

## [Regular Paper]

## Coke Deposition on Furnace Tubes of the Vacuum Distillation Unit Estimated by Stability of Atmospheric Residue Oil

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The stability of residual oil is considered to be one of the major factors in coke deposition onto the inner surfaces of furnace tubes in distillation units, such as the vacuum distillation unit (VDU). This preliminary study investigated the stability of a Middle East atmospheric residue oil and the coke deposition tendency on type 304 stainless steel surfaces and chromium molybdenum steel surfaces. The latter materials are widely used as furnace tube materials. Coke deposition rates were determined using a laboratory scale test apparatus at atmospheric pressure. The oil was fed in once-through mode into the inlet of the test section of the apparatus for 24 h. During the feeding of the oil, the temperature of the metal surface of the test tube was controlled within a range from 500 to 600°C. The stability of the feed oil and effluent oil was evaluated by the *P*-value based on the Heithaus evaluation method, which indicates the tendency of asphaltene flocculation to form sludge. A decrease of *P*-value indicates decreased oil stability with the formation of sludge. Coke deposition experiments were carried out at higher temperatures than the conventional VDU operation to promote coke deposition. The results showed that the coke deposition rate was slightly lower for stainless steel than for chromium molybdenum steel. The coke deposition rates increased exponentially regardless of the materials. The *P*-values of the effluent oil gradually increased with the effluent temperature from 415 to 450°C. This indicates an increase of oil stability with heating temperature. The changes in *P*-values correspond to removal of unstable aggregates of asphaltenes from the oil. The unstable aggregates are thought to be one of the predominant precursors for coke deposition. The results suggest that the analysis of *P*-values of the feed and effluent oils together with coke deposition is useful to estimate the quantity of deposited coke on the furnace tubes before operation.

**Keywords**

Vacuum distillation unit, Furnace tube, Coke deposition, Atmospheric residue, Oil stability

**1. Introduction**

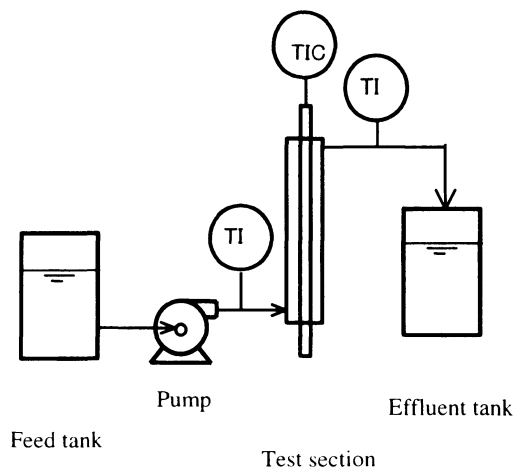
Coke deposition in furnace tubes has recently become a problem for refineries because of the requirements for deep cut and long-term continuous operation of vacuum distillation units (VDUs)<sup>1,2)</sup>. Deep cut operation tends to raise the skin temperature of the furnace tube and promote coke deposition, which makes it difficult to attain long-term operation, as periodic shutdown maintenance of furnace is needed at short intervals. Great efforts have been made to manage furnace tube coke deposition during operation<sup>1)~3)</sup>. Such methods include direct measurement of the skin temperature of the furnace tube, control of the coil outlet temperature, differential pressure between the coil inlet and the outlet, and control of the temperature of the slop oil pull out zone<sup>4)</sup>.

Asphaltenes in petroleum are present as micelles in which light components stabilize the asphaltenes in oil<sup>5)~8)</sup>. Coke formation in residual oils such as vacuum residue from thermal cracking, proceeds *via* flocculation of asphaltenes resulting from the destabilization of the residual oil<sup>9),10)</sup>.

The present study experimentally simulated VDU furnace tube coke deposition to investigate the tendency of coke deposition associated with asphaltene flocculation in a Middle East atmospheric residue using a laboratory scale test apparatus. The effect of oil stability was investigated on coke deposition from the residual oil onto metal surfaces, such as stainless steel. The oil stability can be evaluated by measuring asphaltene flocculation in the residual oil<sup>11)~13)</sup>. The Heithaus stability evaluation method<sup>11),13)</sup>, based on a solvent titration technique, was used to measure the oil stability. This preliminary study was the first step aiming at estimating coke deposition in the VDU furnace tube. Quantitative analyses of the oil stability in various

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TI, Temperature indicator; TIC, Temperature controller.

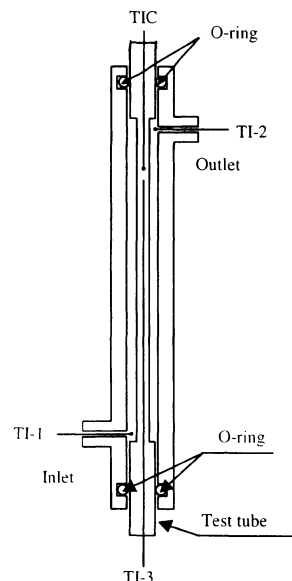
Fig. 1 Schematic View of the Laboratory Test Apparatus (Alcor Hot Liquid Process Simulator) for Coke Deposition of Atmospheric Residue Oil

crude feedstocks and associated coke deposition could be valuable as a database for the production control of residual refinery products and also used as a design basis for the furnace.

## 2. Experimental

### 2.1. Experimental Apparatus and Measurement of Coke Deposition

The amount of coke deposited was evaluated using a laboratory scale test apparatus, Alcor Inc. Hot Liquid Process Simulator (San Antonio, TX, USA) at atmospheric pressure. The experiment was carried out at various temperatures including higher temperatures than the conventional VDU operation to promote coking. The schematic view of the test apparatus is shown in Fig. 1. Detail of the test section containing the test tube is shown in Fig. 2. The oil preheated at about 60°C in feed tank was fed in once-through mode at a flow rate of 1 ml/min, which corresponds to a linear velocity of 1.7 mm/sec, into the inlet of the test section of the apparatus for 24 h. During oil feeding, the temperature of the metal surface of the test tube was controlled over a range from 500 to 600°C using a thermocouple installed on the inner wall of the test tube (TIC in Fig. 2). The test tubes were hollow tubes with 1.5 mm inner diameter, outside diameter of 3.2 mm and wall thickness of 0.85 mm. The fluid was designed to flow along the outside of the test tube in the test section. The length of the test tube in contact with the fluid was 60 mm. The test tube was designed to be heated as a resistance coil by current flow. During the experiment, temperatures were monitored at the inlet and the outlet of the fluid and the metal sur-



TIC, Temperature controller for inside wall of specimen; TI-1, Temperature indicator for feed inlet; TI-2, Temperature indicator for fluid outlet (effluent oil); TI-3, Temperature indicator inside wall of specimen, defined as surface metal temperature.

Fig. 2 Detail of Test Section Containing the Specimen in the Laboratory Test Apparatus Shown in Fig. 1

face of the inside the wall of the test tube (TI-1, TI-2 and TI-3 in Fig. 2, respectively). In the present study, the temperature of the inside wall was defined as the surface metal temperature. The metal temperature had a gradient from the inlet to the outlet and reached the maximum around the outlet. The maximum temperature was used as the surface metal temperature in the series of tests. The amount of coke deposited was measured by comparing the weight of the test tube before and after the experiment and expressed as weight of coke deposited per unit time. Each test tube was washed with acetone and dried in air before the experiment. The test tube was washed thoroughly with hexane before weighing to remove sticky oil bound to the test tube without dissolving the coke deposited. The effluent oil was collected for the determination of the flocculation tendency (*P*-values) of asphaltene in comparison with the fresh feed.

### 2.2. Property of Feedstock

A Middle East atmospheric residue, originating from Kuwait and Basrah crude, was used as feedstock. General properties including the oil stability are shown in Table 1. Details about *P*-values are described below.

### 2.3. Test Materials

Type 304 stainless steel and chromium molybdenum steels (5Cr-1/2Mo and 9Cr-1Mo) were used as the test tube materials. Stainless steel test tube was commercially available. Chromium molybdenum steel test

Table 1 Properties of Feedstock

Properties		Analytical values
Density	[g/cm <sup>3</sup> ]	0.971
S	[wt%]	4.0
Metal	[ppm]	Na 16.8, Fe 6.1, V 43.6, Ni 12.5
CCR	[wt%]	11.1
<i>P</i> -values		2.2

tubes were prepared for the present study by cutting down furnace tubes used in VDUs. The surfaces of the test tubes were mechanically polished to an average roughness of 1.6  $\mu\text{m}$ .

#### 2.4. Analysis of Oil Stability

The stability of the feed and the effluent oil was analyzed by the Heithaus evaluation method<sup>(11)</sup> according to the recent methods using solvent titration technique<sup>(12),(13)</sup>. This method is generally used to predict the stability of heavy oils and is carried out by titration of a solution of aromatic solvent and a solution of paraffinic solvent into the oil to determine the flocculation tendency of asphaltene. The flocculation tendency of the asphaltene was measured by monitoring the particles that become visible with the onset of flocculation under a Nikon DIAPHOT TMD300 microscope (Tokyo). In the present study, the solvents used for measurements of oil stability were  $\alpha$ -methyl-naphthalene as an aromatic solvent and *n*-hexadecane as a paraffinic solvent. The ratios of  $\alpha$ -methyl-naphthalene to hexadecane were in the range of 0.15-0.49. The measurement procedures were as follows: dilution of sample oils with different volumes by aromatic solvent; titration by paraffinic solvent into the diluted sample oils with aromatic solvent; monitoring of the onset of the asphaltene flocculation under a microscope; since the solvent ratio (aromatic solvent *versus* paraffinic solvent) against the reciprocal of the dilution ratio by paraffinic solvent should be a straight line, the intersection point at *x*-axis and *y*-axis by extrapolation corresponds to the dilution ratio at which flocculation starts and the minimum aromaticity required to prevent flocculation, respectively. The minimum aromaticity or maximum flocculation tendency,  $FT_{\text{max}}$ , can be expressed as follows:

$$P = p_o / (FT_{\text{max}}) = p_o / (1 - p_a)$$

From these measurements, the three parameters of  $p_a$ ,  $p_o$  and  $P$  were obtained as an evaluation of the stability of sample oil. The parameters of  $p_a$  and  $p_o$  are the peptizability of asphaltene and the peptizing power or available aromaticity of maltene in heavy oils, respectively. The parameter  $P$  indicates the overall state of peptization of the system. A decrease in  $P$ -values generally means a decrease in the oil stability<sup>(11)~(13)</sup>. Sludge formation is accelerated by asphaltene flocculation when the  $P$ -value is below 1 in case of marine fuels<sup>(12)</sup>. Compositions of the fresh feed and the efflu-

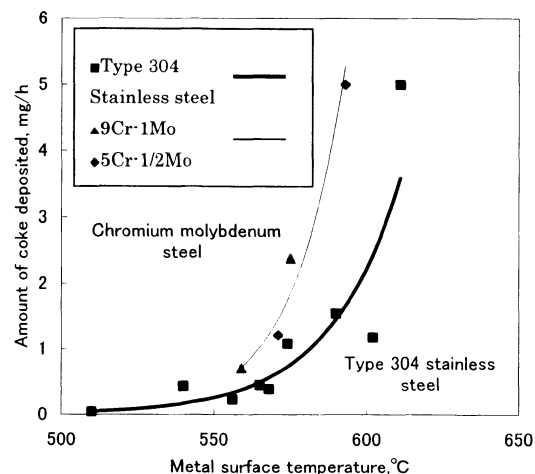


Fig. 3 Effect of Metal Surface Temperature on Coke Deposition Rate for a Middle East Atmospheric Residue

ent oils were analyzed by thin-layer chromatography with a FID detector (TLC-FID) to determine the amounts of saturates, aromatics, resins and asphaltenes. The H/C atomic ratio and the carbon aromaticity  $f_a$  were also determined using a YANAKO MT-5 CHN CORDER (Tokyo) and a JEOL JNM-GS-X270 <sup>1</sup>H-NMR spectrometer, respectively.

### 3. Results and Discussion

#### 3.1. Analysis of Coke Deposition

Figure 3 shows the coke deposition rate *versus* metal surface temperature for Middle East atmospheric residue over stainless steel and chromium molybdenum steel. The coke deposition increased within the whole range of metal surface temperatures, but coke deposition was slightly lower on stainless steel than on chromium molybdenum steel. The difference in the coke deposition rate became more significant by plotting the amount of the coke deposited against the reciprocal of the metal surface temperature as shown in Fig. 4. Linear relationships were obtained for the tested materials, but with different slopes. The results suggest that coke deposition is inhibited by stainless steel compared to chromium molybdenum steels, but the same mechanisms of coke deposition occur over the whole metal surface temperature for both materials. In the case of coke deposition on the furnace tube in ethylene production, the coke may be produced during pyrolyses by a complicated sequence of metal-catalyzed reaction and non-catalytic reaction<sup>(14),(15)</sup>. The metal-catalyzed coke was produced at temperatures over about 400°C<sup>(15)</sup>. Metal-catalyzed coke formation apparently does not occur in the case of heavy oils. In the present test, assuming no catalytic function to accelerate coke deposition on the surface of the furnace

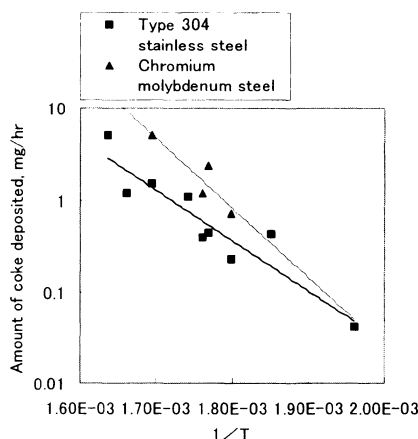


Fig. 4 Amount of Coke Deposited vs. Reciprocal of Metal Surface Temperature

tube, the inhibition in the coke deposition observed over stainless steel may be attributable to a difference in adsorption affinities of the precursors for coke deposits onto the metal surfaces. Filamentous coke is reported to grow by the metal-catalyzed reaction<sup>(14),(15)</sup>. However, electron microscopy observed no such filamentous coke (data not included).

Adsorption models, such as the Langmuir adsorption model, assume reversible adsorption for the adsorbate<sup>(16),(17)</sup>. Adsorption affinity is expressed as a function of the ratio of adsorption to desorption of adsorbate. Stainless steel has relatively good corrosion resistance due to the formation of a chromium-rich oxide surface film called the passive film<sup>(18)</sup>. On the other hand, chromium molybdenum steels do not form such a passive film and the surfaces are susceptible to sulfurization of surface iron in contact with heavy oils. Therefore, the surfaces of the chromium molybdenum steel test tubes may have been sulfurized during the experiment. Such distinct structures of the metal surfaces may have caused differences in adsorption affinities for the precursors of the coke deposits. A full understanding of the mechanism of coke deposition requires information about the surface properties, such as the surface affinities in relation to coke deposition in heavy oils during heating.

### 3. 2. Asphaltene Flocculation and Coke Deposition

The mechanisms of coke deposition occurring in residual oils are thought to differ from those in light components, such as pyrolysis of ethane<sup>(19)</sup>, as described above. The most prominent feature of coke deposition from residual oils in furnace tubes seems to be related to asphaltene flocculation, which leads to the formation of the coke precursor<sup>(6)</sup>. It is generally accepted that coke deposition is affected, regardless of type of oil components, by the mass velocity of the fluid, fluid viscosity, temperature of the fluid film

Table 2 Oil Stabilities of Feed and Effluent Oil Used in the Coke Deposition Experiment on Stainless Steel Test Tubes

Oil	$P$	$p_a$	$p_o$
Feed	2.3	0.85	0.35
Effluent oil			
Effluent temperature [°C]			
415	0.50	0.80	0.10
425	0.79	0.81	0.15
435	1.1	0.82	0.20
445	1.13	0.69	0.35
450	1.35	0.69	0.42

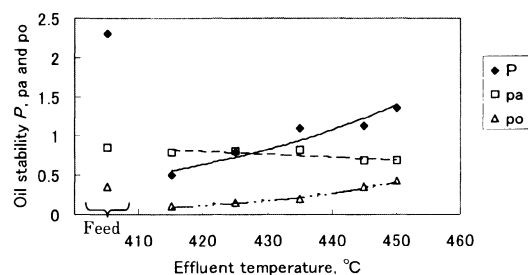


Fig. 5 Oil Stability of Feed and Effluent Oils Measured in Stainless Steel Test Tubes (values also shown in Table 2)

formed adjacent to the furnace inner surfaces, and equipment design<sup>(1)~(3)</sup>. The present study investigated asphaltene flocculation as an indicator of oil stability that leads to the formation of the coke precursor. The stability of the feed and the effluent oils in the case of the stainless steel test tube are summarized in **Table 2**. The stability is also illustrated in **Fig. 5**. The Heithaus stability evaluation method shows that the critical value of parameter  $P$  at which asphaltene flocculation initiates was about 1 in marine fuels<sup>(12)</sup>. According to this criterion, the feed oil in the present study, with a  $P$ -value of 2.2, should be classified as a stable oil. However, the effect of the effluent temperature on  $P$ -values should be noted, since the coke deposition rate increased with metal surface temperature. The  $P$ -values increased with effluent temperature although these values were smaller than that of the fresh feed oil. These trends also coincided with change in the parameter  $p_o$ . However, the change in parameter  $p_a$  according to the effluent temperature was independent of the other parameters,  $P$  and  $p_o$ , showing values relatively close to that of the fresh feed. These changes could result from the improved oil stability caused by the removal of unstable aggregates of asphaltenes from the oil. The decreased oil stability was probably due to the change in the peptizing power of maltene rather than the change in the peptizability of the asphaltene in the heated oil. The occurrence of asphaltene flocculation is the result of reduced solubili-

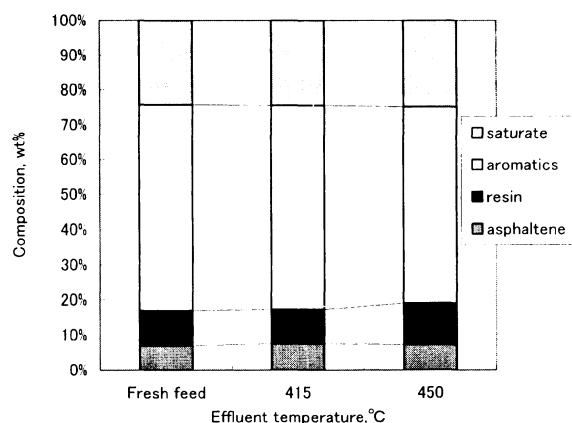


Fig. 6 Composition of Feed and Effluent Oil Analyzed by TLC-FID, for Stainless Steel Test Tubes

Table 3 Chemical Compositions and Carbon Aromaticity ( $f_a$ ) of Feed and Effluent Oil Used in the Coke Deposition Experiment on Stainless Steel Test Tubes

Oil	C	H	N	C/H <sup>a)</sup>	$f_a$
	[wt%]	[wt%]	[wt%]	[—]	[—]
Feed	84.3	11.2	1.4	0.63	0.24
Effluent oil					
Effluent temperature [°C]					
415	84.1	11.1	1.5	0.63	0.25
450	84.0	11.1	1.6	0.63	0.25

a) Atomic ratio.

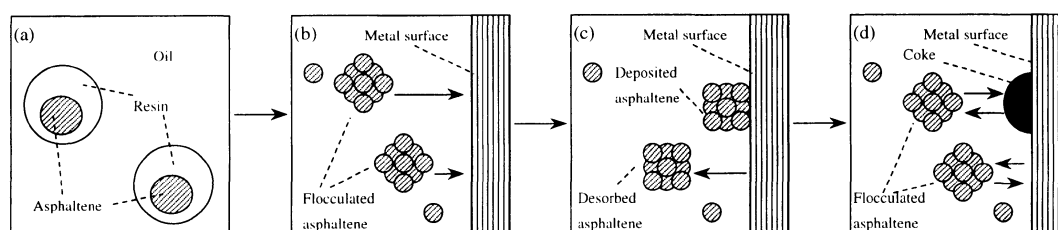
ty of the asphaltene in maltene, especially the decrease in compatibility between asphaltene and resin components. The marked change in  $p_o$  during heating indicates that the effect of maltene to stabilize asphaltene is susceptible to change during heating. **Figure 6** shows the compositional analysis of the feed and the effluent oils in the stainless steel test tube. The compositional change was not conspicuous in the respective components, although the resin component increased slightly with heating temperature. Possibly the

change in the amount of resin may reflect the release of resin bonded to the asphaltene before flocculation. The chemical composition (C, H, N) and the carbon aromaticity ( $f_a$ ) remained practically unchanged during heating, as shown in **Table 3**. The measurements of oil stability suggest that the  $P$ -value is more useful to detect the overall state of the oil than other chemical characteristics, such as the composition and the carbon aromaticity, in particular the sensitivity to detect the stability of asphaltene in the oil.

A possible mechanism for the coke deposition associated with stability of the atmospheric residue oil is depicted in **Fig. 7**. The asphaltene micelles are destabilized by heating and flocculation of the asphaltenes is initiated, which provides the precursors for deposited coke; the flocculated asphaltenes are adsorbed onto the metal surface as a result of the equilibrium between adsorption and desorption of the precursors; the deposited precursors are converted to coke at the metal surfaces by dehydrogenation, which is the main mechanism of formation of the deposited coke; and the coke precursors continue to be deposited onto the surfaces of the matured coke at the metal surface as well as onto the metal surfaces. Based on this coke deposition mechanism, the trends of coke seen in the present study could be interpreted through two processes: the coke precursor/metal surface interaction; and the coke precursor/matured coke deposit interaction. The former interaction would affect the difference in the coke deposition rates between the test tube materials due to the difference in adsorption affinities. The latter interaction would affect the enhancement of coke deposition onto the test tube materials as the metal surface temperature increases, as shown in the exponential increase of the coke deposition rates.

### 3.3. Prediction of Coke Deposition

The thickness of the coke deposited onto the inner surface of the coil can be calculated from difference between the maximum tube metal temperature and bulk fluid temperature based on the following equation of API recommended practice 530<sup>20)</sup>:



(a) Feed oil containing stable micelles consisting of asphaltenes and resins; (b) flocculation of asphaltenes, leading to formation of precursors for coke deposition; (c) deposition of coke precursor onto the metal surface and desorption of coke precursor from the metal surface; (d) coking of the precursor on the metal surface and deposition of the coke precursor onto both the coke formed at the metal surface and the metal surface.

Fig. 7 Presumed Mechanism of Coke Deposition onto Metal Surfaces from Atmospheric Residue Oil

$$T_m = T_b + \Delta T_f + \Delta T_c + \Delta T_w$$

where  $T_m$  is the maximum tube metal temperature,  $T_b$  is the bulk fluid temperature,  $\Delta T_f$  is the temperature difference across the fluid film,  $\Delta T_c$  is the temperature difference across the deposited coke and  $\Delta T_w$  is the temperature difference across the tube wall. In practice, the coke thickness can be obtained by considering the maximum radiant heat flux and the fluid heat transfer coefficient, and the thermal conductivities of the deposited coke and the tube metal. The API method is useful for the prediction of the coke growth during operation and for planning operation. On the other hand, oil stability evaluation of the feed and the outlet oils, as examined in the present study, is an effective approach for the prediction of coke deposition before operation. Although the present study was carried out as a preliminary investigation of the prediction of the coke deposition, it is likely that the quantitative analyses of the stabilities of the feed and effluent oils for various types of crude oil could be used as a database for the production control of the residual refinery products and also as the design basis for the furnace.

The present study demonstrated that  $P$ -values in the oils increased with the effluent temperature. This indicates that oil stability increases with heating temperature, probably through removal of unstable aggregates of asphaltene from the oil. These results suggest that the coke deposition trends for the oils from different crude types could be experimentally analyzed by comparing the  $P$ -values for the feed oils and the effluent oils. The target of our present experimental approach is to fully understand the properties of the crude oil type-dependent coke deposition, which can then be reflected in furnace design. Despite the wealth of information about the structure of asphaltene molecules in various crude oils<sup>(6)~(8)</sup>, there is still little information about how the coke precursor from the heavy oil in the distinct crude type is formed and whether the coke precursor adheres onto the surface of the tube and forms coke on the surface or desorbs from the surface, thus affecting the effluent properties after the heavy oil passes through the furnace tube. The coke deposition trends obtained from the residual oils can help to determine the optimal conditions of furnace operation to prevent coke deposition. Further study using other heavy oils, such as different types of atmospheric residue oils, is under way to evaluate coke deposition in furnace used to upgrade residual oils.

#### 4. Conclusion

The present study investigated the trends of the coke deposition in furnace tubes handling residual oils, such as atmospheric residue. Coke deposition increased exponentially with metal surface temperature. The

coke deposition rate was slightly lower for stainless steel compared to chromium molybdenum steel. The change in the oil stability associated with asphaltene flocculation for the feed and the effluent oils was related to the quantity of the coke deposited on the metal surfaces. These results suggest that quantitative analyses of  $P$ -values for the feed oils and effluent oils together with the coke deposition tendency could be useful to estimate the quantity of coke deposited on furnace tubes before operation and also in the design basis of the furnace.

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## 要 旨

## 常圧残さ油の安定性から見た加熱炉管へのコーク付着傾向

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Vacuum distillation unit (VDU) など, 残さ油の処理装置における加熱炉のコッキングでは, 油の安定性とその促進要因の一つであると考えられている。油安定性からコーク付着を予測する手法を確立するための第 1 段階の研究として, この論文では, 小型実験装置を用いた実験によって, 中東系常圧残さ油のアスファルテン凝集と加熱炉管のコーク付着傾向との関連を調べた。実験では VDU の深絞りの領域となる 450℃ 程度までの流体出口温度が達成されるように試験片を加熱して原料油を供給し, コーク付着速度と原料油ならびに通油後の油の性状を測定した。コーク付着に関しては, SUS304 ステンレス鋼と, 比較のために加熱炉管材質として採用されているクロムモリブデン鋼 (5Cr-1/2Mo あるいは 9Cr-1Mo) も検討した。コーク付着速度は材質によらず試験片の加熱温度とともに指数関数的に増

加した。材質間の付着速度はクロムモリブデン鋼よりもステンレス鋼の方が幾分抑制される結果となった。アスファルテンの凝集性の評価は, Heithaus 法に準じ,  $P$  値を測定することによって行った。 $P$  値はその値が小さいほど油が不安定であり, アスファルテンが凝集してコーク前駆体を形成しやすいことを示す。この油の安定性の評価では, 通油後の油の  $P$  値が流体出口温度とともに逆に大きくなることが示された。通油後の油における  $P$  値の増加は, コーク付着によって流体から不安定なコーク前駆体が除去され, 油が安定化したために生じた変化と考えられる。以上の結果は, 原料油と通油後の油の  $P$  値およびコーク付着傾向の評価が加熱炉管のコーク付着の指標として利用できる可能性を示している。