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Exchanger Fouling in an Aromatics Plant

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ANALYSIS AND STEPS TO MITIGATE FOR HEAT EXCHANGER FOULING IN AN AROMATICS PLANT

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ABSTRACT

A heat exchanger, upstream a distillation tower for the separation of BTX (benzene, toluene, xylene) from crude benzene in an aromatics plant, experiences heavy fouling. The fouling mechanism and countermeasures to mitigate or eliminate it, were investigated. An Alcor Hot Liquid Process Simulator (HLPS)[1] was used for the fouling rate measurement. The main mechanism is a combination of precipitation fouling and chemical reaction fouling. Effects, such as temperature, vapor ratio (vapor mole fraction of the fluid), heater materials, surface roughness and the addition of some different types of chemicals were studied. From the experiments, some countermeasures for this fouling were proposed. A decrease in the vapor liquid ratio and a continuous supply of the more effective antifoulant chemical (dispersant) successfully reduced fouling in the plant.

INTRODUCTION

The Mitsubishi Chemical Co. BTX plant uses two material sources: gasoline from a naphtha cracker, and crude benzene mainly from a coke plant. A heat exchanger which is used as a pre-heater of the distillation tower for the separation of BTX from crude benzene experiences heavy fouling. This fouling causes a loss of production and necessitates cleaning of the heat exchanger every 2 years. The total cost of this fouling is above two hundred thousand dollars per year. To mitigate or eliminate this loss, experiments were carried out to study the mechanism and identify countermeasures using the Alcor Hot Liquid Process Simulator 400 (HLPS400). To study organic fluids fouling of heat exchangers, many methods have already been reported [2,3]. The HLPS400 was chosen because of its easy operation, the small size of equipment and the stability of its results. In addition, deposits on the heater rod surface can be analyzed. The HLPS is commonly used

by anti-fouling chemical suppliers for screening tests of chemicals.

The process around the heat exchanger is shown in Figure 1. Heat exchanger E-2 has much heavier fouling than E-1, and hence is the target for fouling reduction.

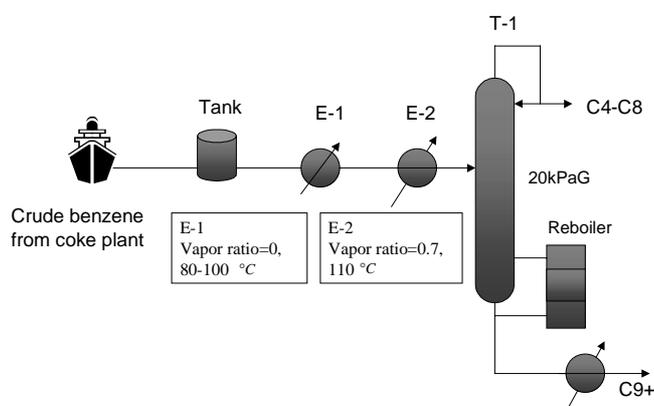


Figure 1. The process around the heat exchanger. E-1: outlet temperature 80-100°C, vapor ratio=0, E-2: outlet temperature 110°C, vapor ratio=0.7, T-1: C9+ separation tower operated at atmospheric pressure.

Crude benzene contains benzene (ca. 60wt%), toluene (ca. 10wt%), xylene (ca. 6wt%) and C9+ (above 8 carbon fractions, ca. 20wt%). It also contains a small amount of particles (we think they are ppm order concentration and mainly composed of inorganic materials such as FeS.), which may be produced by corrosion of tanks and pipes.

First, we tried to identify which types of fouling mechanism dominate in this situation. From the crude benzene analysis, one or two of three mechanisms are expected to be dominant. The three mechanisms are (1) particulate fouling, (2) precipitation fouling and (3) chemical reaction fouling. Second, from experimental results, the kinds of conditions in the heat exchanger which affected the fouling deposition rate most were determined. Some mitigation ideas for the heat exchanger were then

applied.

EXPERIMENTAL METHOD

General Alcor HLPS400 test procedure

The HLPS400 tests were carried out by charging the reservoir (heated up to 50°C) with 300ml crude benzene and pumping the benzene through the annulus formed by a vertically positioned, heater rod (outside diameter of heated section: 3.25mm) and an outer tube (inside diameter: 4.35mm) at a flow rate of 3.0 ml/minute. The heated crude benzene was then returned to the reservoir (Figure 2). The system was pressurized with nitrogen (190-350kPaG) to control the vapor ratio of the heated outlet bulk fluid. The rod surface was heated by applying a voltage to the rod to control the outlet bulk fluid temperature. Thermocouple readings were recorded for the bulk fluid inlet and outlet temperatures as well as the rod surface. The thermocouple for the rod was positioned inside the heater rod.

With constant outlet bulk fluid temperatures (i.e., constant heat flux conditions), as foulant deposited and built up on the heated rod surface, due to its insulating effect the heater rod surface temperature increased over time. However, at vapor ratios above zero from these temperature profile changes, the fouling resistance could not be determined because of the large fluctuations in the temperatures. Consequently, the deposit weight on the rod was measured directly after experiment runs. Usually, the HLPS400 tests were run for 20 hours. For run times below

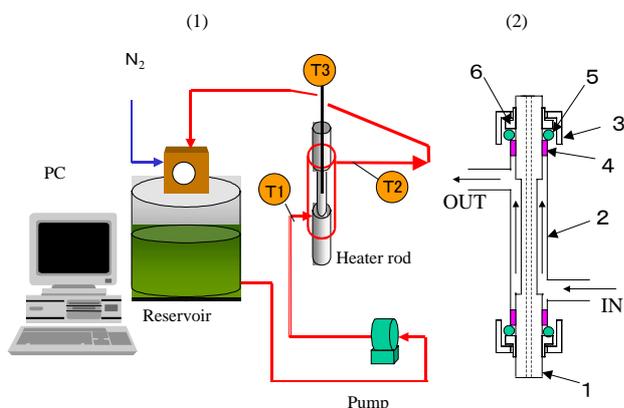


Figure 2. Alcor HLPS400 system(1) and heater rod(2). 1: heater rod, 2: housing, 3: nut, 4: insulation part, 5: O-ring, 6: insulation part.

20 hours the deposit weight increased linearly with the run time in the test temperature range used.

To define experimental conditions, vapor ratio is based on mole fraction, temperature is the outlet bulk fluid temperature and pressure is the reservoir pressure.

The contents of the crude benzene differ slightly each day. So, the crude benzene samples taken on different days show around 40% deposit weight differences. But, using samples from the same day, the reproducibility is good enough for this study (deviation is below 15%). The data shown in the figure are the results from the same day samples.

RESULTS AND DISCUSSION

STEP1: Identification of the mechanism

It was assumed that the total fouling rate could be written as the following equation:

$$\text{Total fouling rate} = (1)\text{particulate fouling} + (2)\text{precipitation fouling} + (3)\text{chemical reaction fouling}$$

To separate mechanism (1) from (2) and (3), fine particles were removed by filtration from the crude benzene, and the deposit amount measured. The filter was PTFE membrane filter (pore diameter 0.2 μ m). The difference between fouling results with filtration and

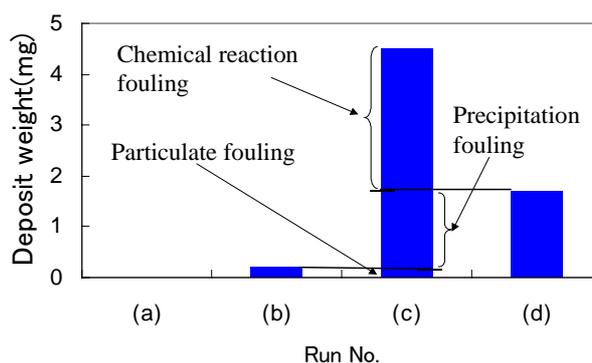


Figure 3. Separation of the contributions from fouling mechanisms (1), (2) and (3). Experimental conditions; temperature 145°C, pressure 330kPaG (vapor ratio=0, and 260kPaG(vapor ratio=0.43), run time 20 hours, heater rod material: carbon steel. (a) with filtration, vapor ratio=0, (b) no filtration, vapor ratio=0, (c) no filtration, vapor ratio=0.43, (d) no filtration, addition of antipolymerant.

without filtration would be the contribution from mechanism (1).

Next, antipolymerant was added until the deposit amount stopped decreasing (Both Hakuto PN2500 and Ondeo-Nalco EC3142A were added each about 40 wtppm. These additives contained no dispersants.), and its effect may be attributed to the contribution of mechanism (3). The remaining amount may be from mechanism (2). The results are shown in Figure 3. From these results, the main mechanisms of the fouling are (2) precipitation fouling and (3) chemical reaction fouling. Of course, this estimation method of the mechanism is rough. In particular, separation of (2) and (3) are difficult just by the addition of antipolymerants. But this is a first step to identify which mechanisms dominate the phenomena.

The outlet temperature of the process fluid at the heat exchanger E-2 was 110°C. But in order to shorten the experiment run time, 145 °C was chosen for the outlet fluid temperature. The actual plant might have slightly different mechanism contributions because of the lower temperature in the plant.

STEP2: Survey of the effects of the heat exchanger conditions

Effects of temperature and vapor ratio

Because the main mechanisms are (2) and (3), the temperature and vapor ratio should have large effects on the fouling weight. The results are shown in Figure 4 and

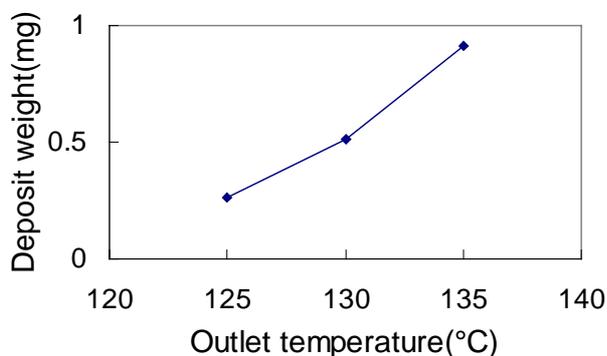


Figure 4. Temperature effect

Experimental conditions; pressure 287kPaG, vapor ratio =zero, run time 20 hours, heater rod material: carbon steel, crude benzene sample: Sept. 13, 2001.

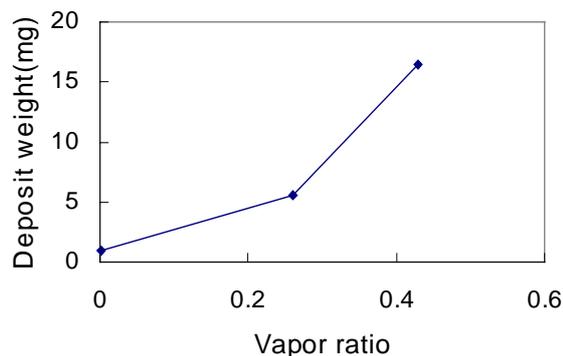


Figure 5. Vapor ratio effect

Experimental conditions; temperature 135°C, pressure 287-190kPa, run time 20 hours, heater rod material: carbon steel, crude benzene sample: Sept. 13, 2001.

5.

The vapor ratio change from 0 to 0.43 was much more effective in increasing deposition than temperature change from 125°C to 135°C. The heater rod surface temperature increased about 20°C when the vapor ratio increased from 0 to 0.43. Perhaps, both polymerization (chemical reaction) and precipitation were enhanced on the heater rod surface by the condensation of high boiling temperature components, and the foulants were easily attached on the heater rod. To reduce fouling in the BTX plant, the most effective method is to decrease vapor ratio.

Effects of heater rod materials and surface roughness

Depending on surface materials, reactions on the surface and attachment behaviors are different. Also, surface roughness may be important. The results are shown in Figure 6.

Compared with carbon steel, type 316 and 304 stainless steels (SS) and aluminum had about 40% less deposit. From experience, when the fluid contains corrosive contents, such as acids, carbon steel has heavier fouling than does stainless steel. (Crude benzene contained some hundreds wtppm acids. We assume this corrosion effect is caused by both dissolved iron salts which act as polymerization catalysts and corroded surface roughness that is easy to attach.)

Both surface treatments by sandpaper (No. 180) and by electrochemical polish increased the deposit amount. Perhaps, because the heater rods bought from Alcor

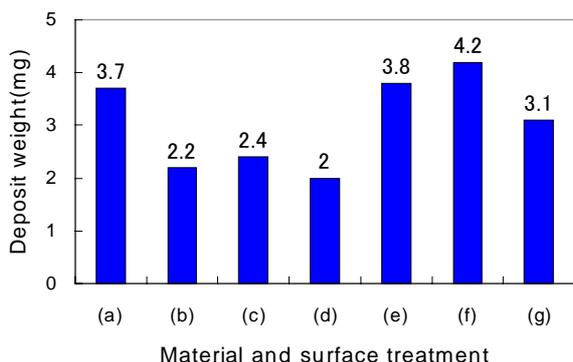


Figure 6. Material and surface roughness effect

Experimental conditions; temperature 145°C, pressure 287kPaG, vapor ratio = 0.43, run time 20 hours. crude benzene sample: May. 25, 2001. (a) carbon steel, (b) SS316, (c) SS304, (d) aluminum, (e) carbon steel (repeat), (f) carbon steel treated by No. 180 sandpaper, (g) SS304 treated by electrochemical polish.

Petroleum Instruments had already quite smooth surfaces, the electrochemical polish did not work well.

Analysis of the deposits

Deposits of the actual plant heat exchanger and Alcor HLPS400 heater rods were analyzed. Elemental analyses of C, H, N, S are listed in Table 1. H/C mole ratio of the deposit of the E-2 process outlet was 0.82, and that of the Alcor heater rod was 0.68. Because the temperature of HLPS400 test was higher than that of E-2, H/C ratio of the heater rod is lower than that of E-2. Infrared absorption charts are almost the same (Figure 7) for each deposit.

Table 1. Elemental analysis of the deposits.

	(wt%)			
	C	H	N	S
E-2	77.2	5.3	4.8	6.4
Alcor heater rod*	67.5	3.8	8.2	8.1

*Alcor deposit is from the experiment of Figure 5, vapor ratio=0.43.

However, E-2 has sharper absorption peaks because of less carbonization and CH₂ and CH₃ group vibration peaks (around 3000cm⁻¹) are seen. Both charts have aromatic ring vibration peaks (around 1000-1800cm⁻¹).

STEP3: Countermeasures and plant test

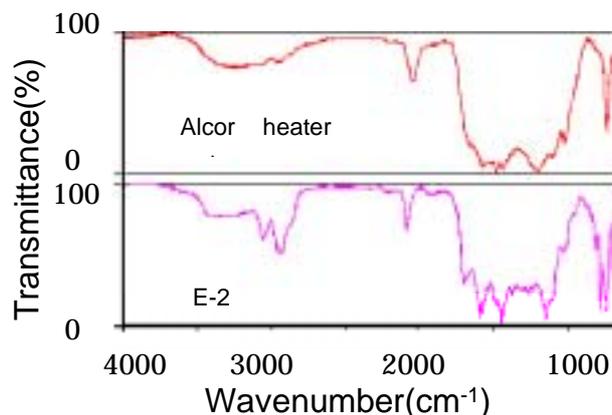


Figure 7. Infrared absorption chart

Screening test of anti-fouling chemicals

The easiest way to mitigate fouling is to use anti-fouling chemicals. First, we tested nine chemicals which include the chemical already used in the plant at that time. Four dispersants, three mixtures of dispersant and antioxidant, one antipolymerant and one mixture of metal deactivator and antioxidant were used. (Experimental conditions: temperature 125°C, pressure 160kPaG (vapor ratio=0), run time 10 hours, heater rod material: carbon steel, crude benzene sample: Sept. 13, 2000. Added

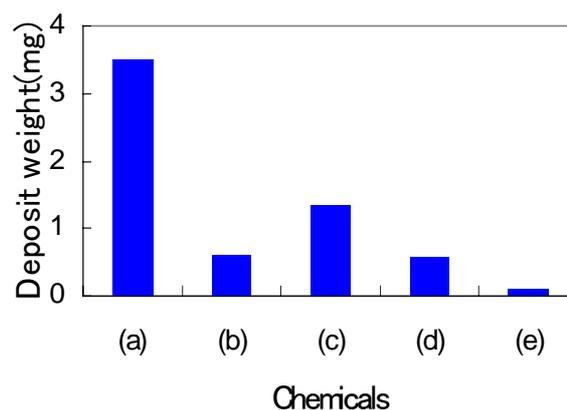


Figure 8. Screening test of the four chemicals.

Experimental conditions: temperature 135°C, pressure 190kPaG (vapor ratio=0.43), run time 20 hours, heater rod material: carbon steel, crude benzene sample: Feb. 2, 2001. Chemicals concentration: 35wtppm. (a) no addition, (b),(c) mixture of dispersant and antioxidant, (d),(e) dispersant.

chemicals concentration: 35wtppm.) From the above screening tests, it was found that four chemicals were much more effective than the chemical used in the plant at that time. All the four effective chemicals contained dispersant.

Next, the selected four chemicals were tested in more severe conditions. The results are shown in Figure 8. From this result and the running charge cost, chemical (c) (dispersant) was selected.

Plant test

From the results above, countermeasures for the fouling are as follows.

- 1) Decrease the vapor ratio
- 2) Use more effective chemicals
- 3) Change material from carbon steel to stainless steel
- 4) Remove small particles by filtration

The plant could easily adopt countermeasure 1) and 2). The chemical was changed to the more effective one, and the outlet temperature decreased from 110°C to 104°C, the lowest temperature to maintain maximum production rate. Then the vapor ratio decreased from 0.7 to 0.5.

After these changes, production was maintained without reduction for two years.

CONCLUSIONS

a) Using Alcor HLPS400, the probable mechanism of heat

exchanger fouling was identified. In the case of the BTX plant, precipitation fouling and chemical reaction fouling are dominant.

- b) Vapor ratio is the most effective parameter for controlling the crude benzene fouling.
- c) Stainless steel has less fouling deposit than carbon steel.
- d) Surface roughness has minimal effect on the deposit amount in the crude benzene case.
- e) By addition of anti-fouling chemicals, and a decrease of the outlet fluid vapor ratio, the heat exchanger has worked for two years without production loss.

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