Evaluation of mineral oils as matrices for AISI/SAE–1020 steel naphthenic corrosion study

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Abstract. Petrochemical industry has suffered great economic impact due to light crude oil reserves reduction, so refineries have been processing high acidity heavy crude oils. Studies of corrosion caused by naphthenic acids are interfered by presence of other corrosive agents contained in real crude oils, so naphthenic phenomenon must be isolated using synthetic crude oils. For this reason, in present work two high purity mineral oils were used to evaluate their efficiency as synthetic crude oil matrices in AISI/SAE–1020 steel naphthenic corrosion study. Temperature levels evaluated were 200 °C, 250 °C, and 300 °C, while exposure times evaluated were 5, 10 and 15 hours. Surface morphological characterization of AISI/SAE–1020 steel was carried out using scanning electron microscopy and X-ray diffraction. Gravimetric tests showed that AISI/SAE–1020 steel naphthenic corrosion rate increases with temperature and exposure time for one of the synthetic crude oils. However, results obtained for the other synthetic crude oil did not show increasing behaviour due to presence of sulfur traces in the oil, which caused an interference with AISI/SAE–1020 steel naphthenic corrosion study, reducing the reliability of gravimetric results so they cannot be extrapolated to operating conditions in distillation units.

1. Introduction
In petrochemical industry, corrosion phenomenon is strongly associated with processing of heavy crude oil due to its high content of corrosive agents [1]. Naphthenic acids are among the main causes of this phenomenon, which are potentially corrosive and affect preheating furnaces, transfer lines and atmospheric and vacuum distillation units, causing fouling and decreasing the quality of middle distillates obtained [2].

Naphthenic corrosion is influenced by multiple variables such as temperature (generally occurs above 220 °C), exposure time, concentration and type of naphthenic acids and the presence of organic sulfur compounds, among others. This phenomenon is caused by reaction of naphthenic acids (RCOOH) with iron (Fe) from metallic surfaces, generating iron naphthenates (Fe(RCOO)₂) that are soluble in crude oil and cause a constant material loss, giving place to appearance of pitting corrosion in the exposed materials [3].

Currently, there are several alternatives for naphthenic corrosion prevention and mitigation such as: blending, which consists of mixing crude oil with others with lower naphthenic acids content to reduce the acidity; chemical neutralization of naphthenic acids; and metallurgy upgrade through selection of materials with greater corrosion resistance [3]. Evaluation of these methods is carried out in its initial
stage through bench scale tests, generally by gravimetry, where fractions of real crude oil or synthetic crude oil can be used.

One advantage of using synthetic crude oils is that it allows to isolate naphthenic acids effect from other corrosive agents present in real crude oil fractions such as organic sulfur compounds, hydrochloric acid, amines and heavy metals, among others [4]. In addition to this, selection of mineral oil matrix is of great relevance during the development of bench scale tests, since its composition must be such that it does not generate any type of interference on the gravimetric results.

For this reason, in present work two mineral oils were used as synthetic crude oil matrices to evaluate the effect of temperature and exposure time on naphthenic corrosion of AISI/SAE–1020 steel in a system that simulates operating conditions of a transfer line in Colombian heavy crude processing.

2. Experimental

Tests were carried out using gravimetric coupons of AISI/SAE–1020 steel with dimensions: 76 mm length, 12.6 mm width, 1.5 mm thickness and 7.9 mm internal diameter for fastening hole. Surface metallographic preparation was carried out according to ASTM G1–03 standard guidelines [5]. Material surface was polished with silicon carbide abrasive paper No. 150, 220, 400, 600, 1500 and 2000; subsequently, gravimetric coupons were cleaned with acetone in ultrasonic bath and weighed on a Mettler AE 240 analytical balance with ± 0.0001 g precision. Chemical composition of AISI/SAE–1020 steel was determined by atomic emission spectrometry according to ASTM E415–15 standard [6] as shown in Table 1.

| Element | C      | Fe    | Mn    | S     | Si    | P     | Ni    | Mo |
|---------|--------|-------|-------|-------|-------|-------|-------|-----|
| Composition (%wt) | 0.17  | 98.61 | 0.82  | <0.15 | 0.04  | 0.01  | 0.01  | <0.01 |

Synthetic crude oils used were called SCO–1 and SCO–2, and they were prepared by adding a mixture of Aldrich analytical grade naphthenic acids on mineral oils MO–1 and MO–2, respectively. The amount of mineral oil and naphthenic acids were calculated to obtain synthetic crude oils with total acid number (TAN) equivalent to 1, which represents the amount of mg of potassium hydroxide needed to neutralize one gram of crude (mgKOH/g) [7].

Gravimetric tests were carried out in a Parr 4848 dynamic autoclave–type batch reactor with pressure and temperature control, where gravimetric coupons were placed immersed in 500 mL of the corresponding synthetic crude oil. Prior to start of each test, a purge with analytical grade nitrogen was carried out to remove oxygen dissolved in the synthetic crude oil and avoid interference from material oxidation reaction. Once the gravimetric test was completed, the coupons were removed from the reactor and weighed on an analytical balance to determine the mass loss, which was used to calculate the naphthenic corrosion rate of AISI/SAE–1020 steel according to Equation (1) [5], where: Δw represents mass loss in (g); A represents the exposed area in (cm²); ρ represents the density of AISI/SAE–1020 steel in (g cm⁻³); and t represents exposure time in (hours).

\[
\text{Corrosion rate} = \frac{3.45 \times 10^6 \times \Delta w}{\rho \times A \times t}.
\]

For each synthetic crude oil (SCO–1 and SCO–2) a 3² design of experiments was carried out, where levels established for temperature were 200 °C, 250 °C and 300 °C while levels for exposure time were 5, 10 and 15 hours. Each set of synthetic crude oil, temperature and exposure time conditions was evaluated in triplicate in order to guarantee the results repeatability. Surface morphological characterization of the exposed AISI/SAE–1020 steel was performed using scanning electron microscopy (SEM) combined with energy dispersive X–Ray spectroscopy (EDS) and X – ray diffraction (XRD).
3. Results and discussion

Figure 1 shows AISI/SAE–1020 steel corrosion rate exposed to SCO–1 and SCO–2 crude oils as a function of system temperature and exposure time, where is observed different behaviours for each synthetic crude oil.

![Figure 1](image_url)

**Figure 1.** AISI/SAE–1020 steel corrosion rate for crude oil: (a) SCO–1 and (b) SCO–2.

For crude oil SCO–1, AISI/SAE–1020 steel corrosion rate increased with both temperature and exposure time. In the first case, phenomenon is associated with the greater reactivity of naphthenic acids when system temperature increases, since corrosion reaction occurs faster and allows forming a greater quantity of iron naphthenates, leading to an increase in AISI/SAE–1020 steel mass loss and corrosion rate [8]. In addition to this, iron naphthenates formed are soluble in crude oil, so they do not form a layer of corrosion products on the material surface that can isolate it from the corrosive environment, and for this reason the naphthenic corrosion reaction occurs continuously and progressively in the system, allowing the corrosion rate of the material to increase with exposure time [9]. In accordance with this trend, it is possible to infer that synthetic crude oil SCO–1 allowed to isolate the AISI/SAE–1020 steel corrosion rate values corresponding to naphthenic acids exposure, and therefore the mineral oil MO–1 can be used as a matrix in the study of naphthenic corrosion phenomenon.

On the other hand, behaviour of AISI/SAE–1020 steel corrosion rate for synthetic crude oil SCO–2 was different from that expected after exposure to a system where naphthenic phenomenon predominates. This was evidenced as a decreasing trend of corrosion rate with temperature for all exposure times, which is a behaviour commonly associated with sulfidic corrosion [10]. In this phenomenon, layers of corrosion products are formed on the material surface and act as a physical barrier that isolates the iron from the corrosive medium, thereby reducing the interaction between the metal surface and the naphthenic acids in the synthetic crude oil [11]. In this way, it is possible to infer that traces of sulfur were found in the composition of mineral oil MO–2 that reacted with AISI/SAE–1020 steel surface to form iron sulfides, and since these are insoluble in crude oil, they led to formation of adhered layers that prevented the advance of naphthenic corrosion reaction.

Figure 2 shows the surface morphological characterization of AISI/SAE–1020 steel exposed to synthetic crude oil SCO–1 at 300 °C for 15 hours, where the damage caused by naphthenic acids to the material is evidenced. As described in Equation (2), naphthenic corrosion reaction leads to formation of soluble iron naphthenates in crude oil, so the material presents an iron loss that is evidenced as an erosion corrosion attack on the metal surface [8].

\[
Fe + 2 RCOOH \rightarrow Fe(RCOO)_2 + H_2. \tag{2}
\]
In addition to this, according to the hydrodynamic conditions of the system there is the possibility that areas where occurs a localized increase of naphthenic acids concentration are generated, as generally occurs in the plates of distillation units, which can lead to pitting corrosion that is difficult to identify on units in service and can cause serious material, economic, safety and environmental damage [12].

In the same way, lack of corrosion products on the material surface leads to the absence of major changes in elemental composition obtained through EDS analysis, where the iron from the material predominates and there are low concentrations of carbon and oxygen associated with both the original composition of the material and the thermal decomposition of naphthenic acids in the system. Finally, analysis highlights the absence of sulfur in the surface elemental composition, which confirms that mineral oil MO–1 oil was sulfur free and can be adequately used as a matrix for preparation of synthetic crude oils in naphthenic corrosion study.

Figure 3 shows the surface morphological characterization of AISI/SAE–1020 steel exposed to synthetic crude oil SCO–2 at 300 °C for 15 hours, where it is possible to observe the simultaneous presence of naphthenic and sulfidic corrosion, with areas with erosion corrosion attack caused by naphthenic acids and areas where iron sulfide–type corrosion products were formed.

As described for synthetic crude oil SCO–1, naphthenic corrosion is represented by Equation (2) where the iron in the material reacts with naphthenic acids to form iron naphthenates that dissolve in the crude and allow continuous attack to the metallic surface. However, for synthetic crude oil SCO–2, the presence of a high sulfur content was also evidenced in the elemental chemical composition of the exposed AISI/SAE–1020 steel. This was caused by the presence of sulfur traces in mineral oil MO–2, generally organic sulfur compounds, which thermally decompose to generate hydrogen sulfide that reacts with the metal surface and forms iron sulfides as shown in Equation (3) [13].

\[
\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2. \quad (3)
\]

Iron sulphides formed as corrosion products are insoluble in crude oil, which is why they remain attached to the surface and generate a mass gain that distorts the gravimetric results. In this way, the mass loss used to determine AISI/SAE–1020 steel corrosion rate does not correspond solely to naphthenic phenomenon, but is interfered by mass gain caused by sulfidic phenomenon. Additionally, the increase in system temperature favours the thermal decomposition of sulfur compounds, increasing the iron sulfides formation and, therefore, reducing the corrosion rate of the AISI/SAE–1020 steel, as observed in gravimetric results [14].
Additionally, it is possible that a third chemical reaction occurs as presented in Equation (4), where interaction between naphthenic acids and the iron sulfides formed is observed, increasing the system complexity [15]. In this way, the presence of traces of sulfur in mineral oil MO–2 generates a great disturbance in the system, and for this reason it should not be used as a matrix for the preparation of synthetic crude oils in naphthenic corrosion study.

\[
\text{FeS} + 2 \text{RCOOH} \rightarrow \text{Fe(RCOO)}_2 + \text{H}_2\text{S}. \tag{4}
\]

Finally, Figure 4 shows the X–Ray Diffraction patterns for AISI/SAE–1020 steel exposed to 300 °C for 15 hours. For synthetic crude oil SCO–1, the presence of only a high intensity peak close to 45 ° is evidenced, corresponding to the iron in the metallic matrix. However, for synthetic crude oil SCO–2 the additional presence of an intense peak at 43° and multiple peaks between 30° and 35° is evidenced, which correspond to iron sulfides formed on the steel surface due to sulfidic corrosion, confirming the results obtained in gravimetric and microscopy analysis [16].

![XRD patterns of AISI/SAE–1020 steel exposed at 300 °C for 15 hours.](image)

**Figure 4.** XRD patterns of AISI/SAE–1020 steel exposed at 300 °C for 15 hours.

4. Conclusions

Naphthenic corrosion rate of AISI/SAE–1020 steel exposed to synthetic crude oil SCO–1 increased with the two operating variables analysed, since the increase in temperature caused a greater reactivity of the naphthenic acids to form iron naphthenates, which did not form a physical barrier that isolated the material from the corrosive environment and therefore the reaction took place continuously over time.

On the contrary, for synthetic crude oil SCO–2 a great difference was evidenced for AISI/SAE–1020 steel corrosion rate trend with the system temperature, due to the presence in the mineral oil of sulfur traces that allowed the formation of iron sulfides on the material surface, increasing the mass of the system and interfering with gravimetric results.

For this reason, gravimetric tests oriented to evaluate naphthenic corrosion that are carried out using synthetic crude oils must start from sulfur–free oil matrices, in such a way that reliable studies of naphthenic phenomenon are obtained, which are very useful for advance and optimization of corrosion monitoring and control systems in the petrochemical industry.

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