Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 55 (1) 57-61, 2013

OPPORTUNITIES TO REDUCE THE FOULING PROCESSES IN HDS INSTALLATION

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Received December 17, 2012, Accepted March 1, 2013

Abstract

Fouling can be defined as an undesirable phase, preventing the processing of feedstock. Typically, this phase is solid. While the fouling phase is often a solid, it could be a liquid when a gas is expected or it could be an emulsion when separate liquid phases are expected.

Contamination during the processing of feedstock is significant and often it is necessary to stop the operation for cleaning. It is a necessary and exigent expense that can be reduced or even removed, offering alternatives for its elimination (because it can usually be significantly reduced or eliminated by a systematic procedure that determines its reason).

Typically, problems with heat exchangers plugging in HDS plants are due to the presence of compounds in the feedstock with high molecular weight, the presence of unsaturated hydrocarbons and inorganic constituents (Fe, Na, Cu, Ni). Obviously, the depth of the problem is directly related to the raw material supplied to the system. The fouling processes are influenced also by other factors such as plant design, mode of operation, method of storage of raw material, the influence of weather conditions, etc.

Key words: fouling; heat exchangers; hydrodesulphurization unit; additives.

1.Introduction

Fouling in pre-heat heat exchangers in HDS plants leads to a significant increase in costs due to reduced efficiency, increased pressure, often shut downs for maintenance and lost productivity [1-3].

In the autumn of 2011 in HDS plant in INSA OIL Ltd. refinery appeared problems with plugging of the heat exchange equipment, in which in the feed is flowing in the tube space and the heat agent – in the inter tube space.

The unit is fed with gasoil bought on the market. The characteristics of the feed are anyhow quite constant. The fouling was localized in particular in the heat exchangers 2 and, in a minor quantity, on the following heat exchanger 1(shown in the scheme of the problem "node" in the plant).

Feed samples have been collected from both tanks and have been analyzed. The analysis PONA (ASTM D1319) is shown in Table 1.

Table 1 PONA analysis

Sample	Saturates, %v/v	Aromatics, %v/v	Olefins, %v/v
Tank R2T	76.8	22.4	0.8
Tank R4T	77.3	21.9	0.8

The feed contains mainly saturated and aromatic hydrocarbons. appears to be mainly based on saturates and aromatics. The very low level of olefins is indicative of a low tendency to polymerize or to give radicalic reactions.

Therefore, the fouling source as complex characteristics. Probably an important role plays the temperature in the heatexchange equipment, the presence of overheated areas and the duration and way of storage of the feed for hydrotreatment [4, 5].

2. Deposits characteristics

Both deposits samples have been analyzes: from heat exchanger 1 and from heat exchanger 2. The characterization of the deposits was made to identify the nature of the deposits and to "connect" it with the other parameters affecting these unwanted processes. Scheme of the HDS plant and the problem "knot" is shown in Figure 1.

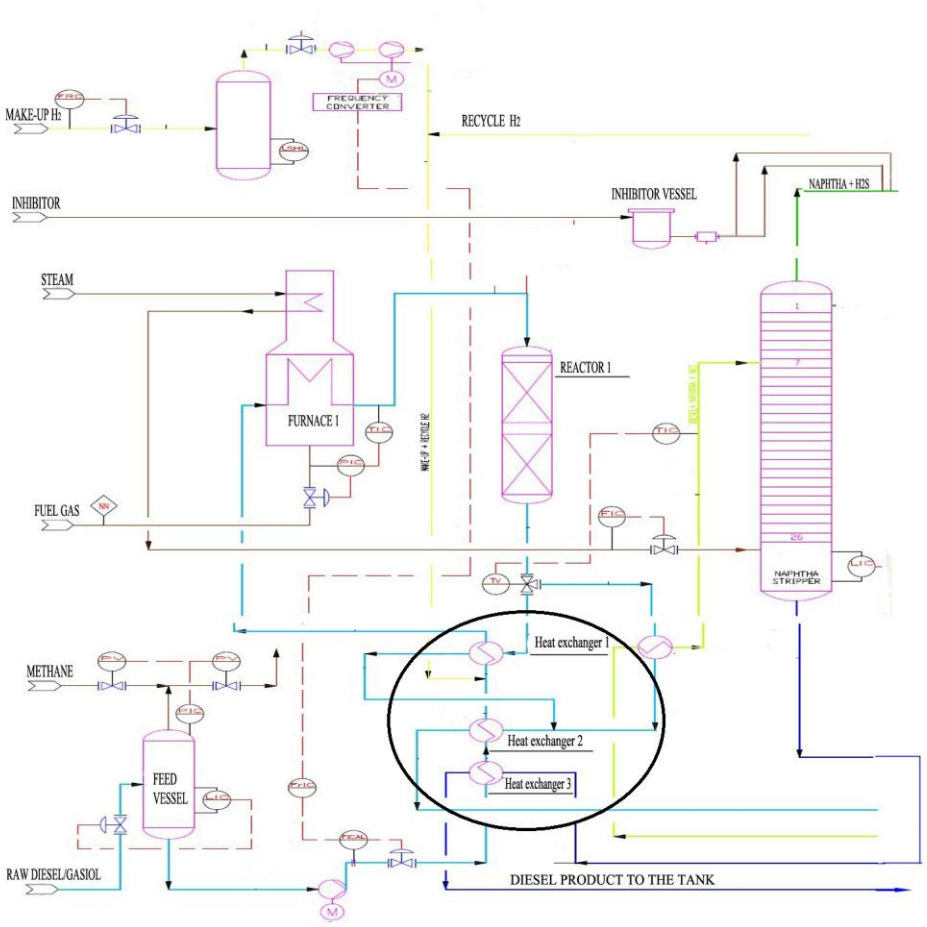

Fig. 1 Scheme of HDS plant in Insa oil refinery

More focus was given to the deposit of the heat exchanger 2, that according to the information appear to be the most critical. Although both deposits seem quite different, appear quite different their composition is very similar.

The deposit taken from heat exchanger 2 contains a higher quantity of trapped gasoil (which depends on how and where the sample was taken), but after its removal the appearance resembles that one of the heat exchanger 1.

The trapped feed removal is performed by washing the deposit with petroleum ether, the residual ether being then removed by evaporation. Both the deposits are based on a predominant part of organic material (95-97%) and a smaller one of inorganic products (3-5%).

The inorganic part consists of corrosion products, particularly iron oxides and iron sulphides. Its presence is not large in comparison with organic components, but in any case cannot be ignored because the inorganic particles are the primary source for developing agglomeration process (which seems to be the main problem of the plant).

The analysis found that the organic fouling is based on high molecular weight compounds (probably gum substances or polymeric products) that are difficult to be dissolved in a solvent and thus to be precisely characterized.

Washing with Toluene and n-hexane allowed to separate only a small quantities of products from the deposit.

On this basis is expected only a little presence (<1%) of aromatics and paraffins. Unfortunately additional washing, also with very strong solvents, didn't lead to further deposit solubilization. This limits the available analysis to characterize the deposit.

Indicative information can be obtained through the elemental analysis of the deposits. The C/H ratio and the presence of N, S and O in fact can provide useful information to define the possible compounds.

3. A simulator test to identify the susceptibility to contamination

This apparatus essentially consists of a closed loop fuel system with a heater tube section including a test filter, together with associated equipment for controlling and measuring the heater tube temperature. There is a differential pressure transducer to measure ΔP.

A constant displacement pump allows the test sample contained in the reservoir to circulate through the test section. The heater tube is connected with two busses and is electrically insulated from the outer housing by a non conductive ferrule. The sample rises vertically in the annular space between aluminium heater tube and its outer stainless steel housing. A low-voltage high current signal is passed through the heater tube in order to obtain a resistance heating. Coming out from the heater tube section, the sample passes through a test filter consisting of a stainless steel cloth with a rated porosity of 17 microns.

The sample reaches the cooler from either routes and proceeds through the metering pump back to the fuel reservoir. A sight gage drip flow indicator allows the flow rate visual monitoring . The heater tube is heated by a current voltage of approximately 200-300 A at 0,3-0,5 V. The heater tube is clamped at each end into busses having a corrosion resistance surface. The collection containers - busses are cooled by internal water lines and they receive electrical power from a low voltage transformer. There is a temperature controller. The input signal to the controller comes from a thermocouple inserted through the top heater tube and placed at maximum temperature point. The system can be pressurised with inert gas as nitrogen.

4. Tests related to the establishment of feed tendency to form deposits in the operating conditions of the plant

In appearance, the feedstock (gasoil) looks clean and bright. However, it has been tested in terms of Total contamination and Microbiological contamination, to exclude the possibility of fouling transportation from the storage tanks to the unit. As expected both the analysis gave negative results. The levels of contaminants already present in the gasoil are negligible and there are no evidences of microbiological activity (see Table 2).

Table 2 Total contamination results

Sample	Total contamination, mg/kg
Gasoil Bottom Drain	12
Gasoil Buffer Vessel	7

Regardless of the conclusions reached with respect to the feedstock quality, it is necessary to apply additional measures for the delivery and storage of the feed. In this regard, the feedstock should be stored in a tank in which is maintained the maximum level to minimize the direct contact with oxygen from the air. The best would be to store the feedstock in tanks under nitrogen blanket. The lower the level in the tank, the more the feed is exposed to the influence of weather – contact with air, high temperatures in the summer, sunlight, etc. All these factors have a significant influence on the stability of the feed and on the rate of development of corrosion processes. Subject to all these requirements, it is not necessary to add anti-oxidation products for maintain the stability of the feedstock to its feeding to the technological process.

The tests continued in direction towards the establishment of the feed tendency to form fouling in terms of operation mode of the plant. This has been achieved by using ASTM - method (D3241), used mainly for jet fuels. The procedure follows the conditions of JFTOT analysis that we applied in this case, to assess the tendency of the hydrocarbon flow to contamination, simulating the operating conditions of the plant. The contamination is measured as ΔP accumulation on the filter with a fixed size of porosity. The test was performed simulating the operative conditions of the heat exchanger 2. The results of the test confirmed the high tendency to contamination of the feed used. The filter in fact was completely plugged already after 25 minutes from the test start.

Based on the deposit characterization and onexperience, 4 antifouling products have been selected to be tested in the simulator in order to evaluate their performances and their tendency to form contamination - Antifouling A, B, C and D. Among the products tested, "Antifouling A", showed the best performances. Other additives, especially those based on antioxidants actives, showed poorer performances in terms of stopping the formation of deposits. In Figure 2 is shown the performance of the feed, while in Figure 3 are shown the curves for the amendment of the pressure in time for the feedstock and the feedstock with an additive at one and the same concentration of the different antifouling products tested.

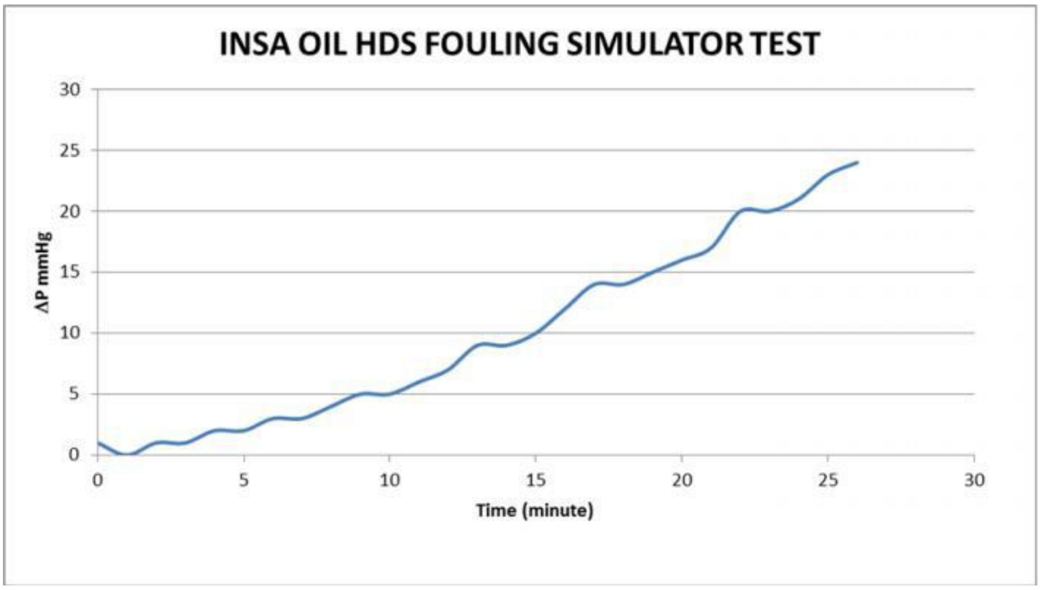

Fig. 2 Feed stock fouling simulator test

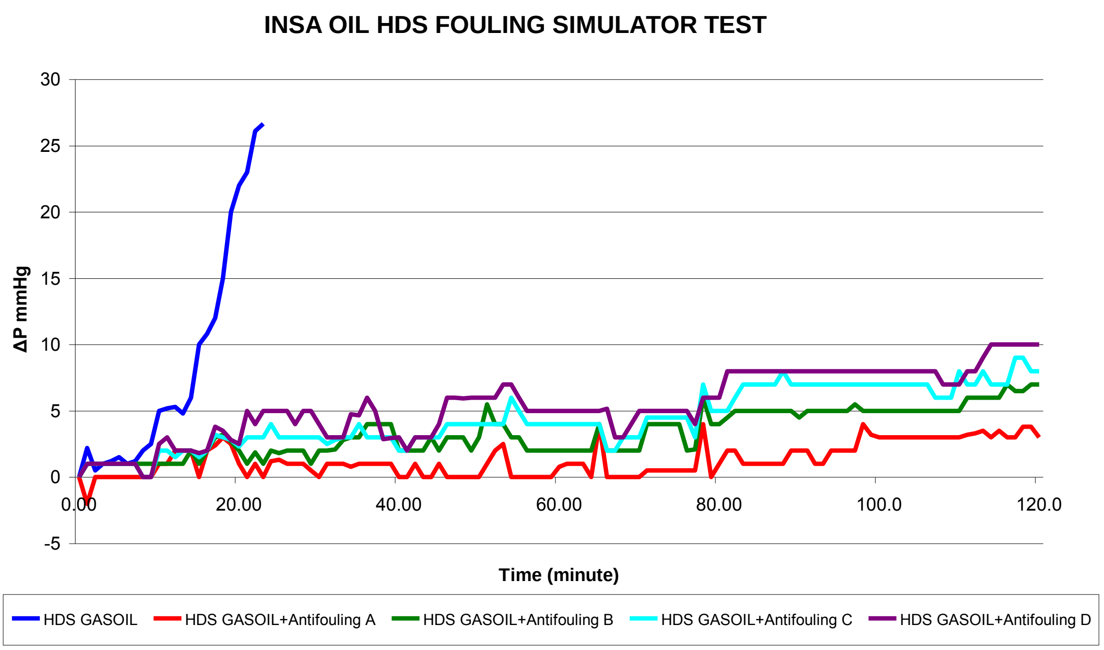

Fig.3 Comparison between the pressure amendment curves between the feedstock and the feedstock with additives

"Antifouling A" is a balanced blend of strong dispersing active compounds for gums and inorganic compounds. The product is able to disperse the fouling into the process stream, without any fouling reallocation in downstream equipment.

This aspect is particularly important as it ensures the purity and activity of the catalyst in the reactor and can be easily checked by monitoring its ΔP.

The effect of more efficient product "Antifouling A", avoiding fouling deposition, will help to increase plant run-length and to reduce operating costs for cleaning of process equipment. This product does not affect the catalyst activity, nor the final product quality, it does not contain halogens nor heavy metals. Besides C and H, the product contains about 1.1% nitrogen, oxygen (not free O_2) of approximately 3.6% and sulfur of approximately 2.4%.

5. Conclusions

1. It was found that the processed feed does not tend to form gums and polymer products during its storage and it contains corrosion products in minimal amounts. The feedstock in this case is not a reason for the fouling of heat exchange equipment.
2. Conditions for fouling processes are created in the very heat exchange equipment. Perhaps there is overheating in certain areas, causing destruction and compaction of hydrocarbons in the problematic equipment.
3. Solving the problem is reduced to the use of appropriate antifouling products.
4. Of the four products tested, Antifouling A showed the highest efficiency in the area of the problem and after it.
5. Antifouling A carries the deposits out of the system without accumulating them in the downstream equipment and on the catalyst or negatively to affect its activity.
6. Based on studies carried out in the HDS plant of INSA OIL Ltd. the abovementioned products are currently used as the most effective one.
7. This treatment will help to reduce the cost for cleaning the exchange equipment, reducing the number and duration of downtime for cleaning the system, increasing the effective run-length of the catalyst, operation of the plant in light mode, reducing the energy costs, mainly due to improved heat transfer, etc.

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