THE MECHANISM AND EFFICIENCY OF INHIBITION OF GALANGAL RHIZOME (*Alpinia Galanga L.*) ON THE CORROSION OF CARBON STEEL IN AN ENVIRONMENT APPROPRIATENESS TO CONDITIONS OF A PETROLEUM WELL

Yayan Sunarya, Heli Siti Halimatul Munawaroh, Iqbal Mushapa and Devi Tristiani
Department of Chemistry Education, Universitas Pendidikan Indonesia, Bandung, Indonesia
E-Mail: yayan_sunarya@upi.edu

ABSTRACT

The mechanism and efficiency of inhibition of the ethanol extract from galangal rhizome on the carbon steel API 5L X65 corrosionin an environment appropriatness to the conditions of a petroleum well had been studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (Tafel plot). The results showed that the ethanol extract from galangal rhizome is good inhibitor. The inhibition efficiency increased as the galangal extract concentration was increased and the inhibition reached its optimum at 200 ppm by 87%. Potentiodynamic polarization studies clearly reveal that galangal rhizome acts essentially as cathodic-type inhibitor. The experimental impedance data were analyzed according to a proposed equivalent circuit model for the electrode/electrolyte interface, its show that the corrosion inhibition mechanism took place through the adsorption process which formed an uneven protective film on the carbon steel surface. The adsorption took place physically following Langmuir's adsorption isotherm with the adsorption energy of -14.96 kJ.mol^{-1}.

Keywords: galangal rhizome, corrosion inhibitor, EIS, tafel plot.

INTRODUCTION

Crude oil which is produced in petroleum mining contains chemicals in the forms of salts, organic acids, and acidic gases[1]. The chemicals, when mixed with water pumped into a well to facilitate the extraction of crude oil, become very corrosive medium towards the metal equipment used. One of the main features of the condition of a petroleum well is that its liquid contains high percentage of NaCl about 2-4% and saturated with CO_2 gas[2]. Accordingly, the salt solution saturated with CO_2 can be considered as to mimic the natural condition of a petroleum production well[3]. In this study, the NaCl 1% solution, as the corrosive medium, was bubbled with CO_2 gas and pH of 4.0 ±0.1 controlled with acetic buffer.

Corrosion can be overcome by adding an inhibitor of the adsorbate type, which is a chemical that is added in a corrosive environment in a very small amount in order to control corrosion[4] through the formation of a protective passive film on the internal surface of the carbon steel pipes. Recently, the development of corrosion inhibitors has been directed to heteroatomic organic compounds containing nitrogen, sulfur, oxygen, or phosphorous. The inhibiting power of the atoms is: P > S > N > O[5]. The inhibiting ability of the organic compunds is based on their adsorption strength on a metal surface which form a passive or protective film. There are three organic compund groups which have a potential to become corrosion inhibitors on metals: (1) amine compound, (2) heterocyclic nitrogen compound, and (3) compounds containing mercapto, phosphoryl, amide, or thiocarbamide[6-8].

Spices contain various heterocyclic carbon compounds and/or compounds containing amine, mercapto, hydroxyl, and conjugated double bond functional groups. That said, several types of spices have the potential to become an alternative material for metal corrosion inhibitor, among others being ethanol extract from nauclea latifolia for light steel corrosion in H_2SO_4 solution[9]; sida acuta extract for light steel corrosion in H_2SO_4 1 M solution[10]; and tinospora crispa extract as a natural light steel corrosion inhibitor in HCl 1 M solution[11]. Based on the description above, this article evaluated the performance of galangal rhizome as a carbon steel API 5L X65 corrosion inhibitor in NaCl solution saturated by continuously bubbling CO_2 with pH of the medium controlled by acetic buffer system.

METHODS

Preparation of working electrode and sample test

The electrode material was carbon steel of American Petroleum Institute (API) 5L grade X65 type. The electrode was made by cutting carbon steel API 5L, lathing it to a diameter of 0.8 cm and a length of 2 cm, connecting (soldering) it to a copper wire and coating it with epoxy resin to obtain an area of exposed surface of 1 cm^2. Before being used as a working electrode, the exposed surface was smoothed with Si-C sandpaper (grade 400 to 1400), washed with distilled water and acetone and dried.

Galangal rhizome was dried under the sun for 7 days, and finely ground and weighed. The dry and fine sample was soaked in ethanol medium/solution for 2 x 24 hours in room temperature. The resultant extract was filtered and the filtrate was separated from its solution with evaporation, and dried with freeze drier. All the chemicals used in this study had the analytical grade and the solution was made using distilled water. The test solution was made from NaCl 1% solution with pH of 4.0 ±0.1 which was regulated with acetic buffer system and during the course of this work the solution was saturated with CO_2 gas by bubbling.

Potentiodynamic polarization parameter and EIS

Into the electrochemical cell, 250 ml of test solution was poured, saturated with CO_2 in the pressure of 0.25 ± 0.05 atm, and stirred with the speed of 250 rpm. The auxiliary electrode (carbon steel), reference electrode (saturated calomel electrode/SCE), and auxiliary electrode (platinum) were immersed into the test solution, and connected to the potentiostat of Radiometer (Voltalab PGZ 3O1). Data processing was conducted using Voltamaster 4.

Polarization data was recorded with the constant sweep rate of 0.5 $mV.s^{-1}$, with potential range applied being ± 50 mV relative to corrosion potential[12]. The corrosion current was determined by extrapolation from polarization curve using Tafel method. The measurement of impedance was conducted in the frequency range of 50 kHz to 50 mHz with ten points per decade. The sinus wave with an amplitude of 10 V which was applied to interfere with the DC system and potential applied was free[13]. The impedance diagram was disclosed in the form of Nyquist plot.

RESULTS AND DISCUSSION

Corrosion rate and inhibition potential

The output from the results of potentiodynamic polarization method measurement was a graph indicating a relationship between polarization current and polarization potential. Further, the graph was extrapolated with Tafel technique to obtain the interface electrical properties such as corrosion potential, E_{cor}, anodic constant, β_a and cathodic, β_c, polarization resistance, Rp, corrosion current density, I_{cor}, and corrosion rate, R_{cor}. The result of Tafel extrapolation is shown in Table-1. Corrosion potential and carbon steel corrosion current density in the solution without galangal extract were respectively -607,8 mV and 542,5 μA per cm^2. This indicated that the energy level of the charged orbitals on the carbon steel surface was excited exceeding the energy level of empty orbitals of the solution. Consequently, a transfer of electrons took place from the carbon steel surface to the solution resulting in a cathodic current, which produced reduction reaction of H^+ ions in the solution which formed H_2 gas. This hydrogen gas evolution reaction was counterbalanced by the the occurence in which iron oxide formed Fe^{2+} ions on the metal surface in the anodic process[14]. The result of Tafel extrapolation is shown in Table-1.

Table-1. Corrosion parameters of carbon steel polarization in NaCl solution saturated with CO_2 with and without galangal extract.

C_{inh}/ ppm	E_{cor}/mV	β_a/mV dec^{-1}	β_c/mV dec^{-1}	I_{cor}/(μA.cm^{-2})
0	-607,8	77	170	542,5
40	-613.1	79	174	257,8
80	-621,4	75	157	180,3
120	-632,5	74	139	128,5
160	-640,3	73	120	93,7
200	-643,8	71	113	79,2

The addition of Galangal extract into the test medium decreased the corrosion current density (I_{cor}). The higher the extract concentration was added, the lower the value of I_{cor} was. The decrease of I_{cor} was related to the decrease of anodic constant value (β_c). This indicated that carbon steel corrosion inhibition process by galangal extract was more likely caused by the increase of hydrogen gas formation energy barrier[15]. In other words, galangal extract played a role as a cathodic-type inhibitor in the corrosion of carbon steel API 5L in NaCl solution saturated with CO_2 with the pH of acetate buffer. In other words, galangal extract could sigificantly decrease the carbon steel corrosion rate. The more galangal extract concentration was added to the test medium, the lower the carbon steel corrosion rate was, and it reached the optimum at 0.85 per year for galangal extract concentration about 200 ppm.

Inhibition mechanism and efficiency

Determining the inhibition mechanism and efficiency can be done through the impedance spectra data resulted from EIS measurement., as illustrated in Figure-1 in Nyquist mode, indicating imaginary impedance plot, $Z_{i(\omega)}$ as the function of real impedance, $Zr_{(\omega)}$ from $\omega \to 0$ to $\omega \to \infty$. At $\omega \to \infty$ the value of $Z_r = R_s$ (solution resistance) and at $\omega \to 0$ the value of $Z_r = R_s + R_{ct}$, with R_{ct} being load transfer resistance. The shape of the impedance spectra obtained was a semi circle with the frequency increase being counter clockwise. The imperfection of the semi circle was caused by the frequency dispersion applied during the measurement[16].

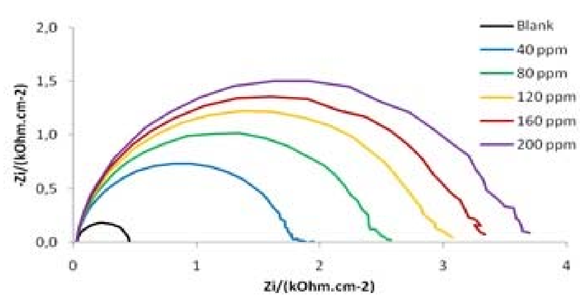

Figure-1. Potentiodynamic polarization curve of APL-5L in NaCl solution saturated with CO_2 with and without Galangal extract.

VOL. 11, NO. 22, NOVEMBER 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

The corrosion parameter resulted from the measurement of electrochemical impedance is shown in Table-2. The solution resistance value (R_s) with and without the presence of galangal extract was not significantly different, whereas the load transfer resistance value (R_{ct}) significantly increased. This indicated that galangal extract added into the test medium was a molecular compound which could resist the electron/ion current from and to the carbon steel surface such that carbon steel corrosion could be inhibited.

Table-2. Electrochemical impedance parameters on the carbon steel API 5L X65 in NaCl solution saturated with CO_2 with varies concentrations of Galangal.

C_{inh}/ ppm	R_s/ Ohm.cm^2	R_{ct}/ Ohm.cm^2	C_{dl}/ µF.cm^{-2}	IE/%
0	11,39	53,5	116.6	-
40	10.31	173,4	120.7	69,15
80	10.97	264,2	88.4	79,75
120	11.39	335,7	75.7	84,06
160	13.10	386,6	69.1	86,16
200	12.88	415,3	65.6	86,80

Electrical double layer capacitance value (C_{dl}) obtained in the maximum frequency f_{max}, when the imaginary component of the impedance reached the maximum ($-Z''_{max}$), was calculated with the following equation:

$$f(-Z''_{\max}) = \frac{1}{2\pi C_{dl} R_{ct}}$$

The value of C_{dl} decreased as the galangal concentration was increased. The decrease was caused by the adsorption of galangal on the carbon steel surface which formed insoluble protective film [17]. This indicated that galangal extract formed an isolator layer on the carbon steel surface which could resist the electrical current. This electrical resistance strength (impedance) was shown by the value of load transfer resistance (R_{ct}). The lower the value of C_{dl}, the higher the strength of R_{ct} was.

From R_{ct} data, information was obtained indicating that the inhibition efficiency value from galangal extract increased as the extract concentration was increased, and it reached its optimum at 200 ppm, by 86.8%. The inhibition efficiency value was not diffferent from that obtained based on I_{cor} data which was measured with polarization (Tafel), as shown in Figure-2. The percentage of the inhibition efficiency illustrated the inhibiting power from galangal extract in covering the carbon steel surface from environmental corrosive attacks, which was in the form of corrosive properties of NaCl solution saturated with CO_2 and pH 4 in room temperature.

The corrosion inhibition mechanism from galangal extract can be observed through adsorption free energy and computer simulation from the equivalent electrical circuit on the metal surface which was supported by the physical data of the metal surface.

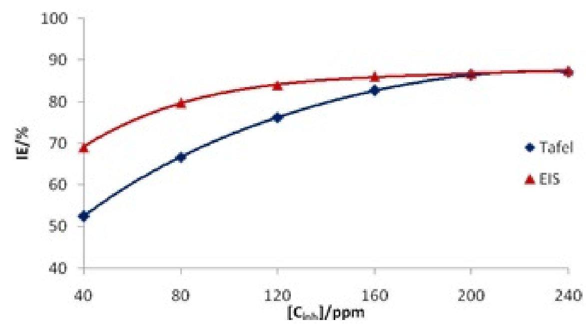

Figure-2. The inhibition efficiency of Galangal extract on the corrosion of carbon steel API 5L X65 in NaCl solution saturated with CO_2 with pH= 4 of buffer control.

Adsorption isotherm and adsorption free energy

Interaction between the carbon steel surface and molecules from galangal extract results could take place physically or chemically. This depended on the energy involved in the carbon steel corrosion inhibition process. If the energy value involved exceeded 40 kJ.mol^{-1}, it was categorized as chemical interaction. If it was less than 20 kJ.mol^{-1}, it was categorized as physical interaction or Van Der Waals force [18]. From the fraction data of carbon steel surface closing fraction by galangal extract, which was represented by inhibition efficiency value, information was obtained indicating that molecules resulted from the extract results followed Langmuir's isotherm, and the adsorption free energy value was -14.96 kJ.mol^{-1}. This value indicated that molecules from the results adsorped galangal extract on the carbon steel surface physically or as an interaction of Van Der Waals type.

Equivalent electrical circuit model

Based on the results of the simulation of equivalent electrical circuit which was developed, it was found that the interface of carbon steel API 5L in NaCl solution without galangal extract yielded a model shown in Figure-3a, whereas when galangal extract was present the model is shown in Figure-3b.

The behavior of carbon steel corrosion corresponds to the model in Figure-3a in which the carbon steel corrosion rate is controlled by the load transfer. The addition of galangal into the solution could form a protective film on the carbon steel surface with isolating properties against the electrical current, as shown in Figure-3b. Based on the simulation results, the protective film formed on the carbon steel surface was uneven. It means that the carbon steel surface stiill could interact with the solution which might cause potentially cause local corrosion.

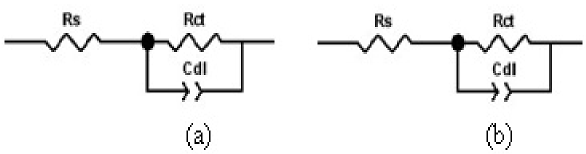

Figure-3. Equivalent electrical circuit model on carbon steel interface and NaCl solution saturated with CO_2. (a) without galangal extract, (b) with the addition of 200 ppm of galangal extract.

The imperfection of the protective film from galangal extract on the carbon steel surface is shown by SEM result, as shown in Figure-4. Figure-4a shows the carbon steel surface soaked in the test solution for 8 hours without galangal extract, and Figure-4b with the addition of 200 ppm of galangal extract. It can clearly be seen that galangal extract can unevenly cover the entire carbon steel surface.

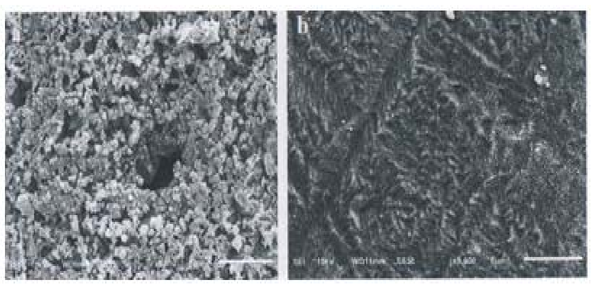

Figure-4. The carbon steel surface image scanned with SEM using 5000X. magnification (a) Soaked in NaCl solution saturated with CO_2 For 8 hours, without galangal extract; (b) with the addition of galangal extract.

CONCLUSIONS

The ethanol extract from galangal rhizome (Alpinia galanga L.)showed high inhibition efficiency on carbon steel API 5L X65 corrosion in the medium corresponding to the condition of a petroleum production well. The value of the inhibition efficiency reached its optimum at 87% for the extract concentration of 200 ppm. Corrosion inhibition mechanism took place through the adsorption process of molecules produced from galangal extract which formed an uneven protective film on the carbon steel surface. The adsorption was of Van Der Waals type following Langmuir's adsorption isotherm with the adsorption free energy of -14.96 $kJ.mol^{-1}$. The ethanol Extract from galangal was of cathodic-type inhibitor.

REFERENCES

[1] Obeyesekere, N., Naraghi, A., Abayarathna, D., Prasad, R., (2000), Environmentally Friendly Corrosion inhibitors for CO_2 corrosion in North Sea Oil Fields, Corrosion 2000, Paper 20, (Houston, TX, NACE, 2000).

[2] S. Seal, K. Sapre, V. Desai, M. Gopal, dan W.P. Jepson (2000): Surface chemical and morphological changes in corrosion product layers and inhibitors in CO_2 corrosion in multiphase flowlines, Corrosion 2000, Paper 046, (Houston, TX, NACE, 2000).

[3] K. Videm (2000), The anodic behaviour of iron and steel in aqueous solutions with CO_2, HCO_3^-, CO_3^{2-}, and Cl^-, Corrosion 2000, Paper 39, (Houston, TX, NACE, 2000) .

[4] Jones, D.A., (1992): Principles and Prevention of Corrosion, Macmillan Publishing Company, New York, 1992.

[5] Raicheva, et.al., (1992): The Efeect of The Chemical Structure of Some Nitrogen and Sulphur-Containing Organic Compounds on Their Corrosion Inhibiting Action, Corrosion Science, 34(2), 343-350.

[6] Şahin, M. Dan Bilgiç, S., (2003): The inhibition effects of some heterocyclic nitrogenous compounds on the corrosion of the steel in CO_2-saturated NaCl solutions, J. Anti-Corrosion Method and Materials, 50(1), 34-39.

[7] Y. Sunarya, C.L. Radiman, S. Achmad, B. Bundjali (2007), Amino acids as Corrosion Inhibitor for Carbon steels., Proceeding of International Conference on Mathematics and Natural Sciences/ICMNS, November 29-30, 2006, Bandung, p 623 – 626.

[8] Wang, H.L., Liu, R.B., dan Xin, J., (2004): Inhibiting effects of some mercaptotriazole derivatives on the corrosion of mild steel in 1.0 M HCl medium, Corros. Sci., 46 2455 -2468.

[9] Uwah, I.E., Okafor, P.C., Ebiekpe, V.E.,(2010): Inhibitive action of ethanol extracts from nauclea latifolia on the corrosion of mild steel in H_2SO_4 solutions and their adsorption characteristics, Arab. J. of Chem., xxx, in.press.

[10] Eduok, U.M., Umoren, S.A., Udoh, A.P., (2010): Synergistic inhibition effects between leaves and stem extracts of sida acuta and iodide ion for mild steel orrosion in 1 M H_2SO_4 solutions, Arab. J. of Chem., xxx, in.press.

[11] Hussin, M. H., Kassim, M. J., Razali, N.N., Dahon, N.H., Nasshorudin, D., (2011): The effect of tinospora crispa extracts as a natural mild steel corrosion inhibitor in 1 M HCl solution, Arab. J. of Chem., xxx, in.press.

[12] ASTM G-5 (1987): Standard practice for making potentiodynamic anodic polarization measurements convention applicable to electrochemical

measurement in corrosion testing, Annual Book of ASTM Standard, Metal Test Methods and Analytical Procedures, American Society for Testing and Materials.

[13] ASTM G-106 (1989): Standard practice for verification of algorithm and Equipment for Electrochemical Impedance Measurement, Annual Book of ASTM Standard, Metal Test Methods and Analytical Procedures, American Society for Testing and Materials.

[14] Sato, Norio, (1987): Some concepts of Corrosion Fundamentals, Corrosion Science, 27(5), 421 – 433.

[15] Wang, H.L., Liu, R.B., Xin, J., Inhibiting effects of some mercapto-triazole derivatives on the corrosion of mild steel in 1.0 M HCl medium, Corr. Sci., 46 (2004) 2455.

[16] Gamry Instruments (2005): Electrochemical Impedance Spectroscopy Primer, http://www.gamry.com. Diunduh pada tanggal 10 Agustus 2013.

[17] Gabrielli, C., (1980): Identification of electrochemical processes by frequency response analysis, Center Nation de la Rercherche Scientifique Physique des Liquides et Electrochimie, France.

[18] Popova, A., Christov, M., Raicheva, S., dan Sokolova, E., (2004): Adsorption and Inhibitive Properties of Benzimidazole Derivates in Acid Mild steel Corrosion, Corros. Sci., 46, 1333-1350.