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Reaction Products of *Crude Palm Oil*-based Fatty Acids and Monoethanolamine as Corrosion Inhibitors of Carbon Steel

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Abstract

Herein we report the application of the reaction products of crude palm oil-based fatty acids and monoethanolamine as sustainable corrosion inhibitors in acidic environments for carbon steels. Reaction products were identified based on FTIR analysis as a mixture of 2-aminoethyl fatty esters and N-(2-hydroxyethyl) fatty amides. Corrosion inhibition effect of these compounds was evaluated by potentiodynamic polarization techniques in 0.5 M HCl. The mixture of fatty esters and fatty amides showed promising potential as an alternative corrosion inhibitor. Inhibition efficiency was found to be 80% at 80 ppm. Thermodynamic and kinetic parameters obtained from the tafel plot displayed an increase in activation energy with a higher inhibitor concentration that led to the decrease in the corrosion rate. Furthermore, physisorption interaction was found to be the main process of the inhibitor's adsorption on metal surfaces and obeyed the adsorption model of the Langmuir isotherm.

Keywords: crude palm oil, acid medium, corrosion inhibitor, fatty ester, fatty amides

Introduction

Indonesia is one of the largest palm oil producers, having produced 26.47 million tons in 2015, and is responsible for 55% of total production globally. Almost all palm oils are exported in the form of low-price crude palm oils (CPO) and palm kernel oils (PKO) [1-2]. In order to add higher economic value to the palm oil industry, there is a need to develop new valuable materials based on the chemical transformation of CPO, e.g., to act as a corrosion inhibitor.

Corrosion inhibitors are chemical compounds that, when added even in small quantities, significantly decrease the corrosion rate of metal surfaces in contact with corrosive media such as acids [3,4]. Addition of corrosion inhibitors to protect metals in acidic media is a very common practice in various industries due to their effectiveness and low cost compared to other methods [4]. A wide range of compounds, both inorganic and organic, have been reported as potential inhibitors to prevent the corrosion process [5-6]. However, most of the published inhibitors are typically toxic, require complicated synthesis methods, are expensive, and are not environmentally friendly. Therefore, it is of huge

interest to design a new, green corrosion inhibitor. Some studies have reported that palm oil-based derivatives have been used as corrosion inhibitors for metals such as amides [7] and surfactants [8]. Herein, we propose the use of products from the reaction of palm oil-based fatty acids and monoethanolamine as environmentally friendly corrosion inhibitors in acidic media. Additional heteroatom groups from monoethanolamine should cause additional interactions with metal surfaces compared to fatty acids or normal fatty esters, thus increasing their corrosion prevention properties.

The present work was conducted to study the inhibitive properties of the reaction products using potentiodynamic polarization measurements on carbon steel surfaces in a 0.5 M HCl medium [9]. Thermodynamic parameters of the inhibition were also examined, and the type of isotherm model responsible for the interaction between metal and inhibitor was elaborated.

Materials and Methods

Relevant materials in this study were: Sodium hydroxide (Merck, German), Hydrochloric Acid (Merck, German), n-heptane (BDH Chemicals, United Kingdom), sodium

sulfate (BDH Chemicals, United Kingdom), Monoethanolamine (Motochem, Indonesia), sulfuric acid (Merck, German), chloroform (BDH Chemicals), sodium bicarbonate (Merck, German), sodium chloride (Teknis), Gas Chromatography (GC-2010 plus, Shimadzu), Fourier Transform Infrared Spectroscopy (FTIR Alpha ATR), Pt auxiliary electrode, Ag/AgCl as a reference electrode, and carbon steel coupon (1.5 cm² surface area) as a working electrode and potentiostat (DY2300 Digi Ivy, Inc.).

Hydrolysis of CPO. 100 g CPO was reacted with 80 mL of 40% sodium hydroxide at 80 °C–90 °C for 4 h. Fatty acid phase was separated from aqueous phase and washed with 4 M hydrochloric acid. Organic phase was dissolved with n-heptane in a separating funnel. The n-heptane layer was separated and distilled water was added to wash the organic layer several times until pH was neutral. Sodium sulfate was added to remove the remaining water. The resulting n-heptane layer was concentrated by means of a rotary evaporator at vacuum pressure. Fatty acid was analyzed using gas chromatography with operating conditions of DEGS 10% column, flowrate of N₂ 20 mL/min, H₂ 30 mL/min, O₂ 220 mL/min, injection volume 20 µL, injection temperature 200 °C, and programmed temperatures of: initial, 150 °C for 5 min, final, I 200 °C for 10 min, and final II, 220 °C for 15 min [10].

Synthesis and characterization of fatty acid esters and amides. Fatty acids and MEA were mixed into a 100 mL round flask at a molar ratio of 1:1 (MEA:fatty acid), and 1% sulfuric acid was added as a catalyst. The mixture was stirred at 120–130°C for 4 h. After the crude reaction cooled to room temperature, 100 mL of chloroform was added to the flask. A 10% sodium bicarbonate solution was used to wash the separated organics, followed with a brine solution and water. The product was obtained by removing the solvent using a rotary evaporator and analyzed using FTIR.

Electrochemical measurements. An electrochemical analysis was carried out in a 0.5 M HCl test solution. Before the analysis, the steel coupons were sanded with silicon carbide (mesh 500–1000) and cleaned with distilled water and acetone. An electrochemical analysis

was undertaken using a potentiostat. Electrochemical measurements used linear sweep voltammetry with a potential range of –1.0 V to 0.3 V, scan rate of 0.05 v/s, and a sensitivity of 0.001, and was performed at room temperature. Corrosion rate data of the inhibitors was used for calculation of the thermodynamic parameters using the Arrhenius equation in transition conditions obtained from the electrochemical analysis at different temperatures.

Results and Discussion

Hydrolysis of CPO. The hydrolysis reaction of CPO was catalyzed by NaOH and resulted in 87% yields of fatty acid mixtures (Figure 1). The hydrolysate were analyzed by GC and showed the main constituents were oleic, linoleic, and palmitic acids (Table 1) and in good agreement with previous published reports. Composition of the fatty acid is an important parameter in designing a corrosion inhibitor because the length and type of hydrocarbon chain contributes to the adsorption mode and inhibition efficiency of the inhibitor [11]. Furthermore, higher content of unsaturated fatty acids in the mixture of hydrolysate could enhance the formation of film protection on metal surfaces from corrosive environments via the phi orbital-metal reaction [12]. Thus, the hydrolysate mixture was a good raw material for corrosion inhibition.

Table 1. Fatty Acid Composition (%) of Hydrolysate

Fatty Acid	%
Caprylic	0.02
Capric	0.02
Undecanoic	0.17
Myristic	0.69
Palmitic	36.67
Palmitoleic	0.13
Cis-10-Heptadecanoic	0.02
Stearic	3.9
Oleic	44.89
Linoleic	12.06
Linolenic	0.3

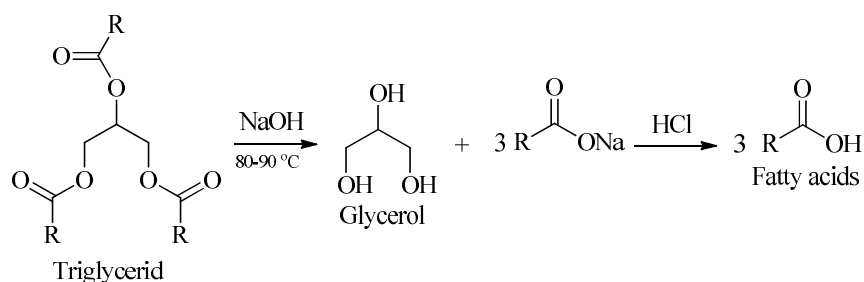


Figure 1. Hydrolysis Reaction of CPO

Reaction of fatty acid and monoethanolamine. Reaction between hydrolysate and monoethanolamine was catalyzed by sulfuric acid in yielding 40% as brown solids. FTIR analysis of the product showed significant differences from the spectrum of monoethanolamine as the starting material, which indicated the reaction had taken place. The peaks of amide at 1640 cm^{-1} and esters at 1732 cm^{-1} and 1181 cm^{-1} were observed in the spectrum, thus indicating the presence of two compounds in the product that probably were 2-aminoethyl fatty esters and N-(2-hydroxyethyl) fatty amides (Figure 2). Also, there was the presence of sharp and strong intensity at 3298 cm^{-1} corresponding to N-H bonds and 1554 cm^{-1} to N-H bonds, with 1464 cm^{-1} peaks indicating C-N amide that supported this argument. Ratio between am-

ides and esters products were found to be around 3:2 based on the relative ratio of FTIR peaks.

Electrochemical measurement. The curve of potentiodynamic polarization was used to estimate the corrosion inhibition effect of fatty esters and amides mixtures on carbon steel in an acidic solution. Figure 4 shows the results of electrochemical measurements on carbon steel metal corrosion (0.5 M HCl solutions) with and without the addition of inhibitor. Current and potential measurements with various concentrations of inhibitor were obtained and were then changed to a Tafel curve to find the equation for the cathode and anode lines as summarized in Table 3.

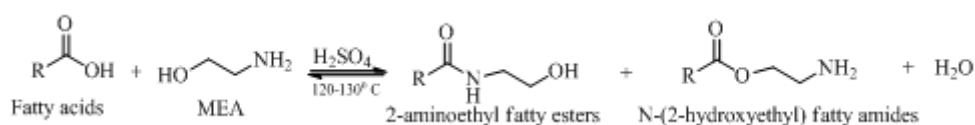


Figure 2. Reaction of Fatty Acids and Monoethanolamine

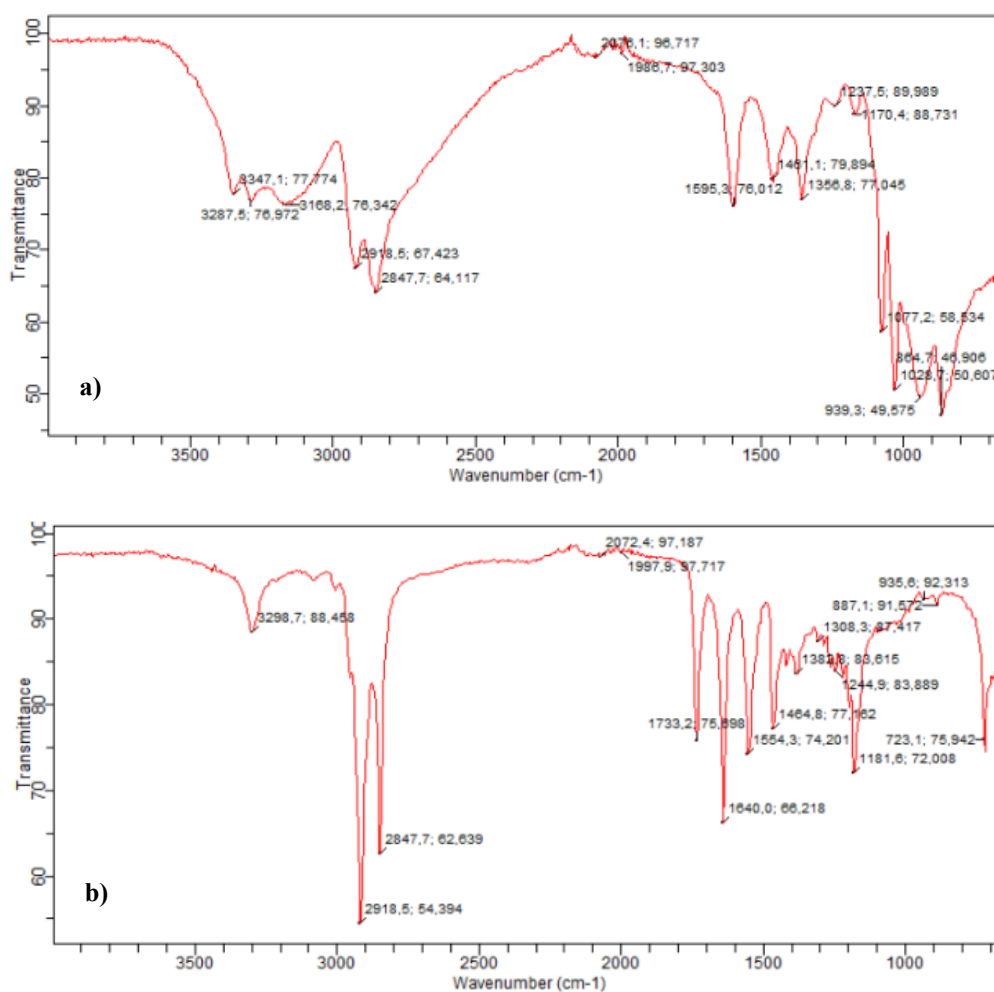


Figure 3. FTIR Spectra of a) Monoethanolamine and b) Reaction Products

Both equations were used to produce corrosion current and then protection efficiency (% IE). The result showed that addition of the inhibitor suppressed the anode and cathode reaction (Figure 4). Corrosion potential was more negative and the density of the cathode and anode currents increased that of the blank. Therefore, the fatty ester and amides were categorized as a mixed-type corrosion inhibitor since they simultaneously affected both the oxidation and reduction reactions [13].

The polarization curve (Figure 4) was used to calculate several important parameters, as summarized in Table 2, such as Tafel equations, corrosion current density (I_{corr}), corrosion potential (E_{corr}), corrosion rate (Cr), surface coverage (θ) and protection efficiency (% IE) [14]. The Cr, (θ), %IE, and θ were calculated using the follow equations:

$$(Cr) = \left[\frac{i \times Ar}{A \times z \times F \times \rho} \right] \quad (1)$$

where i is corrosion current density (Ma), Ar is relative molecular weight (55.85 gmol^{-1}), A is surface area of the specimen (1.5 cm^2), z is number of electrons lost per atom oxidized, F is a faraday constant (96485 C mol^{-1}), and ρ is density of carbon steel (7.87 gm cm^{-3})

$$\%EI = \left[\frac{I_{corr}^o - I_{corr}}{I_{corr}^o} \right] \times 100\% = \theta \times 100\%$$

increase in the corrosion inhibition efficiency directly proportional to the increase in the fatty ester and amide concentrations. This was because of the higher number of inhibitor molecules adsorbed into the metal surface, while the concentration increase [15] was in good agreement with the value of surface coverage (θ) that increased with inhibitor concentration. Optimum efficiency was obtained at concentration 80 ppm with an %IE value of 88% [16]. The mechanism of inhibition probably involved the formation of a protective layer using the interaction between the free electron pairs

from the oxygen and nitrogen atoms of the fatty esters and amides via coordination bond, thus preventing the corrosion reaction between metal and oxygen [12, 17-18].

Thermodynamic parameters. Calculation of thermodynamic parameters was measured by the potentiodynamic polarization analysis in various temperatures with an inhibitor concentration of 80 ppm. The Arrhenius equation was calculated using the following equation [16]:

$$\ln \frac{Cr}{T} = \left(\ln \frac{R}{N_A h} + \frac{\Delta S^*}{R} \right) - \frac{\Delta H^*}{RT} \quad (3)$$

where the parameters ΔH^* and ΔS^* represent the change in enthalpy and entropy, respectively, in the transition state as calculated from the $\ln (Cr / T)$ vs $(1 / T)$ plot. $N_A h$ is the Planck molar constant ($3.99 \times 10^{-10} \text{ JS mol}^{-1}$). Relationship of $\ln (Cr / T)$ vs $(1 / T)$ is showed in Figure 5, and the obtained parameters are presented in Table 3.

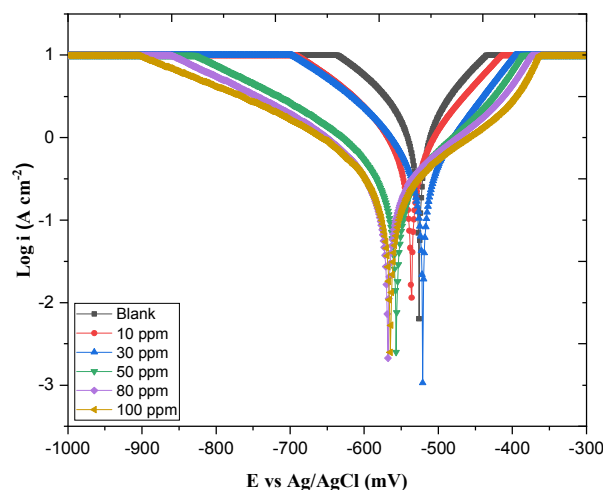


Figure 4. Tafel Polarization Curve of the Corrosion Inhibitor Reaction Product with Various Concentrations in 0.5 M HCl at Room Temperature

Table 2. Tafel Equation of Fatty Esters and Amides Mixtures

Concentration (ppm)	Tafel Equation		E_{corr} (mV)	I_{corr} (mA)	Cr (mm/y)	θ	IE(%)
	Cathode	Anode					
0	$y = -0.0077x - 3.8732$	$y = 0.0094x + 5.0907$	-524	1.4560	11.256	-	-
10	$y = -0.0076x - 4.1964$	$y = 0.0108x + 5.5159$	-528	0.6534	5.051	0.5512	55.12
30	$y = -0.0087x - 4.8426$	$y = 0.0119x + 5.7530$	-510	0.4781	4.140	0.6716	67.16
50	$y = -0.0089x - 5.8173$	$y = 0.0065x + 3.0036$	-573	0.1908	1.475	0.8690	86.90
80	$y = -0.0069x - 4.7618$	$y = 0.0068x + 3.1247$	-576	0.1623	1.254	0.8886	88.86
100	$y = -0.0121x - 8.1490$	$y = 0.0054x + 2.5137$	-609	0.1673	1.293	0.8851	88.51

Table 3 shows that the positive values of the ΔH^* samples were higher than ΔH^* blank. This result indicated that more energy was required for the corrosion reaction to proceed with the inhibitor on the carbon steel metal surface. ΔS^* was higher for the sample compared to the blank, indicating an increase in ΔS^* when the reactant changed into activated complex, making the inhibitor easier to attach to the metal surface [19-20].

The kinetic parameter was determined by reviewing the E_a calculated from the relationship between $\ln Cr$ and $1/T$ based on the following Arrhenius equation [20]:

$$\ln C_r = \ln A - \frac{E_a}{RT} \tag{4}$$

where E_a is activation energy of the corrosion process (kJ mol^{-1}), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and A is the Arrhenius constancy determined empirically from the relationship of slope between $\ln Cr$ vs $(1/T)$ as shown in Figure 5b. Positive value of the E_a sample was higher than the blank from 0.01 to $+12.69 \text{ kJ mol}^{-1}$, indicating the lower probability of a corrosion reaction to occur.

Adsorption isotherm. The corrosion inhibitor, in forming a passivation layer and a shielding layer on the carbon steel surfaces, was studied through calculation of the adsorption isotherm parameters. Isothermal adsorption can be determined by reviewing the constant (K_{ads}), Gibbs free energy value (ΔG°_{ads}), and the value of R^2 . Energy-free adsorption (ΔG°_{ads}) was determined based on [6].

$$k_{ads} = \frac{\exp\left(\frac{\Delta G^{\circ}_{ads}}{RT}\right)}{C_{solvent}} \tag{5}$$

where K_{ads} was obtained from the relationship between C/θ VS C (Figure 6). C is the concentration of inhibitor and θ is surface coverage. T is temperature (K), R is the ideal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), and $C_{solvent}$ is the concentration of the water in solution (55.55 mol L^{-1}).

Table 3. Thermodynamic Parameters of Fatty Esters and Amides Mixtures

Test solution	ΔH^*	ΔS^*	E_a
Blank	2.63	-124.40	0.01
Reaction product	17.69	-96.92	12.69

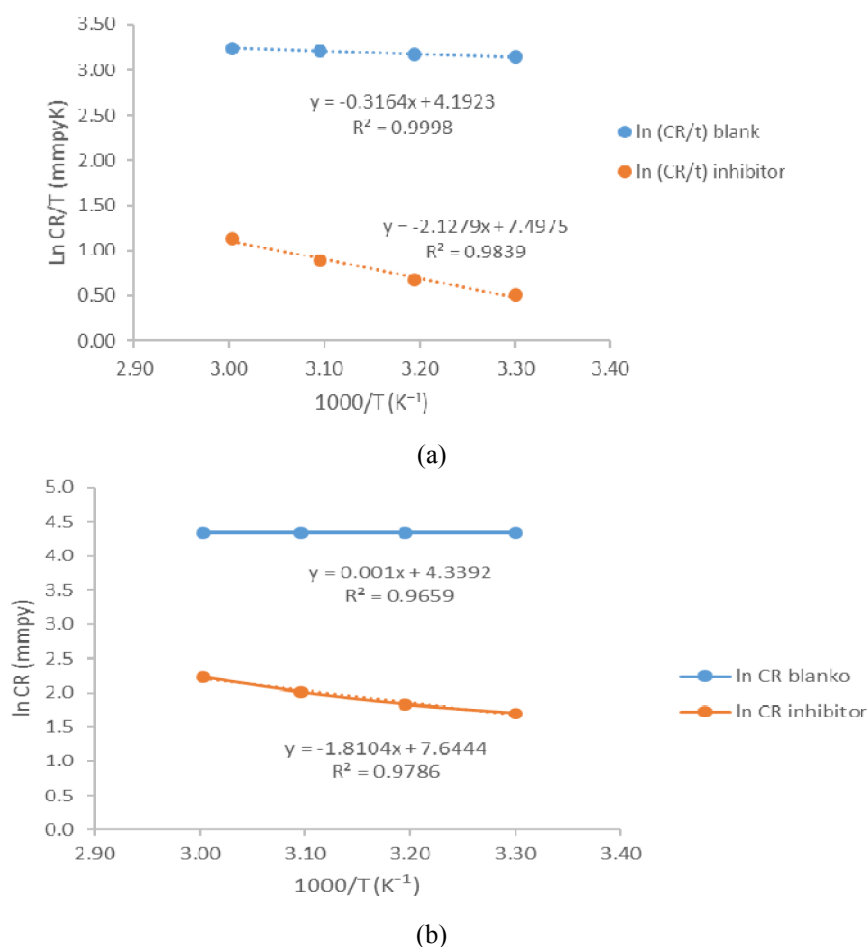


Figure 5. Arrhenius Plot of Fatty Esters and Amides Mixtures

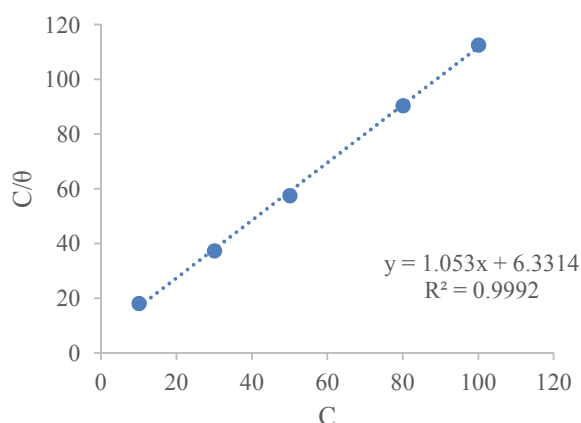


Figure 6. Langmuir Adsorption of Fatty Esters and Amides on Carbon Steel Surfaces

The value of ΔG°_{ads} obtained from the Langmuir equation was -14.52 kJ/mol as shown in Figure 6. Therefore, the adsorption reaction of the product on the metal surface was physisorption because ΔG°_{ads} was < -20 kJ/mol [6].

Conclusion

Reaction products between CPO and monoethanolamine were a mixture of 2-aminoethyl fatty esters and N-(2-hydroxyethyl) fatty amides. Corrosion inhibition properties of this compounds in acidic conditions were determined by the potentiodynamic polarization technique. Results suggested that the fatty esters and amides showed good corrosion inhibition properties on carbon steel in 0.5 HCl, which was more than 80% at 80 ppm. The tafel plot and calculated thermodynamic parameters revealed that the fatty esters and amides were mixed-type inhibitors that obeyed the Langmuir isotherm model.

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