Microwave-assisted synthesis of organic corrosion inhibitor based imidazoline-stearic

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Abstract. Corrosion often occurs in oil and gas industries’ pipelines indicated by a decrease in quality which is harmful to the industries and environment. To slow down the corrosion rate, a corrosion inhibitor is needed. Organic corrosion inhibitors are more widely used than inorganic ones due to its effectiveness and non-toxic. One of the most widely used organic corrosion inhibitors is imidazolines. In this study, imidazoline-stearic was successfully synthesized from triethylenetetramine (TETA) with various purity grade of stearic acid (SA) using 800 W microwave irradiation at 200 °C for 9 min. The obtained products then were separated by a solvent extraction method and identified using thin layer chromatography (TLC). Moreover, the products had also been characterized using FTIR and UV-Vis spectral data. The ability to inhibit corrosion on carbon steel in 1 % NaCl solution was evaluated to obtain inhibition efficiency (%IE). %IE at 500 ppm of imidazoline-stearic from SA pro analysis, technical, and commercial sample were 84.43 %, 75.42 %, and 84.41 %, respectively. Imidazoline-stearic from SA pro analysis revealed a similar corrosion inhibition activity compared with the commercial. Hence, imidazoline-stearic from SA technical grade demonstrated a promising corrosion inhibitor by using economical fatty acid.

Keywords: Microwave-assisted synthesis, organic corrosion inhibitor, and imidazoline-stearic

1. Introduction
Processing equipment for production and petroleum refinery in oil and gas industries requires pipeline operations that susceptible to corrosion [1]. Besides having a potency of gas leaks which triggered the explosions and environmental pollutions, corrosion can also cause industrial losses due to decrease in production and increase in cost production. Until now, carbon steel pipelines are still widely operated to distribute oil and gas since these pipelines are more economical compared with stainless steel modified pipelines [2]. Therefore, compounds having an activity as corrosion inhibitor are needed to slow down the rate of corrosion. This technique is considered as a cost-effective technique which have been developed and widely applied for protecting the metal from corrosion [3].

Imidazoline belongs to heterocyclic organic compound which is widely used as anticorrosive agent in oil and gas industries [4, 5]. This compound is also considered as green inhibitor due to its good biodegradability [3]. Imidazoline represents its ability since this compound has three main parts, i.e. five-ring with two nitrogen atom, long chain of hydrocarbon, and side chain with active functional groups as pendant [6, 7]. Due to a high demand of effective and eco-friendly corrosion inhibitor for industrial purposes, in this present study, we investigate the corrosion inhibition performance of
imidazoline-stearic synthesized from various purity grades of stearic acid (SA). Imidazoline-stearic was synthesized under microwave condition and its corrosion inhibition performance was performed under cyclic voltammetry in comparison with a commercial corrosion inhibitor. This study provides a useful information regarding the utilization of technical grade fatty acid which commonly obtained from industrial waste as a reactant for preparing imidazoline-based corrosion inhibitor.

2. Materials and method

2.1. General
Microwave-assisted synthesis was irradiated using Samsung ME-731K/XSE while UV-Vis Shimadzu UV-2450, FTIR Shimadzu IR Prestige 21, and LC/MS Acquity UPLC tandem with Xevo G2-S QT of Waters were used to characterize imidazoline-stearic structures. The measurement of corrosion inhibition activity was carried out using eDAQ 450 potentiostat and VersaSTAT II operated with working electrode (WE) low carbon steel JIS G3123 grade SGD 400D from PT. Citra Tanamas (Fe 99.276 %, C 0.08 %, Mn 0.40 %, Si 0.19 %, P 0.033 %, and S 0.021 %), reference electrode (RE) SCE, and auxiliary electrode (AE) platinum. Chemicals used for synthesis, identification, and corrosion inhibition test in pro analysis grade were purchased from Merck i.e. triethylenetetramine (TETA), SA (C18), CH2Cl2, NaCl, methanol, NH4OH, art TLC plates, while technical grade of SA was purchased from PT. Wilmar Nabati Indonesia with specification as follows: fatty acid C14 0.4 %, C16 59.2 %, C18 39.8 % and C20 0.6 %.

2.2. Microwave-assisted synthesis of imidazoline-stearic
Imidazoline-stearic from SA pro analysis was synthesized by addition of TETA (5 mmol) and SA (5 mmol) while from technical grade was carried out using TETA/SA molar ratio of 1:1, w/w. Each mixture was irradiated in 800W microwave for 9 min without additional solvent. Temperatures were maintained gradually at 200 °C by using infrared thermometer. After completing the reaction, each mixture was evaporated, identified using TLC with CH2Cl2:MeOH (8:2, v/v) and one drop of NH4OH as mobile phase, and extracted using CH2Cl2:saturated NaCl (1:1, v/v). The organic layer then was collected as imidazoline-stearic and further characterized by using FTIR, UV-Vis, and LC/MS.

2.3. Corrosion inhibition activity test
Measurements were completed using cyclic voltammetry method adjusted to the previous study [7]. NaCl 1 % solution was selected as corrosion medium with various imidazoline-stearic concentrations (100, 200, 300, 400 and 500 ppm) while the absence of sample marked as blank solution. The solution was gassed with CO2 until saturation was reached and three electrodes were arranged. Potentio-dynamic polarization was recorded from -2000 to +500 mV at 50 mV/s scanning rate and Tafel polarization method was chosen to analyze the efficiency inhibition percentage (%IE) using equation:

\[
\%IE = \frac{I_{Blank} \left( \frac{mA}{cm^2} \right) - I_{Sample} \left( \frac{mA}{cm^2} \right)}{I_{Blank} \left( \frac{mA}{cm^2} \right)} \times 100\%
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3. Results and discussion
In this study, imidazoline-stearic from various purity grades of SA were synthesized under microwave irradiation method with solvent-free followed the reaction scheme illustrated in figure 1. Both compounds were obtained as yellowish-brown solid giving Rf value of 0.9 in TLC with CH2Cl2:MeOH (8:2, v/v) and one drop of NH4OH.
FTIR and UV-Vis characterization were carried out to determine if the desired product was formed. Additional LC/MS characterization was also performed to imidazoline-stearic from SA technical grade. FTIR spectra of both imidazoline-stearic compared with SA are shown in figure 2. Imidazoline-stearic from SA pro analysis labeled as TETA-SA pro analysis while from SA technical grade marked as TETA-SA technical. According to figure 2, it can be concluded that both TETA-SA was formed since it showed peaks at the wavenumber of 3300, 2800–3000, 1600, and 1500 cm⁻¹ indicating N-H, C-H sp³, C=N, and C-N-C bonds, respectively. Compared with FTIR spectra of both SA (figure 2), all TETA-SA showed missing peaks at 3300–2700 and 1700 cm⁻¹ representing O-H carboxylic and C=O groups, respectively. Furthermore, a new peak at the wavenumber of 1600 cm⁻¹ indicating C=N bond compared to FTIR of TETA (data not shown) was an indicator that imidazoline had already produced [8].

![Reaction scheme of imidazoline-stearic synthesis.](a)

**Figure 1.** Reaction scheme of imidazoline-stearic synthesis.

![FTIR spectra of (a) SA and TETA-SA pro analysis and (b) SA and TETA-SA technical.](b)

**Figure 2.** FTIR spectra of (a) SA and TETA-SA pro analysis and (b) SA and TETA-SA technical.
Figure 3 summarizes the UV-Vis spectra for both imidazoline-stearic compared with previous study (not yet published). Based on figure 3, all spectra show a similarity in maximum wavelength around 204 nm. Therefore, it indicated that imidazoline-stearic was successfully synthesized.

To analyze the composition of TETA-SA technical, LC/MS spectra was recorded. LC spectra of TETA-SA technical (data not shown) exhibited two dominant peaks at retention time of 11.56 and 12.70 minutes. MS spectra of both dominant peaks are presented in figure 4. According to figure 4,
a peak at 11.56 min represents the imidazoline-palmitic (368.365 m/z) derived from TETA with palmitic acid (PA, C16) while 12.70 min belongs to TETA-SA imidazoline (396.395 m/z). TETA-PA exhibited a lower retention time since it was more polar compared to TETA-SA.

The ability to inhibit corrosion of both synthesized imidazoline-stearic had also been investigated. Commercial imidazoline was also tested as comparison. Specifically, corrosion occurs due to the presence of dissolved CO₂ gas in water. When CO₂ dissolves in water, it will produce carbonic acid which causes more corrosive environment to carbon steel [9, 10]. Imidazoline can be adsorbed physically and chemically onto the metal surface due to the presence of N=C-N bond in imidazoline ring having rich π-electron, as well as lone pair electron in both nitrogen atoms. The existence of π-electron and lone pair electron effects the negative charge of imidazoline. In general, metal surface has a positive charge found on its interface. The charge differences between imidazoline and metal surface cause electrostatic interactions between them and form a layer. The existence of long C-H bonds from hydrocarbon chain as hydrophobic site will prevent water molecules from the environment to interact with metal surface. Therefore, the metal will be inhibited from corrosion [11, 12]. The proposed schematic mechanism of imidazoline-stearic adsorption on metal surfaces is illustrated in figure 5.

The results in corrosion inhibition activity from all samples were plotted in figure 6. Based on figure 6, TETA-SA pro analysis exhibited slightly similar activity in inhibiting corrosion compared with the commercial imidazoline. In contrast, TETA-SA technical showed a lower activity compared with others. Technical grade of SA is consisted of more than one fatty acid, having two majors of PA and SA which different in long hydrocarbon chain. As shown in figure 4, the synthesized TETA-SA imidazoline form SA technical grade was consisted of imidazoline-palmitic (TETA-PA) and imidazoline-stearic (TETA-SA). Therefore, it was proven that hydrocarbon chain plays an important role in the corrosion inhibition activity, which prevents water interaction with metal surface [5].

Figure 5. Proposed schematic mechanism of imidazoline-stearic adsorption on metal surfaces.

![Proposed schematic mechanism of imidazoline-stearic adsorption on metal surfaces.](image)

Figure 6. Corrosion inhibition activity of imidazoline-stearic and commercial in NaCl 1 % solution.
4. Conclusion
Imidazoline-stearic from TETA and various purity grades of SA was successfully synthesized using microwave-assisted method. Imidazoline-stearic from SA pro analysis exhibited a similar activity (84.43 %) with the commercial (84.41 %) in inhibiting the corrosion. However, imidazoline-stearic from SA technical grade also revealed a promise as corrosion inhibitor (75.42 %) due to the economical aspect and effectiveness in scale up production. Replication of corrosion inhibition test is needed for further research.

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