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FOULING MITIGATION OF A REBOILER BY OPTIMIZATION OF ADDITIVE AND OPERATING CONDITIONS

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ABSTRACT

Heavy fouling of a reboiler occurred in a solvent recovery tower of a polyolefin plant. By chemical analysis of the fouling deposits, it was found that the foulant was derived from organic carbonate (OC) which diluted the solvent in order to lower the viscosity of high boiling material in the tower. Also by plant operation condition analysis, it was found that the reboiler operation conditions were not appropriate. To solve this fouling problem, Alcor's HLPS (Hot Liquid Process Simulator) and tube fouling unit (tube diameter: 10 mm) were used. A C8 alcohol was selected as the best dilution solvent from the view points of boiling point, solubility for high boiling point materials, fouling rate and corrosion rate. In terms of reboiler operation conditions, the effect of linear velocity of the fluid was investigated and was found to be too low. The new dilution solvent (additive) and the high linear velocity operation conditions for the plant will be used in the next process development.

INTRODUCTION

Heavy fouling of the reboiler in a solvent recovery tower of our polyolefin plant makes us to stop its operation once for three days in a month in order to clean it. This production loss is large, and cleaning work is hard. Now, it is our urgent task to solve this problem in terms of both our pecuniary benefit and real operation work.

The process flow of the tower is shown in Figure 1. T-1 is the solvent recovery tower and its reboiler has a heavy fouling. Organic carbonate (OC) is fed to the tower as an additive in order to lower the viscosity of the high boiling material at the tower bottom. However, since this additive is expensive, we want to select a better additive to mitigate the fouling and also to lower the additive cost.

The valve opening percentage of the reboiler steam supply and the feed rate to the tower are shown in Figure 2. As shown, the feed rate decreases little by little from full

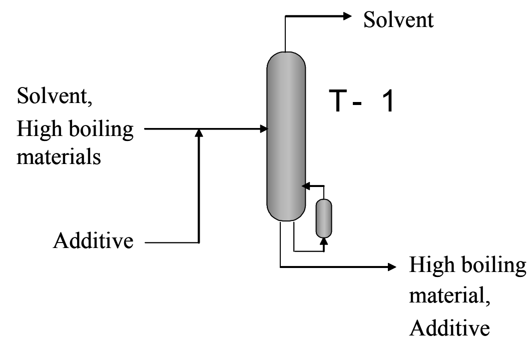

Figure 1. **Process flow of the tower.**

load in about 12 days, and whole plant has to be stopped to clean the reboiler in about one month.

The selection characteristics of an additive are: boiling point, solubility of high boiling materials, the prevention effect to the fouling and no corrosion. Alcor's HLPS [1] (Hot Liquid Process Simulator) was used in order to examine the fouling prevention effect and corrosion in selection of the additive. Moreover, in order to check the effect of liquid linear velocity of reboiler tubes, TFU [2] (tube fouling unit) was used. By examination using these equipments, the optimal solvent, and operation conditions were decided and we are going to apply them to the plant.

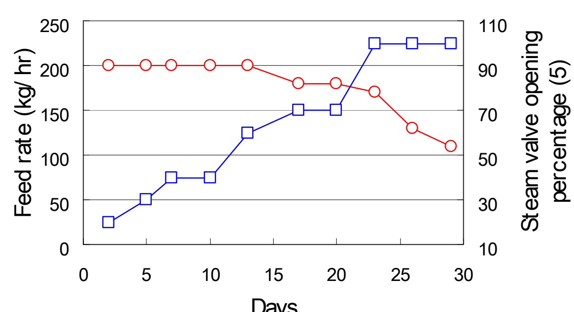

Figure 2. **Reboiler steam supply and feed rate.** Squares: steam valve opening percentage, Circles: feed rate.

EXPERIMENTAL METHOD

Fouling rate measurement by HLPS

The HLPS tests were carried out by charging the reservoir with 300 ml of the stream liquid and pumping the liquid through the annulus formed by a vertically positioned, heater rod (outside diameter of heated section: 3.25 mm) and an outer tube (inside diameter: 4.35 mm) at a flow rate of 0.076 m/s (3.0 ml/minute). The heated liquid was returned to the reservoir (Figure 3). The system was pressurized with nitrogen (190-350 kPaG) to control the vapor ratio of the heated outlet bulk fluid. The rod surface was heated electrically 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 rod thermocouple was positioned inside.

The deposit weight on the rod was measured directly after experiment runs. Usually, the HLPS tests were run for 15 hours. For run times below 20 hours the deposit weight increased linearly with the run time in the temperature range used.

Linear velocity effect test by tube fouling unit

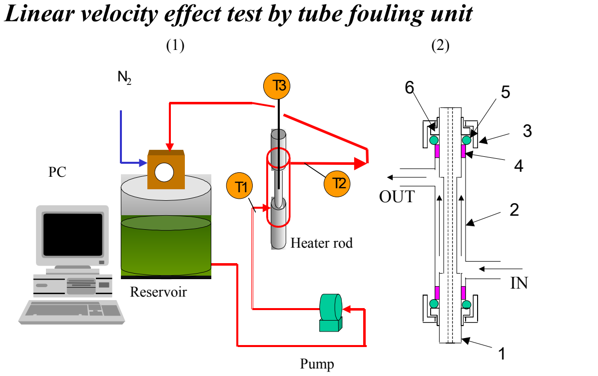

Figure 3. Alcor HLPS system(1) and heater section(2). 1: heater rod, 2: housing, 3: nut, 4: insulation part, 5: O-ring, 6: insulation part.

The tube fouling unit has a tank of 40L. By applying direct voltage to a length of 2m, a diameter 10 mm tube, the fluid which flows inside the tube is heated directly. Because of the heating system, the heater tube has the feature of uniform heat flux along it. The tube has the 1m of heating length in the middle with a run-up section and the rectification section of 0.5 m length before and after the heating section. The 0.2 mm thickness enables the tube to be cut open after experiment to observe the fouling deposit directly. Moreover, the linear velocity in a tube is variable from 0.03 m/s to 1.8 m/s. As shown in Figure 4, eight thermocouples (TC2 – TC9) are installed between the heating electrodes, and two thermocouples (TC1 and TC10) are attached before and after the heating section to measure tube wall temperatures. Bulk inlet/outlet fluid temperatures can also be measured by thermocouples (T1, T2) directly installed in the fluid.

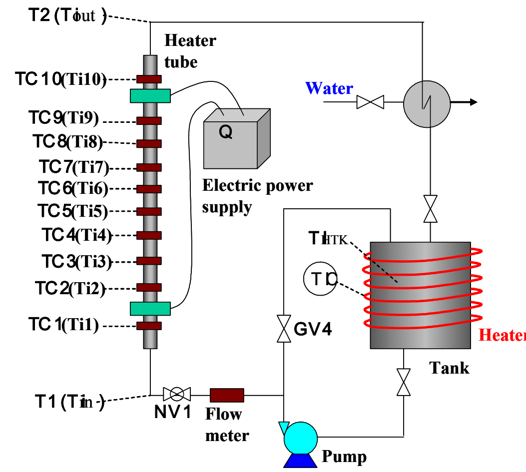

Figure 4. Tube fouling unit (TFU).

RESULTS AND DISCUSSIONS

Fouling mitigation by optimization of an additive

Analysis of fouling deposits in the reboiler

Infrared spectra and chemical element analysis of the fouling deposits in the reboiler were performed, and the main ingredients were the compound of anhydrous organic acid of high boiling materials and an additive (organic carbonate). The viscosity increased, and the gel-like substance was generated when 150°C and 2-hour heat treatment of anhydrous organic acid (high boiling material) and an additive was carried out under nitrogen in a flask. From this, it is needed to change the present additive to what does not generate fouling.

Additive selection: from solubility, boiling point, and the price

The followings are important as candidates of the additive. 1) Suitable boiling point. 2) Dissolution of the anhydrous organic acid of high boiling materials. 3) Low cost. 4) Minimal fouling. 5) Non- corrosive.

Table 1. **Additive candidates.** $\gamma\infty$: infinite dilution activity coefficient to the organic acid of the high boiling materials, Cost: comparing with the present additive, Boiling point: Above 150°C is necessary.

No.	Additive candidates	Organic acid@135 degree C		Cost	Boiling Point	
		LN($\gamma\infty$)	$\gamma\infty$		dgree C	
1	dimethyl sulfoxide	-5.2004	0.0055	H I	194	
2	N,N-dimethylacetamide	-3.4682	0.0312	H I	166	
3	1-methyl-2-pyrrolidone	-3.4104	0.0330	H I	202	
4	N,N-dimethylformamide	-3.3384	0.0355	H I	153	
5	diethylene glycol	-1.7682	0.1706	Good	246	
6	γ-butyrolactone (GBL)	-1.5856	0.2048	Same	205	
7	formamide	-1.2528	0.2857	H I	211	
8	ethylene glycol	-1.1791	0.3076	Good	198	
9	furfural	-0.7002	0.4965	H I	162	
10	organic carbonate (present additive)					
11	ethoxyethanol	-0.3285	0.7200	-	135	LO
12	4-methyl-2-pentanone	0.0760	1.0789	-	116	LO
13	1-pentanol	0.0871	1.0910	-	138	LO
14	acetophenone	0.2263	1.2540	H I	202	
15	dimethylphthalate	0.4016	1.4942	H I	281	
16	butyl acetate	0.4401	1.5529	-	126	LO
17	diethyl phthalate	0.8391	2.3142	H I	305	
18	2-ethyl-1-hexanol (2EH)	1.2636	3.5381	Good	184	
19	dibutyl phthalate (DBP)	1.2684	3.5550	Same	336	
20	anisole	2.4564	11.6628	-	154	LO

The candidates are listed on the Table 1. From the viewpoint of price and boiling point, γ-butyrolactone (GBL), 2-ethyl-1-hexanol (2EH), dibutyl phthalate (DBP) were good candidates. (*See footnote)

Additive selection: Fouling rate and corrosive action

The 2EH was chosen because of the lowest cost and fouling and corrosion were tested using HLPS. Straight chain saturated alcohols, 1-nonanol (HA9) and 1-undecanol (HA11) were also tested as low cost options due to internal transfer pricing. (**See footnote)

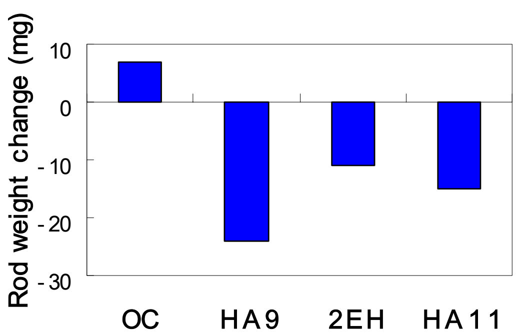

Figure 5. **Fouling rate test for higher alcohols.** Experimental conditions; Outlet bulk liquid temperature 140°C, pressure 0 MPaG (vapor ratio=0), run time 15 hours, heater rod material: carbon steel.

The high boiling materials and additive were mixed up 2:8 ratio [2 (high boiling materials) to 8 (an additive)]. The exit temperature of the heater section was kept at 140°C for 15 hours and the weight of the carbon steel heater rod before and after the experiment was measured. The results are shown in Figure 5. In the case of the present additive(OC), the weight increased because of the fouling deposits. However, the weight of the heater rod decreased in cases of 2EH, HA9 and HA11 caused by corrosion.

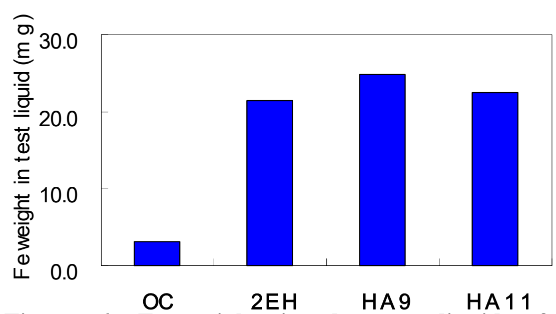

Figure 6. **Fe weight in the test liquid after experiment.** Experimental conditions: same as figure 5. Liquid volume of each experiment is about 300 ml. Before experiment, the Fe weight was about 3 mg in the test liquid.

* The diols were omitted because they were thought to be catalyst poisons.

** HA9 and HA11 have almost the same property as 2EH's solubility and boiling point.

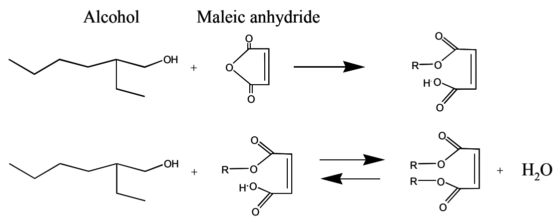

Figure 7. **Presumed reaction of water and acid generation.**

The iron concentration in the liquid of 2EH, HA9 and HA11 increased. (See Figure 6.) On the other hand, there was no change with OC. The presumed acid generation reaction is shown in Figure 7. The anhydrous organic acid (carboxylic acid) of high boiling materials reacts with alcohol, then the anhydrous acid opens its ring and water is generated, producing corrosion.

The result is shown in Figure 8 for the material of a heater rod changed into stainless steel 304 from carbon steel. Before and after the experiment, the iron concentration in liquid hardly changed in both cases. This means there was no corrosion. 2EH was below half the fouling deposit weight of the present additive (OC).

If 2EH were to be used as the additive, the tower of carbon steel needs to be changed to stainless steel 304.

The fouling rate and corrosion behavior of GBL and DBP were checked by HLPS. (However, as for high boiler materials, sampling dates of Figure 8, 9 and 10 are different, and each amount of fouling differed little.) As shown in Figure 9, when GBL was used as an additive the carbon steel corroded. With stainless steel 304, it did not

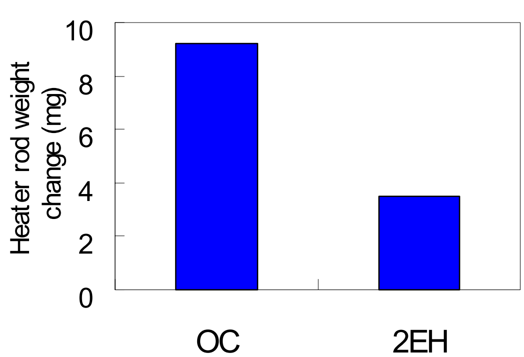

Figure 8. **Effect of stainless steel heater rod.** Experimental conditions: same as figure 5 except heater rod material (stainless steel 304) and HE sampling date.

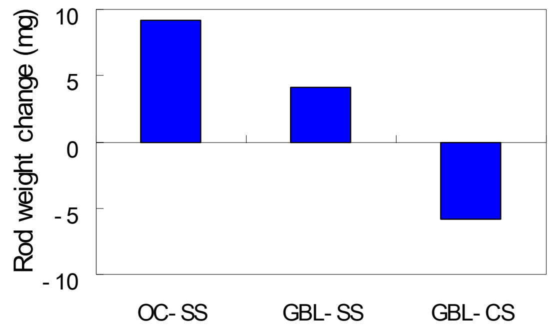

Figure 9. **HLPS test of GBL.** Experimental conditions: same as Figure 5. OC-SS: additive=OC, rod material=stainless steel 304, GBL-SS: additive=GBL, rod material=stainless steel 304, GBL-CS: additive=GBL, rod material =carbon steel.

corrode and there was less fouling than the present additive (organic carbonate). Although the iron concentration in liquid did not increase and corrosion did not occur even with a carbon steel heater rod by DBP, there were more amounts of fouling than the present additive (See Figure 10.)

Determination of an optimal additive

Table 2 shows that is the most advantageous to convert the reboiler and tower bottom into stainless steel

Table 2. **Comparison of additives.**

Additive	OC	2EH	GBL	DBP
fouling	×	O	O	×
corrosion	O	Δ	Δ	O
cost	Δ	O	Δ	Δ

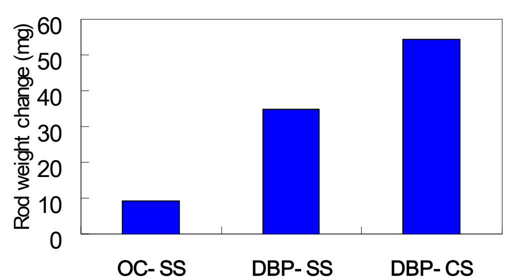

Figure 10. **HLPS test of DBP.** Experimental conditions: same as Figure 5. OC-SS: additive -OC, rod material-stainless steel 304, DBP-SS: additive-GBL, rod material-stainless steel 304, DBP-CS: additive-GBL, rod material-carbon steel.

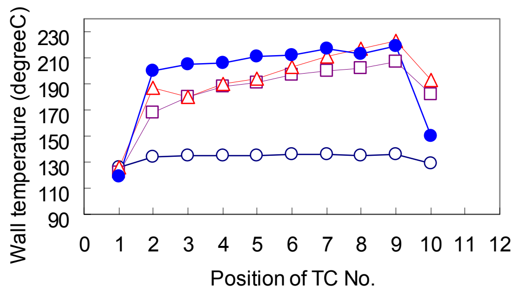

Figure 11. Inside wall temperature of TFU linear velocity test. Open circle: linear velocity =0.6 m/s, inlet temp.=129°C, outlet temp.= 131°C, Q=13,000 w/m^2, Solid circle: linear velocity=0.6 m/s, inlet temp.=123°C , outlet temp.=150°C, Q=180,000 w/m^2, Square: linear velocity=0.1 m/s, inlet temp.=128°C, outlet temp.=140°C, Q=13,000 W/m^2, triangle: linear velocity=0.03 m/s, inlet temp.=130°C, outlet temp.=189°C, Q=19,000 W/m^2. Experimental conditions: pressure 0 MPaG (vapor ratio=0), run time= about 5 hours, tube material=stainless steel 304.

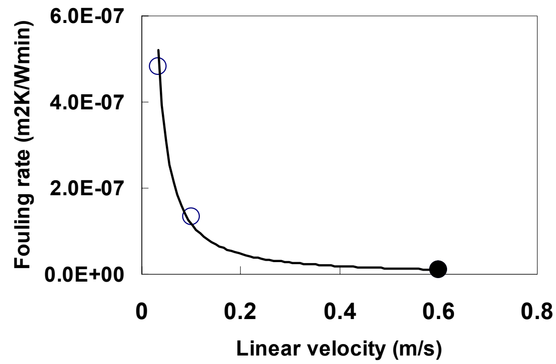

Figure 12. Liner velocity effect. Experimental conditions are described in the caption of figure 11. Open circle: Q=13,000-19,000 w/m^2, Fouling rate of linear velocity 0.6m/s at the low heat flux (Q=13,000 w/m^2) is zero for 5 hours. Solid circle: Q=180,000 w/m^2.

304, and to use 2EH as an additive (from cost and fouling prevention).

Optimization of reboiler operation conditions

The liquid line velocity of the present T-1 reboiler tubes is 0.05 m/s. This is extremely small compared with usual reboilers. In fact, the tower had be converted from some other purposes in the plant. Using T-1 bottom liquid, the relation of velocity and fouling rate was measured by the tube fouling unit. Current and voltage to the heater section was controlled to remain constant heat flux (Q) and the tank was kept at constant around 130°C. The inlet temperature of the heater part was around 130°C.

Since the sensitivity of TFU was high, we could calculate the fouling rate from the overall heat transfer coefficient U of the heater tube for the 5 hour experiments. Because Q is constant, the fouling rate is affected by both linear velocity and liquid temperature. But in the actual plant operation, Q is kept at constant. So, this can simulate that situation. Figure 11 shows wall temperature inside the tube. This inside wall temperature is calculated from outside wall temperature measured by thermocouples attached outside the tube.

Fouling rate is shown in Figure 12. No fouling was measured at the heat flux about 13,000 W/m^2 for a linear velocity 0.6 m/s. For comparison when a high heat flux was applied, the inside wall temperature profile was almost same as the other velocity tests. Even in such a high heat flux and high inside wall temperature condition, fouling rate was quite low.

From Figure 12, fouling rate might be lowered by a factor of 100 when liquid linear flow velocity is increased from present 0.05 m/s to about 0.6 m/s. Laminar flow is below about 0.1m/s, and a turbulent flow region is 0.4 m/s or more. This reboiler flow rate should be increased to this turbulent flow region by converting the circulation pump.

CONCLUSION

1. The current additive (OC) caused reboiler fouling.
2. The optimal additive was chosen by boiling point, solubility, price, fouling rate and corrosive action. 2EH was found to be the best additive from the points of view of fouling rate and price. Some corrosion occurred however in the present carbon steel tower, it will be necessary to change to stainless steel.
3. The linear velocity of the reboiler tubes is too small because the tower was converted from another plant and has affected the fouling rate. Flow velocity has to be increased by converting the circulating pump of the reboiler, and the flow in the tubes must be in the turbulent flow region.

ACKNOWLEDGEMENT

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REFERENCES

[1] Alcor Petroleum Instruments, purchased from Petroleum Analyzer Company, San Antonio, TX, USA.

[2] Wilson, D. I. and Watkinson, A.P., (1996), A Study of Autoxidation Reaction Fouling in Heat Exchangers, *Can. J. Chem. Eng. Vol.74,* pp.236-246.