which it was demonstrated that at a temperature of 80 °C and 6 hours of exposure, the highest percentage of corrosion inhibition of AISI 1020 steel was reached by the Diphenol-based inhibitor. By visual inspection it is possible to detail the protective action of the Diphenol-based Inhibitor on AISI 1020 steel, with less deterioration on the surface as shown in Figure 5. The decrease of iron loss in the exposed coupon is from 48.19 to 27.03% in the 1M HCl system with 200 ppm of GCI.

4. Conclusions

The electrochemical tests performed for Eugenol, *o*-Eugenol and Diphenol, show that all of them have the capacity to inhibit acid corrosion by reducing the deterioration of AISI 1020 steel in a 1 M HCl system at room temperature and 6 h of exposure. The Nyquist diagrams for eugenol-based inhibitors exhibited a double dome, indicating the formation of corrosion products. Otherwise, the diphenol-based inhibitor has a single dome in the Nyquist diagram, which indicates the formation of an interfacial film on the metal surface due to electrostatic bonds of the inhibitor molecules with the surface of AISI 1020 steel, generating a greater resistance against the corrosive medium. For this reason, the inhibition percentage of the corrosion rate was higher for the Diphenol-based inhibitor compared to the Eugenol-based. The Diphenol-based inhibitor demonstrated good electrochemical behavior with respect to its inhibition capacity at 40, 60 and 80 °C temperature conditions and exposure times of 2, 4 and 6 h. The inhibition percentage of the corrosion rate of AISI 1020 steel in a 1 M HCl system increased to 92.23 % at the highest temperature and immersion time conditions. The results of the SEM-EDS analysis performed on the coupons surface showed that the iron content in the AISI 1020 steel decreased about 27 % during the electrochemical test in the presence of the inhibitor, while the decrease was 48 % for the target without inhibitor, which shows that the use of the diphenol-based Inhibitor was able to decrease the iron loss of AISI 1020 steel in 1 M HCl medium, whereby it is possible to increase the useful life of the ferritic materials exposed to a system with high acidity content.

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