CONTRIBUTING FACTOR ANALYSIS AND ITS APPLICATION FOR AN ALCOHOL PLANT REBOILER FOULING PHENOMENA

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Abstract

There were two important fouling problems in an alcohol plant of Mitsubishi Chemical Corporation. One was a gradual U value decrease in a reboiler which might hinder two year consecutive full load operation. The other was a rapid polymerization in a reboiler at the plant start-up time. We measured contributing factor effects of fouling (such as temperature, surface temperature, residence time, high boiler concentration, dissolved metal concentration and so on) using Alcor's HLPS (Hot liquid Process Simulator). We applied some mitigation methods that were derived from analysis results for the plant, and the problems were successfully solved. The first problem (gradual U value decrease) was caused by a high surface temperature of the reboiler. By changing the operation condition, the surface temperature of the reboiler tubes was lowered as much as possible. Then, the U value decrease became slower and now the plant can be operated for two consecutive years.

The second problem (rapid polymerization) was caused by the combination of three factors. They were a high concentration of dissolved iron which arose from corrosion, long residence time because of a low production rate at the start-up time, and presence of high boiling materials. After removing these factors, the plant started smoothly.

Introduction

At an alcohol plant, there were two important fouling problems in the distillation column reboilers. Because the production loss by such troubles was large, preventing these troubles and solving them quickly was quite an important mission for our plant operation. In this work, we studied important factors to solve these fouling troubles.

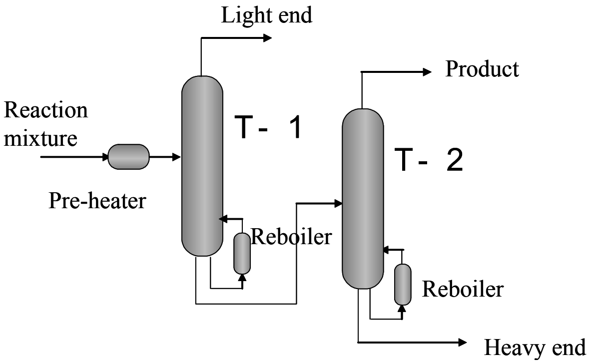

Figure 1. **Distillation process flow of the plant.**

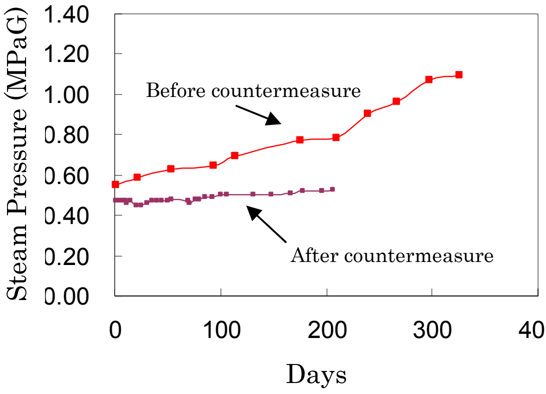

Figure 2. Shell steam pressure of T-1 reboiler.

The distillation process flow of the plant is shown in the Figure 1. Two fouling problems are as follows.

Problem 1: The T-1 reboiler was gradually fouled and overall heat transfer coefficient U value decreased. This U value decrease made it difficult to continue operation for two consecutive years. As shown in Figure 2,

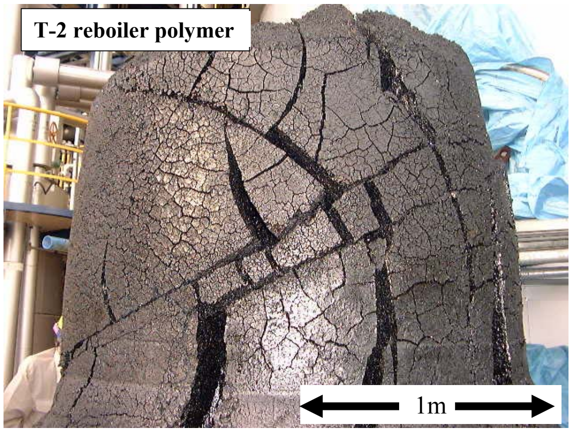

Figure 3. Polymer of T-2 reboiler.

because of the U value decrease, the shell steam pressure was gradually increased to the upper steam pressure limit to keep its heat flux. Then, the plant had to lower the production rate in the second year.

Problem 2: At the plant start-up time, rapid polymerization occurred suddenly and the T-2 reboiler was plugged and the plant completely stopped. (See Figure 3.)

When we try to mitigate this kind of reboiler fouling problems, there are some important affecting factors to be taken into account, such as temperature of the stream, surface temperature of reboiler tubes, concentrations of polymer source, residence time, and polymerization catalyst (dissolved metals) and so on. So, the fouling rate can be expressed as the following formula.

Fouling rate = f(Bulk and Surface Temperature, Catalyst Concentration, Polymer Source Concentration, Residence Time, Others) (1)

To measure the contribution of the factors above mentioned, we used Alcor's HLPS400. This is usually used for quality check of jet fuels, and also used for screening tests of anti-foulant chemicals.

Experimental method

The HLPS400 tests were carried out by charging the reservoir with 300ml of the stream liquid and pumping the liquid 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 liquid was then returned to the reservoir (Figure 4). The system was slightly pressurized with nitrogen to control the vapor ratio of the heated outlet bulk fluid. The heater 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. The thermocouple for the rod was positioned inside the heater rod at the center of the length.

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

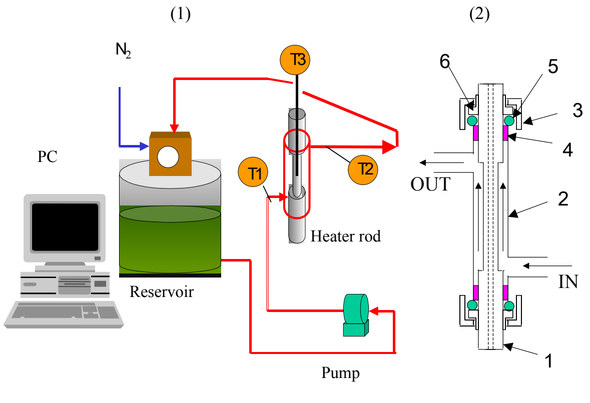

Figure 4. Alcor HLPS400 system(1) and heater section(2). 1: heater rod, 2: housing, 3: nut, 4: insulation part, 5: O-ring, 6: insulation part.

Results and discussion

Chemical analysis of T-1 reboiler deposit

From the results of Infrared measurement and elemental analysis of the deposit of the reboiler, it was mainly polymer of the product. Iron was detected as the main metallic component.

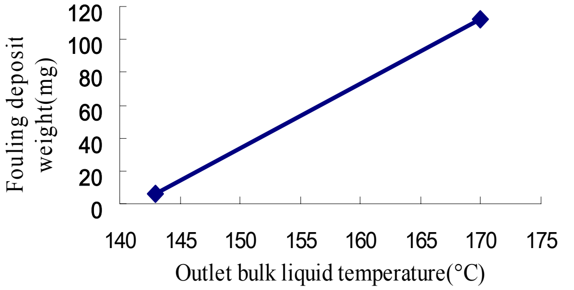

Figure 5. Effect of bulk liquid temperature. Experimental conditions; pressure 0MPaG (vapor ratio=0), run time 20 hours, heater rod material: carbon steel. Sample: T-1 bottom liquid.

Effect of bulk liquid temperature

Using T-1 bottom liquid, the effect of bulk liquid temperature was measured. (See Figure 5.) As the outlet liquid temperature of the heater section (Figure 4, T2) was changed from 143°C to 170°C, the amount of fouling deposit increased more than 20 times. This means that the bulk temperature strongly affects fouling rate.

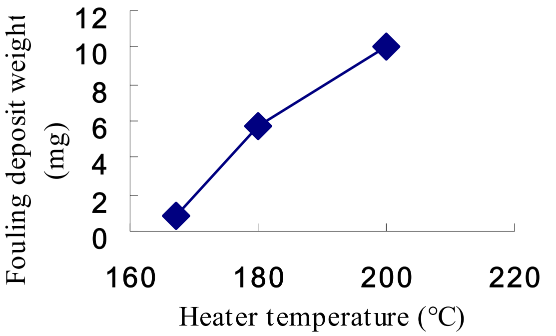

Figure 6. Effect of heater temperature. Experimental conditions; Outlet bulk liquid temperature 143°C, the other conditions are the same as Fig. 5. Heater temperature means heater rod temperature which roughly corresponds to the heater rod surface temperature.

Effect of reboiler tube surface temperature

Bulk liquid temperature test results contain both bulk liquid temperature effects and heater surface temperature effects. So, we kept the outlet temperature constant, and by changing liquid flow rates we changed heater rod surface temperature. As shown in Figure 6, about 30°C change of the surface temperature doesn't affect deposit amount so much compared to the bulk liquid temperature change. But, in actual plant long term operation, this surface temperature effect must be taken into account.

Catalyst effect of dissolved metals

The alcohol plant is mainly made of stainless steel. But, in our experiment we tested both carbon steel and stainless steel 316. As shown in Figure 7, only carbon steel obtained heavy deposits on the heater rod.

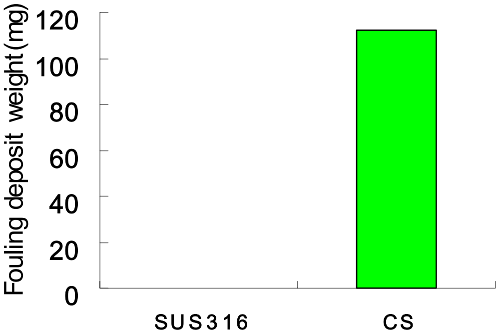

Figure 7. Effect of heater rod material. Experimental conditions; Outlet bulk liquid temperature 170°C, the other conditions are the same as Fig. 5 except heater rod materials.

Although the difference in the surface roughness of carbon steel and stainless steel was considered, it was thought that this effect was too large to be caused by roughness alone. A small amount of organic acid was present in T-1BTM(bottom) liquid, therefore the effect of the corrosion by the organic acid was also considered. The amount of fouling was checked by HLPS similarly after separating organic acid by distillation. The result is shown in Fig. 8.

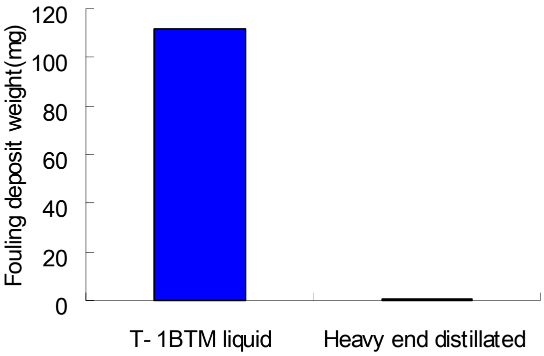

Figure 8. Effect of heavy end (containing organic acid). Experimental conditions; Outlet bulk liquid temperature 170°C, the other conditions are the same as Fig.5.

In the absence of organic acid, fouling could not be detected on the heater rod. When the metal concentration was measured after the experiments with carbon steel heater rods, iron was found to be present at dozens of ppm in the liquid due to corrosion.

Then, iron was added and fully dissolved into T-1BTM liquid, and it was checked whether the amount of fouling would increase. The result is shown in Table 1.

Additive metal	Iron conc. (wtppm)	Fouling deposit weight (mg)
Blank	0.3	0.6
Fe(acac)$_2$	330	3.9
Fe(acac)$_3$	100	7.7

Table 1. Additive iron effect. Experimental conditions; outlet temperature 170°C, the other conditions are the same as Fig. 5.

By iron addition, the fouling amount increased. From this, we concluded that the dissolved iron accelerated generation of polymerization fouling.

Furthermore, in order to test the polymerization acceleration effect by iron, we measured viscosity change of T-2 bottom liquid with and without iron addition using 100ml stirred flasks. The results of 170°C heated tests are shown in Fig. 9. With addition of both iron(II) and (III), the degree of viscosity rise was rapid compared with the additive-free case and with iron(III)the increase was more rapid corresponding to the result of HLPS.

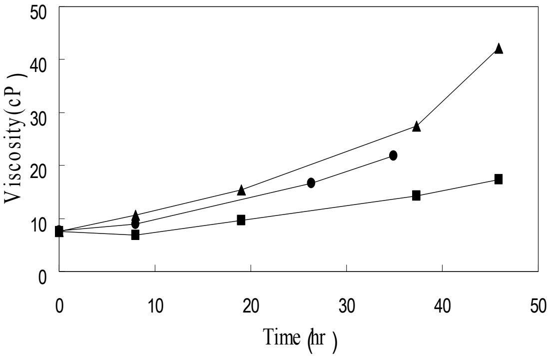

Figure 9. Viscosity change with iron additives. Experimental conditions; sample T-2 bottom liquid, temperature 170°C, under nitrogen atmosphere. Square: blank. Circle: Fe(acac)$_2$ 500ppm. Triangle Fe(acac)$_3$ 500ppm.

Polymer source concentration

Although in the case of Problem 1, the polymerization source was the main product, in the case of Problem 2 the main polymerization source was high boiling point materials (high boiler). In order to check this, we measured the viscosity change when adding high boiler to T-2 bottom liquid. The result is shown in Figure 10. As a result of using the liquid which contained about 35% high boiler (usually T-2 bottom liquid contains about 20% high boiler), even if it was iron additive-free, a viscosity of 1,000cp was exceeded in about 40 minutes. Furthermore, by iron addition, the viscosity rise was remarkably accelerated, and in the case of iron(III) addition it became impossible to measure viscosity after 25 minutes because of solidification.

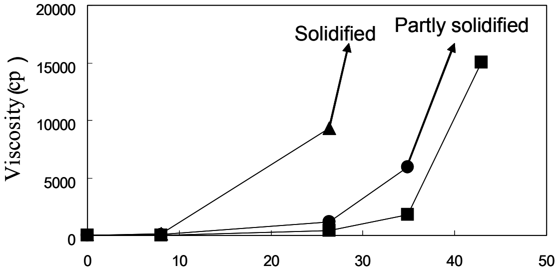

Figure 10. **Effect of high boiler (polymer source material concentration).** Experimental conditions; sample T-2 bottom liquid (high boiler was added), temperature 170°C, under nitrogen atmosphere. Square: blank. Circle: $Fe(acac)_2$ 500ppm. Triangle $Fe(acac)_3$ 500ppm.

Residence time effect

As shown in Figure 9 and 10, it is obvious that polymerization will advance if the time that the liquid is heated in the tower bottom becomes long, and generation of fouling will increase.

Effect of other factors

As other factors, flow rate, surface roughness, material of the reboiler, vapor – liquid ratio of the reboiler, etc. are considered. Although detailed examination for them is important, in this study these were omitted because it is difficult to change these factors this time in the actual plant. However, we think that the effects of flow rate and vapor–liquid ratio are especially large.

Cause and countermeasures

Problem 1

About U value decrease of T-1 reboiler, it was thought from factors of formula 1 that the factor which could be applied was only the surface temperature of the reboiler tubes in the system. We converted the reboiler and the shell side steam pressure was lowered slightly (from 0.55MPaG to 0.47MPaG), and the surface temperature of tubes(product flow is in the tubes) was reduced. Consequently, U value decrease of the reboiler was reduced and full load operation of the plant for two years was achieved.

Problem 2

Among the factor of a formula 1, the rapid several hours polymerization plugging problem during the plant start-up time occurred by the combination of three important factors which were catalyst concentration (iron), residence time of the tower bottom, and polymerization source concentration (high boiler concentration).

First, about the catalyst effect by iron, a very small quantity of chlorine leaked from the newly installed catalyst in the plant and from the corrosion by this chlorine, the reaction mixture contained iron, and that iron was condensed at T-2 bottom. Although the concentration of the contained iron was not measured (of course, iron was detected in the plugging polymer), we cut the iron mixing route.

Second, since the method of raising production rate gradually from the low load was taken at the start-up time, the residence time of T-2 bottom which was usually less than 1 hour had been 3 hours or more and was long enough to start polymerization. We think that the high boiler concentration of the bottom liquid of T-2 was more than twice the usual by this long residence time. When the three above-mentioned factors overlapped, the rapid polymerization reaction occurred. At the next start-up, the iron route was cut, and the plant started from the high production rate to avoid long residence time and concentration of high boiler. Then, it was able to carry out start-up satisfactory.

CONCLUSIONS

In order to solve reboiler fouling problems quickly, it is important to examine each effect in consideration of the following factors of the formula 2.

Fouling rate = f(Bulk and Surface Temperature, Catalyst Concentration, Polymer Source Concentration, Residence Time, Others(Flow Rate, Vapor – Liquid Ratio, Material, Surface Roughness, etc.)) (2)

The two problems of the reboiler fouling and plugging could be explained by four factors of the above-mentioned formula 2, and solutions of them were completed by its application. It is thought that each factor needs to be compared quantitatively in future.

ACKNOWLEDGEMENT

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