

Synthesis and Anti-corrosion Evaluation of Inhibitors for Top Cycle of Fractionating Tower

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Abstract. The top circulation reflux system of atmospheric and vacuum towers, catalytic towers and coking towers suffer from the phenomenon of pipe wall thinning and leakage as well as salt formation in the pump body over the past few decades. This can be attributed to the increased processing volume of high acid crude oil. The most severe corrosion among them threatens the long-term safe operation of the units, particularly the top cycle of the catalytic fractionation tower. Herein this study synthesised a corrosion inhibitor that is appropriate for processing high-acid crude oil in the fractionation tower's top cycle, primarily to prevent catalytic corrosion. In addition, the electrochemical measurement and the weight loss method were employed to evaluate the corrosion inhibition of the water-soluble and oil-soluble imidazoline inhibitors, respectively. The results indicated that corrosion inhibition of water-soluble imidazoline was $WCI \approx WBI > WAI$. Based on assessment results in the simulated oil-running environment of the HCl-water system and the HCl-H₂S water system, the synthesised oil-soluble inhibitor ($OBI > OCI > OAI$) has a better overall corrosion inhibition than the water-soluble inhibitor. The most effective corrosion inhibition on the catalytic top running oil are demonstrated by OBI, an oil-soluble corrosion inhibitor that is synthesised on-site.

Keywords: Fractionating tower; catalytic distillation top circulation reflux; corrosion; water-soluble imidazoline corrosion inhibitor; oil-soluble imidazoline corrosion inhibitor.

1. Introduction

The thinning and leakage of pipe wall and the salt formation of pump body in the top circulation system of fractionating tower in many refineries greatly affect and hinder the normal operation of the plant. This is due to the processing of high acid crude oil resulting in increased corrosion of the top of the fractionating column units such as atmospheric and vacuum, catalysis and coking^[1]. The corrosion of catalytic top cycle is more serious.

Long carbon chain alkyl imidazolines, imidazoline amide compounds, etc. are the main types of corrosion inhibitors^[2]. A thorough explanation of the characteristics, isolation, and characterisation of corrosion inhibitors of the imidazoline class was given by Chen et al.^[3]. Density functional theory (DFT) was utilised by J.F. Ramírez-Pérez et al.^[4] to investigate the performance of imidazoline-based corrosion inhibitors for protecting iron surfaces under aggressive environment.

JYH-2004 Oil soluble corrosion inhibitor is tested in the second set of atmospheric and vacuum equipment before industrial application. The test results show that the iron ion content in the sewage discharged from the initial top, normal top and reduced top has decreased significantly, and an excellent effect has been achieved^[5]. However, most of these imidazolinamide corrosion inhibitors should be combined with neutralizing agents in order to play a better corrosion inhibition performance. Therefore, inorganic ammonia neutralizer is currently gradually replaced by organic amine neutralizer.

Li et al. analyzed the corrosion factors in oil wells and evaluated corrosion inhibitors on site^[6]. They revealed that the optimal corrosion inhibition concentration of imidazoline corrosion inhibitors is 30 mg/L to 160 mg/L, and the dosing cycle can be extended by 1 to 2 days. Polymers with higher molecular sizes can be used as better corrosion inhibitors for the carbon steel/1.0 M HCl solution system by comparing six different types of inhibitors according to Zhang et al.^[7].

These compounds can cover the larger metallic surface area at lower concentrations than those with smaller molecular sizes.

Excellent thermal stability, good corrosion inhibition performance, low toxicity, and the absence of distinctly unpleasant odours are all displayed by imidazoline-type corrosion inhibitors^[8]. They typically consist of a hydrophobic side chain and a nitrogen-containing five-membered heterocycle with a variety of active functional groups on the heterocycle. In order to separate the metal from corrosive reactants and prevent their migration at the corrosion interface, the hydrophobic side chain may create a hydrophobic layer on the metal's surface. Effective coverage can be achieved by hydrophilic side chains chemically adhering to the metal surface by coordination^[9].

Diethylenetriamine and a number of fatty acids (A, B, and C) were chosen for the reaction. First, the fatty acid-type imidazoline intermediate was created. Then the imidazoline intermediate underwent distinct reactions with anhydride and benzyl chloride. A water-soluble imidazoline corrosion inhibitor was created by quaternizing the imidazoline intermediate with benzyl chloride^[10]. Oil-soluble imidazoline amide (OI series) corrosion inhibitors are produced via acylation of the imidazoline intermediate with anhydride. These imidazoline corrosion inhibitors feature several electron-donating groups in them as a result of C=C double bonds, benzene rings, and nitrogen-containing five-membered heterocycles. These groups help the molecules create excellent films. The findings of the experiment show improved corrosion inhibition.

In this study, some of the selected corrosion inhibitors and synthesized imidazole corrosion inhibitors were applied to the atmospheric pressure tower top circulation system, based on the on-site investigation of tower top circulation oil. The aim is to efficiently prevent or mitigate corrosion in the upper cycle of the fractionator.

2. Evaluation Methods for Corrosion Inhibitor Performance

2.1 Weight loss method

The static weight loss method was employed to examine the impacts of corrosion. The mass difference between the pre- and post-corroded steel samples is measured in order to calculate the corrosion rate. This method provides a quantitative evaluation of the material's anti-corrosion properties by calculating the mass loss.

The A3 steel samples were cleaned with acetone and anhydrous ethanol, polished with sandpaper, and then either air-dried or blow-dried with cold air. Samples were weighed after being dried for thirty minutes in a drying oven. The samples were subsequently immersed in a three-necked flask containing the corrosive medium and a reflux condenser attached for a specific amount of time at a predetermined temperature. After being removed, the samples were cleaned with anhydrous ethanol and acetone. They were then dried and put in a drying oven for about half an hour. This process was repeated until the samples were weighed again, this time with an accuracy of 0.0001 mg. The loss weight of the steel sample due to corrosion was measured and recorded.

The corrosion rate and the anti-corrosion efficiency for inhibitor were calculated based on the weight loss of the samples.

$$v = \frac{w_o - w_1}{st}$$

Where v is the Corrosion rate, $\text{g} \cdot (\text{m}^2 \cdot \text{h})^{-1}$; w_o , the Initial weight loss, g; w_1 , the Final weight loss, g; s , the Surface area of the metal specimen, m^2 ; t indicates the Corrosion time, h. The calculation of inhibition efficiency is given as follows:

$$\eta\% = \frac{v_o - v_1}{v_o} \times 100$$

Where v_o is the Corrosion rate of the steel specimen without the addition of corrosion inhibitor, $\text{g} \cdot (\text{m}^2 \cdot \text{h})^{-1}$; v_1 indicates the Corrosion rate of the steel specimen after the addition of corrosion inhibitor, $\text{g} \cdot (\text{m}^2 \cdot \text{h})^{-1}$; $\eta\%$ is the Inhibition efficiency.

2.2 Electrochemical Measurement

Electrochemical measurements were carried out by an electrochemical workstation (Reference 3000, Gamry, Warminster, PA, USA) with 3.5 wt.% NaCl solution. A three-electrode system was employed with the sample as the working electrode. A platinum mesh was regarded as the counter electrode. The reference electrode was selected as an Ag/AgCl electrode (3M KCl). Potentiodynamic (DP) measurements were conducted with the scanning rate of 1 mV/s over ± 0.1 V vs. open circuit potential.

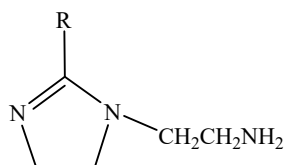
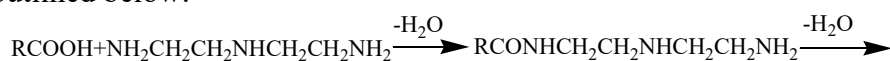
3. Synthesis and Performance Evaluation of Fatty Acid Type Imidazoline Corrosion Inhibitors

3.1 Synthesis of Fatty Acid Type Imidazoline Corrosion Inhibitors

3.1.1 Synthesis of Fatty Acid-Type Imidazoline Intermediate

An imidazoline intermediate was initially synthesized through a two-step process by utilizing fatty acids (A, B, C) and diethylenetriamine as raw materials. The imidazoline intermediate was subsequently quaternized using benzyl chloride to produce three water-soluble imidazoline corrosion inhibitors. Furthermore, three oil-soluble imidazoline corrosion inhibitors were obtained by reacting the imidazoline intermediate with acetic anhydride. The performance of these inhibitors was then evaluated in the corrosion system mentioned above.

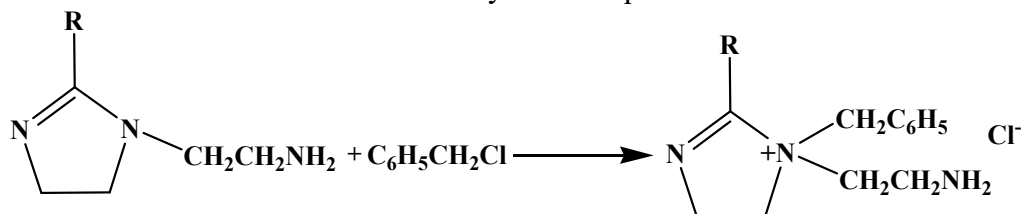
The synthesis of the fatty acid-type imidazoline intermediate commenced with fatty acids and diethylenetriamine as raw materials. The diethylenetriamine was added to a three-necked flask that included a thermometer, reflux condenser, and separator. 5 ml xylene and a specific amount of fatty acid were added once the temperature was increased to about 150°C. The mixture was refluxed and heated rapidly to 170°C under a nitrogen environment to initiate the acylation dehydration process. After a certain period, no water was observed in the separator. The temperature was slowly raised to 210°C by using a programmed temperature increase for cyclization dehydration until no more water was produced. The heating was stopped when the water volume in the separator reached the theoretical amount, and the mixture was allowed to cool under a nitrogen protective atmosphere. Excess xylene-water azeotrope and surplus diethylenetriamine were removed by vacuum distillation, and the product was dried in a vacuum drying oven. The resulting reddish-brown, viscous imidazoline intermediate was weighed to calculate the yield. The synthetic route for the intermediate is outlined below:



Reaction yields or water separation are used to calculate the cyclization conversion rates during the imidazoline intermediate's manufacture. The ideal synthesis conditions for the intermediate are found by investigating the effects of material ratios, reaction times, and reaction temperatures on the synthesis reaction. The ideal synthesis parameters for the imidazoline intermediate (also known as AI) resulting from the reaction between fatty acid A and diethylenetriamine, using fatty acid A as an example, are as follows: a reaction temperature of 230°C, a reaction time of 7 hours, and a material ratio of A to diethylenetriamine of 1:1.2.

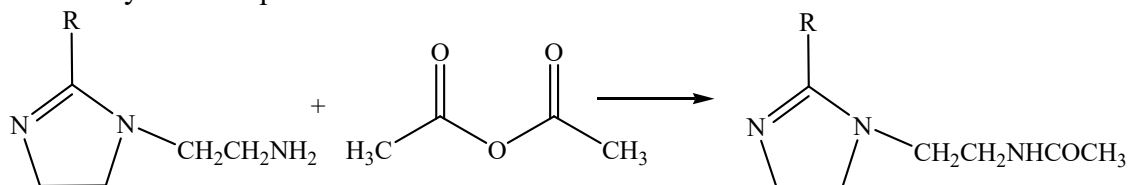
3.1.2 Synthesis of Water-Soluble Imidazoline Quaternary Ammonium Salts

The imidazoline intermediate was introduced into a three-necked flask and heated in an oil bath to 100-120°C. Equimolar benzyl chloride was then added for quaternization to enhance the water solubility of the imidazoline. After a 4-hour reaction, the WI series of water-soluble imidazoline quaternary ammonium salts were obtained. The synthesis equation is as follows:



3.1.3 Synthesis of Oil-Soluble Imidazoline Amides

A certain amount of imidazoline intermediate was mixed with acetic anhydride and reacted in a water bath using DMF as the solvent. After a specified period, the solvent DMF and unreacted reactants were removed by vacuum distillation, resulting in a brownish viscous solid product, the OI series of oil-soluble imidazoline amides. The product was dried, weighed, and the yield was calculated. The synthesis equation is as follows:



The optimal conditions for synthesizing OAI from the AI intermediate were determined to be a reaction temperature of 80°C and a molar ratio of AI intermediate to acetic anhydride of 1:0.6.

Products were individually synthesized from fatty acids A, B, and C, resulting in the following compounds: imidazoline intermediates AI, BI, CI; water-soluble imidazoline quaternary ammonium salts WAI, WBI, WCI; and oil-soluble imidazoline amides OAI, OBI, OCI.

3.2 Anti-corrosion Evaluation of Synthesized Imidazoline Corrosion Inhibitors

3.2.1 Anti-corrosion Evaluation of Water-Soluble Imidazoline Corrosion Inhibitors

Different corrosion inhibitors were added to a hydrochloric acid solution containing 1000 µg·g⁻¹ at room temperature (20°C) at a concentration of 100 µg·g⁻¹. The evaluation was conducted using the polarization curve method, and the results are shown in Figure 1. The corrosion currents of the three inhibitors can be obtained by extrapolating the Tafel lines, from which the inhibition efficiency can be derived.

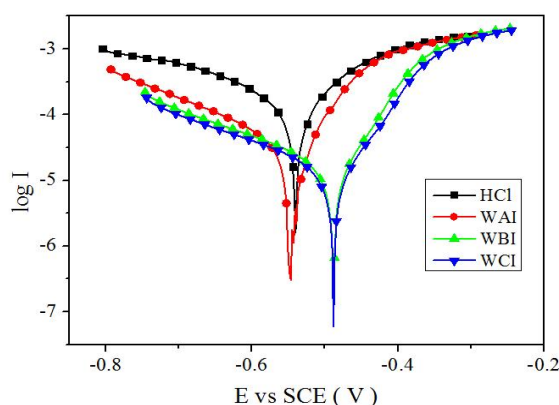


Fig 1. Determination of corrosion inhibition of three kinds of corrosion inhibitors by electrochemical method

Table 1. Evaluation of corrosion inhibition performance of the WI system of corrosion inhibitors for HCl-water system(Polarization curve method)

	HCl	WAI	WBI	WCI
$I_c/(A \cdot cm^{-2})$	3.19E-04	3.76E-05	1.50E-05	1.45E-05
Inhibition rate /%	—	88.2	95.3	95.5

This observation demonstrates that WAI performs noticeably poorer than the other two inhibitors, WBI and WCI, in terms of corrosion inhibition effects. An analysis reveals that WAI's less effective performance may be primarily caused by its inadequate water solubility.

The water-soluble corrosion inhibitors were evaluated using the weight loss method. Different corrosion inhibitors were added to 450 ml of water containing $1000 \mu g \cdot g^{-1}$ hydrochloric acid at a concentration of $100 \mu g \cdot g^{-1}$. Considering that the actual temperature of the top reflux system exceeds $80^{\circ}C$, the assessment of the inhibitors was conducted at $90^{\circ}C$, as indicated in Table 2.

Table 2. Evaluation of corrosion inhibition performance of the WI system of corrosion inhibitors for HCl-water system(Weight loss method)

	WAI	WBI	WCI
Corrosion rate $/g \cdot (m^2 \cdot h)^{-1}$	8.680	2.057	1.906
Inhibition rate /%	Aggravated corrosion	65.54	68.10

Hence, it is evident that both electrochemical methods and the weight loss technique yield consistent evaluations for the three water-soluble corrosion inhibitors, with WBI and WCI exhibiting relatively superior corrosion inhibition effects. However, the assessment of the inhibitors using the weight loss method at $90^{\circ}C$ reveals that the corrosion inhibition efficiency of the synthesized water-soluble imidazoline inhibitors is all below 70%. The synthesis of oil-soluble fatty acid-type imidazoline corrosion inhibitors was pursued in an effort to increase the corrosion inhibition efficiency.

3.2.2 Anti-corrosion Evaluation of Oil-Soluble Imidazoline Corrosion Inhibitors

The corrosion inhibitor was added at a concentration of $100 \mu g \cdot g^{-1}$ (dissolved in ethanol) to a hydrochloric acid (HCl) water solution that was used as the corrosion system, with a concentration of $1000 \mu g \cdot g^{-1}$. For eight hours, the corrosion assessment was carried out at a temperature of $90^{\circ}C$. Table 3 provides specifics on the synthesised compounds' corrosion inhibition capabilities.

Table 3. The corrosion inhibition of synthesizing oil-soluble imidazoline inhibitors in HCl- water system

	AI	BI	CI	OAI	OBI	OCI
Inhibition rate /%	69.15	54.11	72.60	76.35	87.08	84.65

It can be observed that the corrosion inhibition performance of the synthesized OI series oil-soluble corrosion inhibitors is superior to the WI series water-soluble corrosion inhibitors. The corrosion inhibition efficiency of the synthesized imidazoline imide inhibitors is better than that of the intermediates, with $OBI > OCI > OAI$. This is probable that the molecule contains many electron-donating groups due to the presence of nitrogen-containing pentacyclic rings, benzene rings, and $C=C$ double bonds in its structure. the longer carbon chains further contribute to better film-forming properties, and the introduction of an anhydride enhances the stability of the corrosion inhibitor.

4. Summary

Three different types of fatty acids were employed to synthesise the water-soluble and oil-soluble imidazoline corrosion inhibitors in this study. This is more appropriate for the fractionation tower top circulation system than the water-soluble corrosion inhibitor, which is

mainly employed in industrial atmospheric pressure tower tops. The corrosion inhibition property of the synthesised water-soluble imidazoline corrosion inhibitor, as measured by electrochemical measurement and weight loss method, is $WCI \approx WBI > WAI$ in the HCl water system. The synthesised oil-soluble inhibitor exhibits enhanced corrosion inhibition effectiveness over the water-soluble inhibitor ($OBI > OCI > OAI$). In the corrosion environment of catalytic top cycle oil, the synthesised corrosion inhibitor OBI exhibits excellent anti-corrosion performance.

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