

Formation of fouling deposits on a carbon steel surface from Colombian heavy crude oil under preheating conditions

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Abstract. Fouling in heat exchangers is produced by the deposition of undesired materials on metal surfaces. As fouling progresses, pressure drop and heat transfer resistance is observed and therefore the overall thermal efficiency of the equipment diminishes. Fouling is mainly caused by the deposition of suspended particles, such as those from chemical reactions, crystallization of certain salts, and some corrosion processes. In order to understand the formation of fouling deposits from Colombian heavy oil (API \approx 12.3) on carbon steel SA 516 Gr 70, a batch stirred tank reactor was used. The reactor was operated at a constant pressure of 340psi while varying the temperature and reaction times. To evaluate the formation of deposits on the metal surfaces, the steel samples were characterized by gravimetric analysis and Scanning Electron Microscopy (SEM). On the exposed surfaces, the results revealed an increase in the total mass derived from the deposition of salt compounds, iron oxides and alkaline metals. In general, fouling was modulated by both the temperature and the reaction time, but under the experimental conditions, the temperature seems to be the predominant variable that controls and accelerates fouling.

1. Introduction

The fouling is defined as the deposition of unwanted materials on heat transfer equipment, which results in an increase in thermal resistance to heat transfer and loss of the equipment thermal efficiency. Fouling in crude oil pre-heat trains is a complex phenomenon with several mechanisms interacting with each other [1]. The phenomenon is mainly caused by deposition of particles, chemical reactions, crystallization and some corrosion processes [2-4].

The causes of fouling include:

- Impurities from the crude, gum or polymeric species formed through oxidation of reactive species in the oils.
- Insoluble asphaltene.
- Iron sulphide formation.
- Coke formation.

A lot of research has focused on the study of fouling generated in units of heat transfer in the petrochemical industry. These studies were performed at high temperatures ($T > 350^\circ\text{C}$), where the fouling is generated mainly by coke formation [5-8]. The present work aims to study the fouling phenomenon at temperatures below 300°C using Colombian heavy crude oil (CHCO) like fouling agent.



2. Experimental

Fouling experiments were performed using a 1L Parr instrument Model 4848 stirred batch reactor. The reactor is shown schematically in Figure 1.

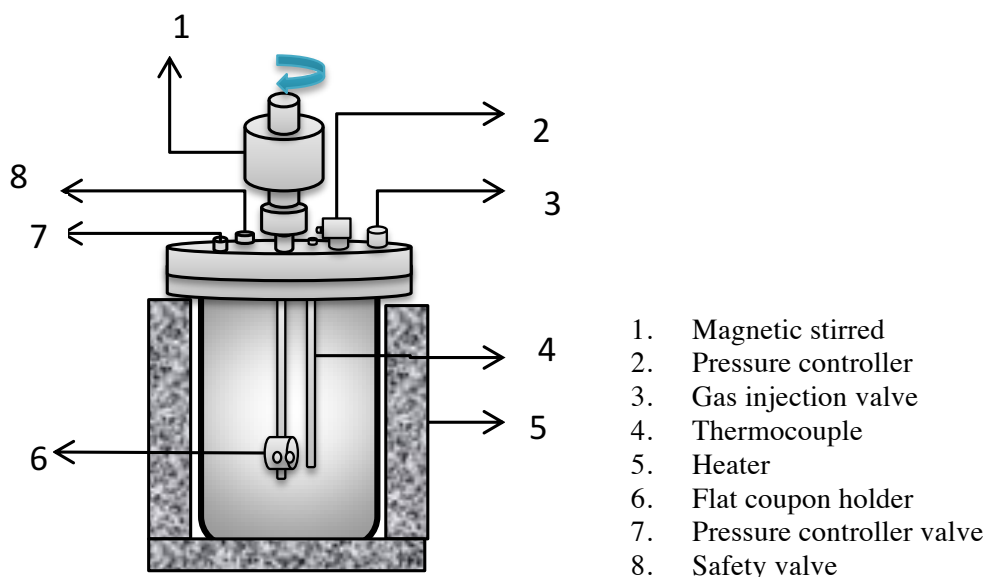


Figure 1. Diagram of stirred batch reactor.

The carbon SA 516 Gr 70 steel (CS) coupons were prepared according to the NACE SP0775 2013 norm [9]. They were processed by 120 grit sand paper, rinsed with acetone and dried in hot air.

CHCO used for the tests contains about 1.6%wt sulphur; API gravity approx. 12.2 and total salt content about 9 Pound/1000Bl.

Tests were carried out at temperatures of 220, 260 and 300°C, using for each experiment 750mL of CHCO in the reactor. Pressure and the rotation speed were maintained constant at 340psi and 15rpm, respectively. For each selected temperature, three different exposure times were used: 25, 30 and 35 hours. After each experiment, the coupons were washed with acetone to remove oil and dried in warm air. To evaluate the formation of deposits on the metal surfaces, the steel samples were characterized by gravimetric analysis and Scanning Electron Microscopy (SEM). After each run, spent oil was analysed to determine salt contents [10].

3. Results and discussion

The Figure 2(a) shows the relationship between final mass and initial mass of the coupons (mass gain) at different experimental conditions. The major mass gain of coupons occurs at temperatures of 220°C. This behaviour is proportional to the increase of experimental time. However, as the temperature increases the behaviour of the curve is different. Both intermediate and high experimental temperature (260 and 300°C), present a major mass gain at 25 hours and decrease at 30 hours. At 35 hours, the mass gains increase significantly at temperature of 260°C while at 300°C the mass gain presents a similar value that at 30 hours. The lowest point occurs at 30 hours for the two higher temperatures.

Figure 2(b) shows the salt intake for each temperature after 35 hours. Salt intake is expressed as the difference between total salt content of crude before the test and total salt content of crude after the test. The major intake was at 220°C. This result indicates that the fouling mechanism may be related to the crystallization of salts.

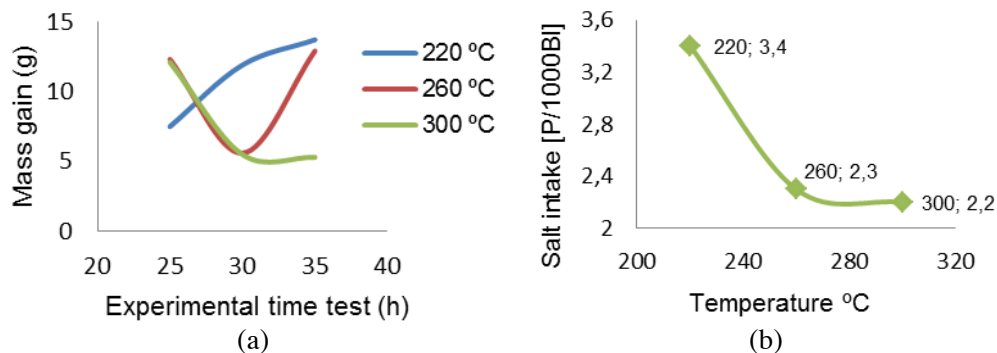


Figure 2. (a) Mass gain of coupons at experimental conditions and (b) Salt intake after 35 hours experiment at 220, 260 and 300°C.

The results of coupon surface characterization are shown in Figure 3(a) and (b). Crystal deposits on coupon surface are observed in Figure 3(a). Energy Dispersive X-ray Spectroscopy (EDS) analysis (Figure 3(b)) shows the presence of sodium and chlorine on carbon steel surface probably by deposition and crystallization of crude salts. This result explains the decrease of the total percentage of salt present in the crude after each experiment (Figure 2(b)).

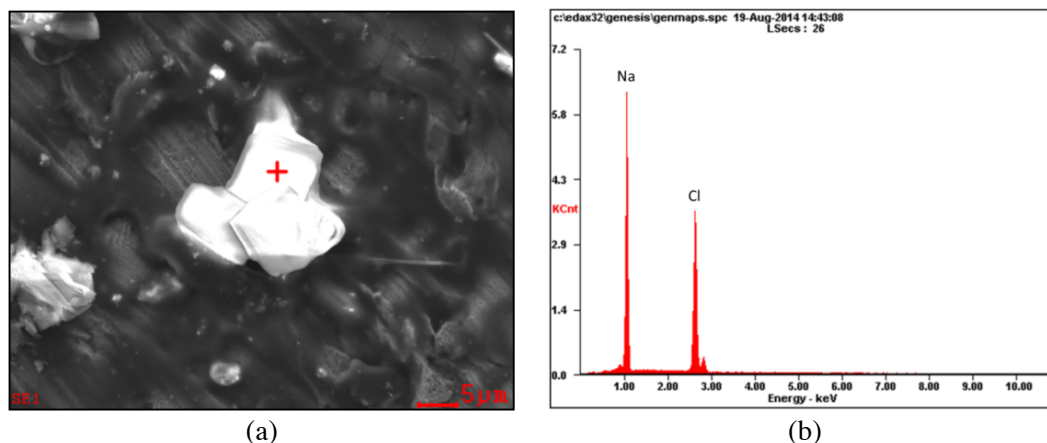


Figure 3. SEM image of crystal deposit on CS after 35 hours experiment at 300°C. (a) Crystal deposit and (b) EDS of crystal deposit.

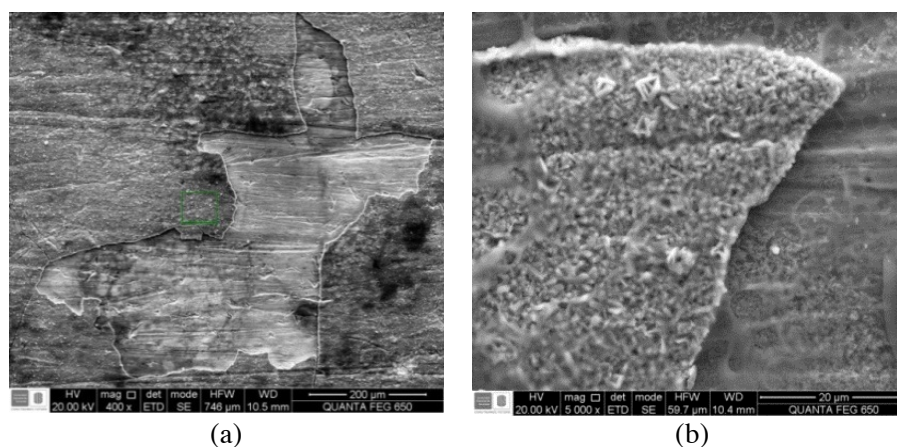


Figure 4. SEM images of deposits on CS after 35 hours experiment at 300°C. (a) Mag 500x and (b) Mag 5000x.

Qualitative assessments of coupon surfaces by SEM (Figure 4) showed formation of a layer, which could have been produced by the reaction between the sulphur from the oil and the iron atoms in the alloy [11-12]. Layer formation occurred at 300°C. No layer formations on metal surface at the other two temperatures occurred. This result confirms the temperature effect on fouling processes.

4. Conclusions

At 220°C, the fouling is related with decreasing of total salt content in the crude. Crystal deposits on metal surface are evidence of the results.

According to the results, both temperature and time have influence on fouling, however under these experimental conditions, the temperature seems to be the predominant variable that controls and accelerates the fouling.

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