Naphthenic Acid Corrosion in Petroleum Refineries

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Abstract

Present review article aims to highlight corrosion problems in refinery processing environment due to low molecular weight carboxylic acids commonly known as naphthenic acids. Various components like vacuum unit distillation column, pumps, transfer lines and exchangers are affected due to naphthenic acid corrosion in refinery environment. Naphthenic acids cause more severe corrosion in vapor phase when compared to liquid phase and velocity has an effect on the corrosion rate through wall shear stress. Corrosion intensity also depends on the physical state of the acids present in the operating system. Suitable corrosion monitoring is invariably required to check the effectiveness of any corrosion control measure. Various modern instrumental techniques for the determination of the nature of the naphthenic acids present can provide vital information such as acids’ sizes and composition, which may be used in the battle against corrosion and also used to fingerprint samples from different oil fields. Different corrosion preventive measures like blending, material up gradation, use of resistant alloys and chemical treatment using corrosion inhibitors have been taken into account while discussing the problem in detail.

Keywords: Corrosion, Naphthenic acids and Refinery.

Introduction

Corrosion in petrochemical industries varies widely with different refinery processes and on the nature of the constituents in the process streams [1]. Although major of the crude consists of non-corrosive hydrocarbons but a part of it consists of sulphur compounds, inorganic salts, water, organic acids and oxygen that initiate corrosion [2]. Among these impurities, carboxylic acids, commonly known as naphthenic acids create corrosion problems during high temperature operations in petroleum refiner. Naphthenic acid content in the different crude oils may vary in the range of 0-4%. These naphthenic acids which are relatively low molecular weight compounds are the problematic substances as these have been started coming even in crude oils from China, India, Africa etc. where these are not expected [3-4]. Naphthenic acid corrosion was observed for the first time in 1920 during the processing of some specific crude oils. Earlier naphthenic acids were readily accepted chiefly in the form of metal soaps, for use as driers, lubricant additives, fungicides etc. [5-6]. It was reported in literature that naphthenic acid corrosion was observed in the petrochemical industries in China, India, Europe, Russia USA, Venezuela etc. [2, 6-7]. Naphthenic acids are naturally occurring surfactants, which play a role in the bitumen extraction in the oil sand industry [8]. Another case was with the Sun Marcas Refinery which runs sweet crude and expecting no corrosion due to naphthenic acids. But in December turn-around during 1990, when vacuum tower was opened, it was found corroded due to naphthenic acid [4]. To overcome naphthenic acid corrosion California refinery used metallurgical solutions by cladding vacuum column in 317SS. From a report in 1983 it was seen that the Amuay refinery in California was running naphthenic acid crude since last 30 years and detected a lot of corrosion in different parts of the process systems including the lube plant and the desulphurization units [9].

Mostly naphthenic acid corrosion is seen at higher temperatures and is significant. Sometimes corrosion is increased when these acids interact with other species like acid gases etc. Even the products like lower organic acids (formic, acetic, propionic and butyric), which are formed by the thermal degradation of naphthenic acids, attack the process equipment [1, 10].

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Naphthenic acids
Structural Composition
These are the low molecular weight carboxylic acids ($C_nH_{2n+z}O_2$) present in the crude along with hydrocarbons. These carboxylic acids are complex mixtures of acyclic and cyclo-aliphatic compounds with alkyl substitution. Where
$n =$ No. of carbon atoms & $Z =$ specifies homologous series (0 or negative even integers)

Fig. 1 gives the various naphthenic acids found in different crude samples [3, 8]. Naphthenic acids with $z = 0$ are acyclic acids but prefer to be branched structures. The value $z = -2$ family corresponds to single ring, $z = -4$ family correspond to 2 rings and $z = -6$ corresponds to 3 rings structures.

<table>
<thead>
<tr>
<th>$Z$</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0</td>
<td>R-COOH</td>
</tr>
<tr>
<td>-2</td>
<td>R-CCOOH</td>
</tr>
<tr>
<td>-4</td>
<td>R-CCOOH</td>
</tr>
<tr>
<td>-6</td>
<td>R-CCOOH</td>
</tr>
<tr>
<td>-8</td>
<td>R-CCOOH</td>
</tr>
</tbody>
</table>

Fig. 1: Various naphthenic acids present in the crude.

Determination of naphthenic acid
Crude oils with a total acidity greater than 0.5 mg KOH/g, generally contains enough naphthenic acids to cause corrosion. There are special test methods available to determine the total acidity as well as naphthenic acid content in the process stream [11-14]. These test methods comprise following procedures:

ASTM procedures:
These procedures were used to determine the oxidation of petroleum products and lubricants. ASTM D 974 is a coulometric titration method whereas ASTM D 664 is a potentiometric titration with reproducibility of 15% and 20-44% respectively.

UOP procedures:
Two methods UOP 565 and UOP 587 are used, which are potentiometric and calorimetric respectively. Apart from these conventional procedures, literature indicates various instrumental analysis techniques like liquid chromatography, I.R spectroscopy and Fast atom bombardment-Mass spectroscopy (FAB-MS). These modern techniques are mainly used to fingerprint crude oil corrosivity [15]. Jones et al. have developed a practical, rapid and quantitative method for analyzing carboxylic acids in oil using solid phase extraction (SPE) based method [7].
Affected areas
Naphthenic acid corrosion normally takes place when the crude has a neutralization number greater than 0.5 mg KOH/g [16]. The corrosion due to naphthenic acids is quite significant, varying from sharp-edged holes to streamlined grooves [1, 10, 17-18]. Some of the corrosion affected areas are:

Vacuum distillation column
Severe naphthenic acid corrosion was seen in vacuum towers of distillation column at temperature 290°C to 350°C and the damage was in the form of pitting. It was seen that these acids are highly active when in the vapour state but severe corrosion is seen in the condensation process. In this part, corrosion limit depends on the content, molecular weight, and the boiling point of naphthenic acids present and is independent of the velocity. The places where severe corrosion is seen are the condensing point [19]. Some items, which are neglected but prone to naphthenic acid corrosion, are tray support rings, tray bolting, support clips etc. [20-21].

Furnace tubes and transfer lines
The intensity of corrosion depends on the temperature of the system, velocity and the degree of vapourization. Also, parameters like load & steam rate and turbulence do affect the corrosion rate. The mechanism is an accelerated corrosion mechanism. To avoid this, carbon steel piping clad with 317SLSS is used. The most affected areas are the thermo-wells in the furnace outlets and the transfer lines [19-20].

Side cut piping
Here if the velocity increases, corrosion also increases and it was seen that the presence of sulphur reduces the corrosion. 317L SS up-gradation reduces the corrosion. Also, the orifices, valves, thermo-wells, and other instruments are affected and need to be up-graded [19-20].

Exchangers
The components of exchangers like shell, tubes, baffles, tie rods, leaf-seals etc. are affected due to naphthenic acid corrosion [20].

Monitoring of naphthenic acid corrosion
As per Gutzeit [22], the laboratory evaluation of naphthenic acid corrosion is carried out using various methods like:

i. Continuous flow unit
ii. Rocking autoclave
iii. Distillation equipment

This type of tests for evaluating naphthenic acid corrosion suffers from following drawbacks:

a. These tests are used only for the determination of corrosion at different velocities in either a liquid environment or in a vapour phase as in distillation unit.

b. These tests use either pressurized autoclave or in distillation unit working at atmospheric pressure. White oil naphthenic acid blends are used in all these studies. Under these conditions, the actual refinery feed containing naphthenic acid cannot be used because of the likely-hood of cracking of the feed which in turn changes the composition of the feed.

Jayaraman and coworkers have developed a device useful for conducting controlled velocity corrosion test in a vacuum distillation unit [23]. This ensures no change in the composition of petroleum feed during the distillation, such as the decomposition of naphthenic acid of the feed at high temperatures. It is reported in literature that thermal decomposition of naphthenic acid can occur which may lead to corrosive low carbon number organic acids. Reference may be made to the article by Batra et al. [17] in which the authors indicated thermal decomposition of naphthenic acids. Based on NACE Standard TM 01-69, "Laboratory Corrosion Testing of Metals for the Process Industries," Kibala et al. have developed a standard test method for monitoring the corrosion of process stream [4].
Factors affecting naphthenic acid corrosion

Neutralization number

Naphthenic acid corrosion normally occurs when the crude being processed has a neutralization number greater than 0.5mgKOH/g. However there are many cases including high velocity, high TAN and others where these rules of thumb break down. Earlier Gutzeit [22] had reported that the corrosion rate of carbon steel, 7Cr-0.5Mo steel and 9 Cr-1Mo steel increases about 2.5 times when the neutralization was doubled (Fig.2). In contrast, the corrosion rate of AISI 410 SS is increased nearly 4.6 times doubling the neutralization number (Fig.3) [22].

![Fig. 2 Corrosion isotherms for 9Cr-1Mo in White oil/naphthenic acid blends](image1)

![Fig. 3 Corrosion isotherms for AISI 410 (12Cr) SS in white oil/naphthenic acid blends](image2)

Operating temperature

Naphthenic acid corrosion is found to occur in the temperature range from 230-420°C in high velocity areas. In the Q&A session of NPRA congress in 1990, it was reported that several refineries experienced naphthenic acid corrosion at temperatures as low as 177°C [10]. Gutzeit has tentatively concluded that naphthenic acid corrosion continues to increase with temperature up to 385°C provided naphthenic acid are not lost through vapourization [22]. No corrosion damage is usually observed at temperatures above 400°C, due to decomposition of naphthenic acid and protection due to coke formation on the metal surface [24].

Physical state

Gutzeit in his paper indicated that liquid phase corrosion decreases slightly with increase in velocity due to loss of naphthenic acid as vapours whereas vapour phase corrosion increased drastically with increase in velocity because of more vapours are formed due to agitation and thereby caused more of condensation. But increasing velocity above 4m/s-vapour phase corrosion rate decreased as formation of naphthenic acid rich condense film is prevented due to centrifugal force [22, 24].

Velocity

Velocity is also involved directly in this parameter. Corrosion rates are directly proportional to shear stress and was seen that even low level of naphthenic acid causes severe corrosion at high temperature and high velocity [24].
Mitigation

Blending

Blending is performed in a way that the crude, which enters the distillation column, should not have a neutralization number more than 0.5 to 1.0 but blending is not useful for vacuum tower internals operating in temperature range of 290-350°C. The sulphur content can also be increased using blending which reduces the naphthenic acid corrosion. Blending also changes shear stress parameters and reduces corrosion [1, 9].

Use of inhibitors

Literature survey indicated some organic corrosion inhibitors that are effective even at temperatures above 200°C whence the naphthenic acid corrosion problems become significant [4]. These comprise of two categories: P series and non-P series. P series include inhibitors like thiozoline, thiophosphate, phosphate esters etc and non P series includes sulfonated alkyl phenols, organic polysulfide, thio-hydroxy triazine, fatty acid amino amide etc, all of which have been claimed to be effective (in hydrocarbon rich phase) against naphthenic acid corrosion. As regards the phosphorus compounds, scanning electron microscope, studies revealed the presence of phosphorus on metal surface [25]. Interaction of phosphate esters with metal (iron) surface has been postulated in the following manner:

\[
\begin{align*}
\text{Fe or Fe}^{2+} + \text{OH}^- + \text{PO(OH)}_2^- & \rightarrow \text{Fe} \text{PO}_4^{3-} + \text{OR}^- \\
\text{Fe} \text{PO}_4^{3-} + \text{OR}^- & \rightarrow \text{Fe} \left(\text{PO}_4\right)\text{OR} + \text{OH}^-
\end{align*}
\]

The above mechanism interferes with the reaction of iron with naphthenic acids. Instead of forming a hydrocarbon soluble iron naphthenate, insoluble iron phosphate is produced. This interaction eventually results in the formation of a tenacious film on the metal surface, which prevents naphthenic acid attack [4, 26-27].

Neutralization

This is another important method of reducing the naphthenic acid corrosion. If the crude is treated before to get rid of the corrosivity, it could be a good measure. In neutralization chemical like caustic soda is added to the crude oil that neutralizes the naphthenic acids before distillation. But it has a drawback that it leads to the formation of emulsions, which in any cause caustic racking of the carbon steel equipment [9].

Process control changes

Ernesto and Brian have concluded that when a refinery is in processing naphthenic crude oils, operational changes can affect corrosivity, much more than with non naphthenic crude oils. Any proposed operational changes should be reviewed with material specialists to evaluate their impact [9].

Equipment material up-gradation

Most of the equipment use construction materials (carbon steel, 5Cr-1/2 Mo and 9Cr-1 Mochrome steel, 410SS) which are resistant to sulphur corrosion, so these need to be up graded to better quality construction materials like 316SS, 5Cr-1 or 2Mo, 9Cr-1 Mo chrome steels, 317SS, aluminized steel etc. [1, 9, 24]. Ernesto Blanco F et al. listed all the parts and the type of construction material used in Amuay refinery to avoid naphthenic acid corrosion. According to a survey by Cathleen Shargay et al. (USA), at least 317 SS should be used in high velocity areas like furnaces and transfer lines. He also indicated that some places like side stream piping may require up-gradation to 317 SS or 316L SS with 2.5% Mo [9, 20].

Alloy

Nickel alloys containing high amount of Ni like Inconel 600 and Incoloy 800 are resistant against naphthenic acids but these have limited operational conditions [9]. In the Q&A session of NPRA (1990)
representatives of different refineries mentioned their precautionary measures taken in respective refinery and was seen that some used up-gradation of equipment and some used blending, topping crude and neutralization methods to overcome the problem [18].

Conclusions

Though present in small amounts, naphthenic acid causes significant amount of corrosion in process equipment in a temperature range of 230-450°C. Literature indicates that in vapour phase naphthenic acids cause more severe corrosion than in liquid phase. Velocity has an effect on corrosion rate through wall shear stress and corrosion also depends on the physical state of the acids present in the operating system. Various control measures have been discussed to mitigate naphthenic acid corrosion including up-gradation of equipment, blending, topping, neutralization and chemical treatment using corrosion inhibitors. These measures can be applied depending on the type of crude and process conditions. Suitable corrosion monitoring is invariably required to check the effectiveness of any control measure.

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