A TUBULAR FOULING MODEL FOR RESIDUE CRACKING FURNACES

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Key Words: Chemical Reactor, Tubular Fouling, Furnace, Thermal Cracking, Residual Oil, Coking, Reaction Model, Mass Transfer, Sedimentation, Compatibility

Tubular fouling by coke deposition on its inner wall has restricted the development of a high-conversion furnace for residual oil. Such a furnace is desirable from the viewpoint of economics and operability. The proposed tubular fouling model well represents the complex phenomena of tubular fouling of a residue conversion furnace by modeling a sedimentation of coke precursor and its reaction into coking material in and out the boundary film. The model was developed from the experimental data of a bench unit which was specially equipped to generate a high linear velocity and conversion at the same time, and was verified by data collected in a commercial unit.

Introduction

In most residue thermal cracking processes vessel-type reactors are usually employed for high conversion, though a greater extent of conversion in the preheating furnace is desired for more economical and flexible operation. The conversion in the tubular reactor is moderately designed, because the ability to control the complex phenomena of tubular fouling is limited.

For the design of furnaces, the concepts of keeping away from "critical zone"⁶⁾ and "dried wall" are still widely accepted. The former indicates that there exist inhibiting temperature zones depending upon feed properties. The latter is considered as the fouling initiator, and design flow patterns¹⁾ in the tube are adjusted to avoid it. But, these points represent only limited aspects of the complex tubular fouling phenomena.

Variables which should all be taken into consideration in developing a new type of reliable residue cracking furnace with a high extent of conversion are:

(1) feedstock properties, (2) heat flux,⁷⁾ (3) linear velocity of fluid,⁷⁾ (4) flow pattern of fluid, (5) temperature and (6) pressure. Addition of the proposed tubular fouling model to the conventional tools of furnace design makes it possible to develop a reliable residue cracking furnace by a simulator. The model predicts all aspects of the complex phenomena of tubular fouling and the simulation can predict all the effects of the six variables listed above on the operation results of furnaces.

1. Experimental Method

Generally, a tubular reactor in a bench-scale unit has a very low linear velocity. The flow is far from turbulent and the reactor is very easily fouled by coking on its inner wall.

The laboratory unit employed in the present experiments is equipped with a pulsating pump, as shown in **Fig. 1**, which permits a high linear velocity of up to 4 m/s in the tubular reactor, as illustrated in **Fig. 2**, though feed rate is nominally 1000–2000 cc/h at bench scale size.⁴⁾ The flow pattern was observed to be a reciprocate piston flow in mock-up tests because of the small tube diameter (4 mm ϕ). The ratio of gas to

Received June 21, 1988. Correspondence concerning this article should be addressed to T. Takatsuka.

Fig. 1. Experimental tubular cracking unit

Fig. 2. Mechanism of linear velocity

liquid corresponded to the ratio of V_G to V_L in the tube as shown in Fig. 3.

A high linear velocity brings about a turbulent flow in the tube and restricts coking on its inner wall. It allows stable operation of experiments and makes it possible to obtain data on reactor fouling in the range of high linear velocity.

The feedstock employed in the experiments is vacuum residue from Middle East crude, and its properties are shown in Table 1.

2. Theory

2.1 Tubular cracking model

Figure 4 shows the reaction mechanism model of residue thermal cracking employed in tubular cracking. The model is very similar to that used for residue cracking in vessel-type reactors,⁸⁾ but is rather simpler. All the cracked products are assumed to come from the *n*-heptane-soluble component of the feedstock. This assumption is valid in the range of relatively low conversion in tubular cracking and has been confirmed in experiments with the vessel-type reactor. Cracked products from *n*-heptane-insoluble components were observed to be of negligible amount in that range of conversion.

Fig. 3. Flow pattern in tubular reactor

Table 1. Properties of feedstock

Sp. Gr.	(d15/4)	1.032
C	(wt%)	85.19
H	(wt%)	10.27
S	(wt%)	3.89
N	(wt%)	0.65
V	(wtppm)	460
Ni	(wtppm)	95
C.C.R.	(wt%)	21.1
Distillation	(deg.C)	
IBP		442
5%		516
EP (9%)		540

$$X k_1 = k_{12} + k_{15} + k_{16} + k_{17} + k_{18}$$

$$\begin{aligned} R_1 &= -X k_1 \cdot C_1 \\ R_2 &= k_{12} \cdot C_1 - k_{23} \cdot C_2 \\ R_3 &= k_{23} \cdot C_2 - k_{34} \cdot C_3 \\ R_4 &= k_{34} \cdot C_3 \\ R_5 &= k_{15} \cdot C_1 \\ R_6 &= k_{16} \cdot C_1 \\ R_7 &= k_{17} \cdot C_1 \\ R_8 &= k_{18} \cdot C_1 \end{aligned}$$

Fig. 4. Reaction mechanism model

Fig. 5. Tubular reactor model

The reactor model is shown in Fig. 5. The solution is obtained by simultaneously integrating differential equations of mass balances for the defined com-

ponents by the Newton-Raphson method. In the tubular reactor the overall density of reactant varies greatly with temperature, pressure and degree of conversion. The degree of vaporization of cracked products was estimated by use of the predicted distillation curves of whole products and the atmospheric equivalent temperature.⁸⁾ The results were calibrated by the SRK method.

2.2 Tubular fouling model

The coking rate, X , can be derived according to the model depicted in Fig. 6.

$$-[\pi r^2 - \pi(r - \Delta r)^2] \cdot Z \cdot \rho_c = X \cdot \Delta t \cdot 2\pi r \cdot Z$$

Then X is defined by the next equation.

$$-\frac{dr}{dt} = \frac{X}{\rho_c}$$

The diameter of the coked tube is calculated by the following equation.

$$r = R - \frac{X}{\rho_c} \cdot t$$

It has been observed in various types of furnace cracking operations that the coking rate depends upon temperature, pressure, linear velocity and properties of the cracked oil. All those variables can now be predicted in advance for any location along the reactor by the tubular cracking model.

The coking rate is actually the result of very complicated phenomena but it can be predicted on the assumption that it is proportional to the concentration of hypothetical coking material, C^* .

$$X = \alpha \cdot C^*$$

It is formed in the boundary film. It easily sticks and accumulates on the inner wall to cause tubular coking.

The concentration of coking material, C^* , is predicted by the model described in Fig. 7. As mentioned, the properties of cracked oil in a tubular reactor are estimated by a tubular cracking model. When residual feedstock is cracked, polycondensation takes place at the same time, as indicated in the reaction mechanism. The polycondensed product is dissolved stably in the liquid phase of the product when the conversion is low. But compatibility decreases as conversion increases, and polycondensed material as a coke precursor is easier to be separated in a bulk flow because the polycondensed product becomes more aromatic while the matrix portion of the cracked oil becomes more paraffinic.

Recently, it was found that the solubility of a coke precursor to a bulk matrix oil could be calculated by the regular solution theory of Hildebrand with binary parameters.⁹⁾ But the concentration of sedimented coke precursor, C_{BS} , was predicted by the following

Fig. 6. Tubular fouling rate

$$X = \alpha \cdot C^*$$

- 1) Separation of coke precursor in bulk flow
- 2) Diffusion of coke precursor into boundary film
- 3) Formation of coking material C^* in boundary film
- 4) Diffusion of coking material out of boundary film

Fig. 7. Tubular fouling mechanism

empirical equation with solubility parameters,³⁾ δ and concentrations of residual components, C_i in the model, for simplicity. This represents the tendency toward a rapid decrease of compatibility from the limited conversion level.

$$C_{BS} = A \cdot \phi_1 + B \cdot \phi_2$$

$$\phi_1 = (\delta_{TI} - \delta_{TS}) \cdot (C_{TI}/C_{HITS})^3$$

$$\phi_2 = (\delta_{HI} - \delta_{HS}) \cdot (C_{HITS}/C_{538-HS})^3$$

where

$$C_{TI} = C_3 + C_4$$

$$C_{HITS} = C_2$$

$$C_{538-HS} = C_1$$

The solubility parameters actually depend upon temperature by definition. But they were predicted by the next empirical equation²⁾ in the model, because the values of their differences can be regarded as independent of temperature.

$$(1000)^{1/2} \cdot \delta = -11.8 \cdot \{1/(1 + C/H)\} + 14.8$$

The coke precursor sedimented in a bulk flow diffuses into the boundary film formed on the inner wall of the tubular reactor with a diffusion rate F_1 . The concentration of coke precursor turns out to be C_S on the inner surface of the tubular reactor.

$$F_1 = 2\pi R \cdot Z \cdot D_s \cdot \rho \cdot \frac{C_{BS} - C_S}{\epsilon}$$

where film thickness is predicted by the equation⁵⁾

$$\varepsilon = \frac{10R}{Re} \left(\frac{2}{f} \right)^{1/2}$$

On the surface of the tubular reactor the coke precursor is further polycondensed and coking material is formed at a reaction rate F_2 .

$$F_2 = 2\pi R \cdot Z \cdot \rho \cdot K_S \cdot C_S$$

Coking material is also allowed to diffuse out of the film at the rate F_3 , where the same diffusion coefficient was employed as for the coke precursor.

$$F_3 = 2\pi R \cdot Z \cdot D_s \cdot \rho \cdot \frac{C^*}{\varepsilon}$$

where the concentration of coking material was considered negligible in the bulk flow.

When all the material balances in and out of the boundary film are calculated simultaneously, a very simple solution is obtained to predict the concentration of coking material C^* . Then the coking rate X is finally stated as follows:

$$X = \frac{\beta}{1 + \beta} \cdot (P_1 \cdot \phi_1 + P_2 \cdot \phi_2)$$

$$\beta = (K_S/D_S) \cdot \varepsilon$$

3. Experimental Results and Discussion

3.1 Effect of linear velocity on tubular fouling

In general, most furnaces for residual oil heating or cracking are operated with steam injection, so-called velocity steam, against tubular fouling.

In the experiments, fouling rates were observed by weighing coke accumulation in the tubes. **Figure 8** shows fouling rates at three levels of linear velocity. In the case of 0.5 m/s linear velocity very fast coking was observed, while fouling was indicated to be much suppressed in the case of a higher linear velocity of 4 m/s.

High linear velocity makes film thickness very thin. It is interpreted according to the theory that coking material was well diffused out of the boundary film and the content of coking material was kept sufficiently low, resulting in moderate tubular fouling in the case of high linear velocity.

Predicted results also fell within the observed data and showed clearly the effect of linear velocity on fouling rates.

3.2 Effect of conversion on tubular fouling

The experiments shown in **Fig. 8** were carried out with a moderate conversion of 35%, while the experiments shown in **Fig. 9** were conducted at higher conversion of up to 43%. It is shown that very rapid fouling took place even at the lowered cracking temperature. The pressure was adjusted to achieve the

Fig. 8. Effect of linear velocity on tubular fouling

Fig. 9. Effect of residue conversion on tubular fouling

same phase equilibrium in the tubular reactor as that of previous experiments to avoid inclusion of its effects in the experiments.

When conversion increases, a toluene-insoluble component is formed in the oil. That component was rather hard to dissolve stably in the bulk flow in the cracking condition, and the compatibility became worse with increased conversion. It is assumed that amounts of coke precursor were produced in the bulk flow and that they accelerated fouling in the experiments. The calculated result also supports the theory as it matches the experimental results.

3.3 Effect of temperature on tubular fouling

Temperature affects tubular fouling, as is commonly experienced. But the mechanism is more complex than usually thought. As found in the examination of the fouling equation, all the variables involved in the phenomena are functions of temperature.

The terms in the fouling equation regarding mass transfer rate such as film thickness and diffusion coefficient are favorable at higher temperature against fouling. And a higher temperature results in increasing vaporization of lighter components in cracked oil, which have a lower value of solubility parameter against coke precursor with a large value of solubility parameter. It improves the compatibility of cracked oil. However, the reaction to convert coke precursor

to coking material is accelerated more than others. A greater amount of coking material was formed in the boundary film and the tubular reactor was rapidly fouled at higher temperatures as shown in Fig. 10.

The experiments shown in Fig. 10 were carried out at the same conversion by adjusting space time. In actual operation in commercial furnaces the conversion will increase further when the temperature is raised, and more severe fouling is anticipated than that observed in these experiments.

3.4 Effect of solvent addition on tubular fouling

According to fouling theory, the addition of aromatic solvent to the feedstock was expected to improve the compatibility of cracked oil and suppress coking in the tubular reactor. Figure 11 shows a lower fouling rate in experiments with FCC heavy cracked oil (CSO) employed as a solvent. Since the solvent was very aromatic ($C/H=1.1$) and a heavy distillate (bp 420–538°C), it should have remained in the liquid phase and the solubility parameter of the liquid phase should have increased according to the rate of addition of solvent, reaching a value closer to that of polycondensed components.

Predicted results shown in the figure did not quite fit the experimental results, but the trends were well represented by the model calculations.

4. Fouling Analysis of Commercial Furnace

A fouling model was developed on the basis of the data from the laboratory unit. Calculations on the operation data of large-scale furnaces have indicated that the same scale-up factor as that of the model worked sufficiently for furnaces with very different conditions, as shown below. The feedstocks were mixture of vacuum residue from various crudes, mainly from the Middle East.

Type	Visbreaker	Eureka Furnace	ET-II Pilot Furnace
feed rate, tons/h	30–70	33 × 2	0.3
outlet pressure, kPa	1000–3000	490	380
outlet temperature, °C	430–470	490	480–490

Figure 12 shows analytical results of a commercial Eureka furnace. No direct measurements of coke thickness were available, but the increase of skin temperature and Δp against operation time were well predicted by the simulation model.

In the ET-II process a very high furnace conversion is aimed at.¹⁰ From the conventional concept of furnace design it may seem to be beyond practical scope, but studies of furnace design with the tubular fouling simulator indicated the realization of a new

Fig. 10. Effect of temperature on tubular fouling

Fig. 11. Effect of solvent addition on tubular fouling

Fig. 12. Simulation of tubular fouling in a commercial furnace

type of furnace.

Conclusion

The fouling mechanism in a tubular reactor for thermal cracking furnaces for residual oil was in-

vestigated, and a simulation model was proposed.

The tubular fouling data required for the model development were obtained in a new type of experimental unit in which residual oil was cracked thermally under a reciprocated high linear velocity of fluid.

The model exactly predicts the effects of major operation conditions of cracking furnaces on tubular fouling, and the performance was successfully verified by commercial operation data.

Acknowledgement

This research was conducted in the development program of the ET-II process and a part was financially supported by the governmental research organization RAROP (Research Association for Residual Oil Processing).

Nomenclature

A	= constant	
B	= constant	
P_1	= constant	
P_2	= constant	
C_i	= concentration	[kg/kg]
C/H	= carbon to hydrogen atomic ratio	[kgmol/kgmol]
D_s	= diffusion coefficient	[m ² /h]
f	= friction factor	[—]
k_{ij}	= reaction rate constant	[1/h]
K_s	= reaction rate constant	[m/h]
R, r	= tube radius	[m]
Re	= Reynolds number	[—]
u	= mass flux	[kg/m ² h]

t	= operation time	[h]
x	= coking rate	[kg/m ² h]
z	= tube length	[m]
δ	= solubility parameter	[(cal/cm ³) ^{1/2}]
ϵ	= film thickness	[m]
ρ	= density	[kg/m ³]
ϕ	= compatibility parameter	[—]

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