Synthesis of imidazoline-palmitic derivative using MAOS (microwave assisted organic synthesis) method

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Abstract. In this work, imidazoline-palmitic derivative had been successfully synthesized by reacting triethylenetetramine (TETA) with palmitic acid (PA). Synthesis process was performed with solvent free using MAOS (Microwave Assisted Organic Synthesis) method with variation of time reactions. Dean-Stark and reflux methods using xylene as a solvent were also performed as comparisons. The percentage yield of TETA-PA imidazoline was obtained from Dean-Stark at 13 hours (95.80 %), reflux at 13 hours (88.53 %), and MAOS at 11 min (87.74 %). TETA-PA imidazoline then was identified by using thin layer chromatography and melting point analyzer followed by characterization using Fourier Transform Infrared (FTIR), UV-Vis, Proton Nuclear Magnetic Resonance (H-NMR), and Mass Spectrometry (MS) spectral data. This study provides information regarding comparison method for imidazoline derivative synthesis. For further research, TETA-PA imidazoline can be used as corrosion inhibitor towards carbon steel.

Keywords: corrosion inhibitor, imidazoline, MAOS, palmitic acid, triethylenetetramine.

1. Introduction

Corrosion is a natural process occurring in metals including carbon steel in petroleum and natural gas mining industries. The dispensing pipes are components which prone to corrosion because of corrosive media such as CO₂ and H₂S. To reduce the corrosion effect, corrosion inhibitors are given regularly to dispensing pipes. Corrosion inhibitors, which widely used in industry, are organic compound containing nitrogen, sulfur, or oxygen atom on its structure [1].

Imidazoline is a five-ring heterocyclic compound having two nitrogen atoms. According to its structure, imidazoline is often used as corrosion inhibitor due to its good adsorption properties and its ability to form layer on metal surface [2]. In the last decade, imidazoline synthesis using polyamines and fatty acid has grown rapidly since MAOS (Microwave Assisted Organic Synthesis) as novel method of imidazoline synthesis was invented. MAOS can facilitate green chemistry with solvent free, faster reaction time, and higher yield compared with reflux method [3].

Based on previous research, it is important to modify imidazoline structure in order to increase the corrosion inhibition activity [1, 4–5]. Therefore, in this research, imidazoline-palmitic derivative was synthesized by reacting triethylenetetramine (TETA) and palmitic acid (PA) using MAOS method with reflux and Dean Stark methods as comparison. PA was chosen because this compound is one of major components in tall oil, a commercial fatty acid mixture for corrosion inhibitor [2]. The aims of this study are to compare various methods on synthesizing imidazoline derivative and determine the structure of synthesized imidazoline using various spectral data. For further research, imidazoline-palmitic derivative can be developed as corrosion inhibitor towards carbon steel.
2. Materials and methods

2.1. General

The chemicals used were palmitic acid (PA), xylene, Thin-Layer Chromatography (TLC) plates, CHCl₃, MeOH, NHOH 25 %, Ce(SO₄)₂, H₂SO₄ 98 %, and Na₂SO₄ anhydrous purchased from E. Merck, while triethylenetetramine (TETA) from Sigma Aldrich. Synthesis of imidazoline-palmitic derivative, TETA-PA imidazoline, using MAOS was carried out by using microwave oven domestic Samsung ME-731K/XSE. Melting point was measured using Electrothermal Melting Temp. Apparatus. Structure elucidation of TETA-PA imidazoline was conducted using Fourier Transform Infrared (FTIR) Shimadzu IR Prestige 21, UV-Vis Shimadzu UV-2450, Proton Nuclear Magnetic Resonance (H-NMR, Agilent 500 MHz), and Mass Spectrometry (MS, Shimadzu Prominance 20-Abiesciex).

2.2. Synthesis of TETA-PA imidazoline using reflux and Dean Stark methods

TETA (5 mmol) and PA (5 mmol) were mixed with 20 mL xylene in a three-neck round-bottom flask. The mixture was heated using reflux at 100–230 °C for 13 hours. Reaction was monitored by TLC with CHCl₃:MeOH 8:2 and one drop of NHOH 25 % as an eluent, visualized under UV₂⁵₄, and stained with Ce(SO₄)₂/H₂SO₄. After reaction was completed, the mixture then was evaporated to remove water as by-product and xylene as solvent. The mixture was dissolved in CHCl₃ and extracted three times with aquabidest. The organic layer then was collected, dried with Na₂SO₄ anhydrous, evaporated, and stored in desiccator. TETA-PA imidazoline then was characterized using FTIR and UV-Vis. A similar reaction was also conducted using Dean Stark method by using Barret distilling receiver on the top of condenser.

TETA-PA imidazoline from reflux method was obtained as dark brown oily solid, Rf 0.70 in CHCl₃:MeOH 8:2 with one drop of NHOH 25 %; FTIR with KBr ν₁ (cm⁻¹): 3303.2, 3078.3, 2918.4, 2850.0, 1656.9, 1550.8, 1467.9; UV-Vis in MeOH λₘₚ (nm): 230, 270 (sh).

TETA-PA imidazoline from Dean Stark method was obtained as dark brown oily solid, Rf 0.70 in CHCl₃:MeOH 8:2 with one drop of NHOH 25 %; FTIR with KBr ν₁ (cm⁻¹): 3304.2, 3081.4, 2850.0, 1656.9, 1550.8, 1467.9; UV-Vis in MeOH λₘₚ (nm): 230, 270 (sh).

2.3. Synthesis of TETA-PA imidazoline using MAOS method

TETA (5 mmol) and PA (5 mmol) were mixed in a porcelain crucible with no solvent added. The mixture then was heated to microwave (800 watt) for 9, 11, 13, and 15 min. Similar monitoring, working up and characterization were also conducted. Furthermore, TETA-PA imidazoline from MAOS method was subjected to determine its melting point and additional characterization using H-NMR and MS.

TETA-PA imidazoline from MAOS method was obtained as dark brown oily solid, Rf 0.69 in CHCl₃:MeOH 8:2 with one drop of NHOH 25 %; mp. 77-29°C; FTIR with KBr ν₁ (cm⁻¹): 3303.2, 3076.5, 2915.7, 2850.0, 1638.6, 1551.8, 1467.8; UV-Vis in MeOH λₘₚ (nm): 230; H-NMR (500 MHz, CDCl₃) δ (ppm): 3.17-3.50 (4H, m), 2.65-2.88 (4H, m), 2.31-2.59 (4H, m), 2.15 (2H, t, J = 7.0 Hz), 1.59 (2H, p, J = 7.0 Hz), 1.22-1.26 (24H, m), 0.85 (3H, t, J = 7.0 Hz); MS (M+H) : 367.3316 m/z.

3. Results and discussion

In this present work, imidazoline-palmitic derivative synthesis was performed using MAOS method and compared with other methods i.e. reflux and Dean Stark methods. In general, imidazoline synthesis consisted of two-stage reaction, i.e. amidation to form amide and cyclization to form imidazoline ring (Figure 1). This two-stage reaction eliminates HO as by-product in both stages. To our knowledge, although this is not the first reported TETA-PA imidazoline synthesis [6], this is the first reported results on comparison methods of TETA-PA imidazoline synthesis along with its H-NMR and MS spectral data.
Table 1. Comparison of TETA-PA imidazoline synthesis using various methods.

| Parameters     | MAOS  | Reflux | Dean Stark |
|----------------|-------|--------|------------|
| Reaction Time  | 11 min| 13 h   | 13 h       |
| Temperature (°C) | 200    | 180    | 170        |
| Solvent        | -     | Xylene | Xylene     |
| % Yield        | 87.74 | 88.53  | 95.80      |

Figure 2. The percentage yield of TETA-PA imidazoline from MAOS method

Synthesis of TETA-PA imidazoline using MAOS method was carried out with variation of reaction time (9, 11, 13, and 15 min). Figure 2 showed the percentage yield of TETA-PA imidazoline as a function of reaction time. According to figure 2, the highest yield of TETA-PA imidazoline from MAOS method was obtained at 11 min with 87.74%. TETA-PA imidazoline was yielded as dark brown oily solid with the IUPAC name of \( N_1-(2-(2-(2-pentadecyl-4,5-dihydro-1H-imidazol-1-yl)-ethyl)-ethane-1,2-diamine \). TETA-PA imidazoline showed melting point at 77-79°C when measured with melting point analyzer, which indicated imidazoline derivative, was produced [2].

Comparison of TETA-PA imidazoline synthesis using MAOS, reflux, and Dean Stark methods were summarized in table 1. According to table 1, TETA-PA imidazoline from reflux and Dean Stark methods exhibited higher yield than MAOS method. According to previous research, the highest yield of synthesized imidazoline using various polyamines and fatty acids was 94.24% for MAOS method whereas reflux method yielded a lower yield of 92.37% [4]. The difference of experimental results may be caused from incomplete evaporation process of xylene and water as by-product. Even though MAOS method produced the lowest yield compared to others, MAOS method still revealed the percentage yield in above 80%, facilitated shorter reaction time, reached higher temperature, and provided green chemistry with solvent free synthesis. Therefore, it can be concluded that MAOS method is the most effective and efficient method on synthesizing imidazoline derivative.

TLC analysis of TETA-PA imidazoline from MAOS, reflux, and Dean Stark methods showed a similarity on \( R_f \) value of 0.69-0.70. Furthermore, FTIR spectra of TETA-PA imidazoline from various methods also showed the same pattern indicating similar functional groups (figure 3a). Based on figure 3a, the absorption peaks of N-H, C-H sp\(^3\), C=N, and C-N-C bonds were appeared at 3075-3304, 2850-2918, 1639-1657, and 1467 cm\(^{-1}\), respectively. These FTIR spectra revealed the characteristic absorption peaks for imidazoline and showed an agreement with previous research [2, 4–6]. UV-Vis spectra of TETA-PA imidazoline from various methods (figure 3b) also showed peaks appeared at the same wavelength of 230 nm which characteristic of C=N absorbance peak in imidazoline ring [2]. A shoulder absorbance peak at 270 nm on reflux and Dean Stark method indicated that xylene was still presented. Based on TLC analysis, FTIR, and UV-Vis spectra, three methods of TETA-PA imidazoline synthesis afforded the same compound.
Figure 3. Comparison of (a) FTIR and (b) UV-Vis spectra of TETA-PA imidazoline from MAOS, reflux, and Dean Stark methods.

Figure 4. (a) H-NMR in 500 MHz (CDCl₃) and (b) MS spectra of TETA-PA imidazoline from MAOS method
Since TLC analysis, FTIR, and UV-Vis spectral data revealed that TETA-PA imidazoline from MAOS, reflux, and Dean Stark methods was similar compound, therefore \textit{H}-NMR and MS spectral data to elucidate its structure were recorded only for TETA-PA imidazoline from MAOS method (Figure 4). According to \textit{H}-NMR spectra of TETA-PA imidazoline (500 MHz, CDCl$_3$) in figure 4a, the characteristic peak of proton in imidazoline ring appeared at chemical shift of 3.17-3.50 ppm. Other peaks were showed at chemical shift of 2.31-2.88 and 0.88-2.15 ppm indicated proton of pendant groups and hydrocarbon chains, respectively. \textit{H}-NMR spectra of TETA-PA imidazoline showed the similar pattern with \textit{H}-NMR spectra of imidazoline derivative from saturated fatty acid [4]. Furthermore, MS spectra of TETA-PA imidazoline in figure 4b shows [M+H]$^+$ at 367.3316 m/z which correspond to TETA-PA imidazoline, C$_{20}$H$_{46}$N$_4$. Based on all spectral data, therefore TETA-PA imidazoline had a structure as illustrated in figure 1. TETA-PA imidazoline is expected to be applied as corrosion inhibitor towards carbon steel in further research.

4. Conclusions
This work had studied imidazoline-palmitic derivative synthesis by comparing three methods i.e. MAOS, reflux, and Dean Stark. The percentage yield of TETA-PA imidazoline was obtained from Dean-Stark at 13 hours (95.80 %), reflux at 13 hours (88.53 %), and MAOS at 11 min (87.74 %). Imidazoline synthesis using MAOS method performed faster reaction time and higher reaching temperature in compare with reflux and Dean Stark methods. Structure elucidation of TETA-PA imidazoline was also conducted using various spectral data together with identification data. For further application, imidazoline-palmitic derivative can be developed as corrosion inhibitor towards carbon steel.

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