

Predicting Corrosion of Successive Feeds in Distilling Units – An Experimental Approach

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ABSTRACT

Cheap heavy crudes become attractive for oil refineries to increase their benefit margins but the corrosivity of heavy crudes compels the refinery engineers to blend them with the more expensive light sweet crudes. Crude oil blends with complex composition including organo-sulfur compounds, fatty acids, nitrogen and chlorine compounds become corrosive when processed at high temperatures due to these reactive species. Therefore, maintaining corrosion control is a constant effort in oil refineries, and it involves the use of dedicated corrosion models combined with specific experimental lab procedures and methods. This work is presenting the practical application of a lab testing procedure used for predicting the high temperature corrosivity of different crude fractions that were run successively for different time periods in a specific “flow-through” apparatus. The testing procedure consists of two distinct phases performed in the same apparatus, at the same temperature, and for different time durations. During the first phase of the test, scales are formed using a distilling fraction on metal samples and further, in the second test phase, these preformed scales on samples are exposed without interruption to a different distilling fraction. Thus, the two successive test phases, each using a different distilling fraction, are associated with the “changing feeds” in the distilling tower. Corrosive effects are evaluated by sample weight loss measured in successive fraction tests and in separate tests performed with each of the selected fractions. Experimental results are compared to predictions of a corrosion model for sulfidation and naphthenic acid corrosion.

Keywords: sulfur, hydrocarbons, naphthenic (NAP) acid, corrosives in refining process, laboratory methods.

INTRODUCTION

Crude oil with its processing final products remains one of the main sources of energy in the world. The 2023 forecasts for oil global supplies were of 100.9 mb/b, an estimation that was falling short of oil global demand which was of 102 mb/d for the same year.^{1,2} The high crude oil

demand constrained the refining industry to process oils of different quality, to optimize the production, and adopt more complex refinery configurations. Thus, the new capacity additions changed the refinery configurations from simple to deep conversion which enabled them to process low, medium, and high quality oils and biofuels.^{3,4} Crude oils have a complex chemical composition and for refining industry they are characterized based on density in “light”, “medium” and “heavy” oils, degrees of quality expressed in “API gravities”, and based on oil sulfur content in “sweet” with less than 1 wt.% sulfur and “sour” crude oils when their sulfur content is higher than 1 wt.%. Some varieties of crude oils (Canada, Venezuela) contain also naphthenic acids that are very important as these acids together with the sulfur compounds represent serious corrosion challenges when such oils are processed in refineries. The types of crudes that are processed influences the yield in final products, therefore the use of “sweet” and “light” crudes is preferable, but their high prices force the refineries to use cheaper “medium” and “heavy” crude oils too in order to improve their margins.⁵ However, processing heavy crudes creates economical and technical challenges as these oils are highly corrosive. The corrosive effects of heavy crude oils are mitigated and controlled in refineries by blending the low quality with higher quality oils, using corrosion inhibitors, and/or upgrading the construction materials of distilling units where possible.⁶⁻⁸ All these strategies for mitigating corrosion imply further production costs therefore reducing the economic margins. Other methods like laboratory tests, corrosion models, and specific methods of optimizing the blends are largely used in the efforts to control corrosion.

Heavy crude oils processed in refineries typically have high concentrations of sulfur compounds naphthenic acids (NAP) that become extremely corrosive at the high temperatures of the distilling units. The corrosive processes generated by sulfur species and NAP acids in oil at high temperatures are very complex and as a consequence, it is generally accepted to describe them by three distinct chemical reactions.



NAP acids react with the metal forming iron naphthenates, a corrosion product that is oil soluble and hence being entrained constantly by the oil flow (1). The sulfur compounds in oil, especially the mercaptans and the sulfides thermally decompose generating hydrogen sulfide (H_2S) which reacts with the metal forming iron sulfide (FeS), a solid reaction product that builds up on the metal surfaces where it forms (2). The thermally generated H_2S reacts with iron naphthenates restoring the NAP and forming more FeS according to Reaction 3.^{9,10} Thus, the NAP acids are reintroduced in the corrosive cycle and generate more damage to the metal. The complex mechanism of NAP acids and sulfur corrosion is very complex and insufficiently understood and known. Therefore, many research studies were dedicated to decipher the complex reaction mechanism of these two corrosive species. The present experimental work was an attempt to evaluate the effect on FeS scales of changing the oil corrosive species in sequence or order, similarly to changing the feeds in distilling towers.

EXPERIMENTAL

Experimental Procedure

The effect of running successively different crude fractions through the same apparatus was evaluated at lab scale by applying specific experimental methods and dedicated instrumentation. The experimental method that was considered appropriate for this work – the “pretreatment-challenge” - was developed to assess the integrity of the FeS scales exposed to NAP acid attack and consists of two distinct phases.¹¹ In the first phase FeS scales are formed at high temperatures (“pretreatment”) on metal samples exposed to crude oil fractions or model compounds solutions. In the second phase, also done at high temperatures, the scales covering the samples are exposed to naphthenic acid solutions – the acidic “challenge”. The corrosion rates are calculated based on samples weight losses. Separate “pretreatment” only tests were performed to evaluate the sample weight loss corresponding to this phase of the procedure. These weight losses of “pretreatment” were subtracted from initial weight of samples that were submitted to the complete experimental procedure. Thus, it becomes possible to separate and precisely evaluate the corrosive effects of each of the two experimental phases.

Similar to the “pretreatment - challenge” method, it was considered that the two crude fractions pumped successively through the same apparatus can be assimilated to the two phases described above. The first fraction, Feed 1, will form the scale (pretreatment) and the second fraction, Feed 2, will challenge the scale formed during the first phase.

Experimental Instrumentation and Materials

The “pretreatment - challenge” procedure can be done “ex-situ” when the two phases are performed in different experimental apparatuses or “in-situ” when the complete procedure is performed without interruption in the same apparatus. The present work was done in a “flow through” apparatus. The Flow Through Mini Autoclave (FTMA) allowed the experimental procedure to carrying on without interruption – “in-situ”. For this experimental work simulating the “changing feeds” in oil refineries, the “pretreatment” phase was considered as “Feed 1” and the “challenge” phase as “Feed 2”. Thus, in “Feed 1” a specific crude oil fraction (VGO) was pumped into reactor and in “Feed 2”, a different VGO was pumped through the system.

The FTMA system presented schematically in Figure 1, has the metal samples inserted in a reactor and exposed to a constant flow of testing fluid that is supplied from different feeding tanks. The testing fluid is pumped through heated lines to the reactor which is also heated and kept to a constant high temperature during the test. The constant oil flow through the reactor ensures a constant fresh concentration of corrosive species on the sample surfaces and simultaneously removes the soluble reaction byproducts that might accumulate in the system. The oil flow rate can be controlled by the pump, and it is set to a very low value that creates flow conditions in the reactor close to those of a stagnant flow similar to those of the autoclaves. Thus, the samples are not exposed to the shear stress effects but only to the fluid corrosive species. A backpressure valve located after the FTMA reactor keeps the volatiles in the liquid during the tests preventing any gaseous phase formation. The FTMA apparatus also includes a sampling port located after the reactor fluid outlet where oil samples are collected during the tests.

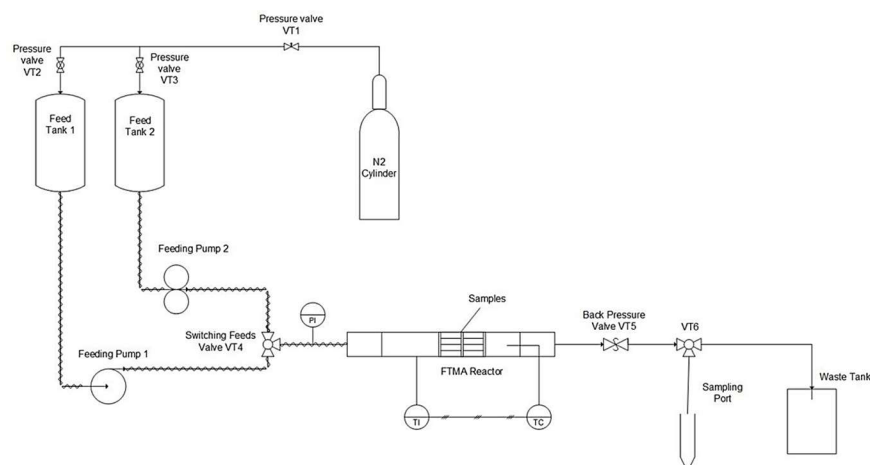


Figure 1: Schematic representation of the Flow Through Mini-Reactor (FTMA) experimental apparatus

All metal samples used in this experimental work had a rectangular shape, with geometrical dimensions of 16.2 x 15.3 mm and were made of UNS K03006 carbon steel. Four samples were used in every test, three samples for weight loss evaluations and the fourth sample for scale microscopic analysis. Before the tests, samples were polished with 400 and 600 grit silicon carbide (SiC) paper under constant isopropanol flush. After polishing the samples were cleaned and degreased with acetone, dried under nitrogen flush, their dimensions were measured precisely with a caliper, and then they were weighed on an analytical balance (initial weight). At the end of the test, samples were extracted from the reactor and the corrosion byproducts (scales) were removed mechanically and chemically from their surfaces. The superficial scale layers that formed on samples were very fragile and loose. Therefore, these scale layers were removed mechanically by brushing the samples with a stiff plastic brush under toluene flush. The strongly adherent scale that persisted on sample surfaces after the mechanical procedure were chemically removed by dipping successively the samples in Clarke solution (ASTM G 1-90).¹² Following every solution dip, the samples were dried under nitrogen flush and weighed. The sample weight at the end of the Clark solution procedure was recorded as the sample final weight and used for corrosion rate calculations.

Table 1
List of the VGO used in tests simulating the “changing feeds” in oil refineries

	Test Fluid	TAN (mg KOH/g oil)	Sulfur content (wt. %)
1	Fraction A	7.7	2.4
2	Fraction B	6.88	0.76
3	Fraction C	4.88	0.11
4	Fraction D	4.43	3.65
5	Fraction E	2.7	0.74
6	Fraction F	2.41	1.17
7	Fraction G	2.16	1.44

The experimental fluids used for this work were all crude distilling fractions – vacuum gas oils (VGO) – and they were part of a research project dedicated to NAP acid and sulfur corrosion in oil refineries. All VGO were provided from different sponsors who shared only the fractions total sulfur content (wt. %) and their total acid number (TAN) with the research group. Table 1 summarizes the total sulfur content and TAN of the selected VGO for the “changing feeds” tests.

The experimental conditions of the “changing feeds” tests are listed in Table 2.

Table 2
Experimental conditions in tests simulating the “changing feeds” in oil refineries

Test Phase	TAN (mg KOH/g oil)	Sulfur content (wt. %)	Temp.	Time (h)	Pressure (psig)	Oil Flow rate (cm ³ /min)
Feed 1	7.7 – 2.16	3.65 – 0.11	343°C (650°F)	24, 168	100	1.5
Feed 2	7.7 – 2.16	3.65 – 0.11	343°C (650°F)	24, 48, 168	100	1.5

The complex chemical composition and structure of the scales formed on metal surfaces were analyzed in a scanning electron microscope (JEOL JSM-6390) coupled with an energy dispersive X-ray spectrometer (EDS).

Experimental Data Processing

The corrosive effects of the VGO TAN and sulfur content were evaluated by calculating the sample corrosion rates according to the formula (1).

$$CR = \frac{(IW - FW)}{\rho_{Fe} \cdot A_s \cdot t} \cdot 24 \cdot 365 \cdot 1000 \quad (1)$$

where

CR - corrosion rate [mm/y]

IW – initial weight [kg]

FW – final weight (after last clarking) [kg]

ρ_{Fe} – Steel density [kg/m³]

A_s – sample area exposed to corrosive fluids [m²]

t – time of the experiment [h]

These samples weigh losses were calculated as differences between their weight measured before and after the test. As the experimental goal was to separate the corrosive effects of two different feeds processed successively, when calculating the corrosion rates for second feed, the metal weight losses measured in a separate test done with only first feed were subtracted from initial weight of the samples exposed to the complete two feeds sequence.

The scales built up on the metal surface in a multilayered structure with a complex chemical composition. The top layers of the scales were loose and fragile therefore they were easily removed from the sample surfaces during the solvent rinsing procedure. Thus, in order to quantify the scales, it was assumed that they all formed uniformly on the metal surfaces and had the same thickness in every considered point. With the superficial layers lost during sample