

A LUMPING MODEL FOR KINETICS OF RESIDUUM HYDROCRACKING

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ABSTRACT

The Hydrocracking reaction kinetics of Gudao Vacuum Residuum was investigated in a 100 ml autoclave with crushed ICR-130H Catalyst in a temperature range of 390-420°C. A lumping model with five parameters for the prediction of the product distribution curve for residuum hydrocracking was proposed as modification of the narrow-boiling point lumping model developed originally for distillate hydrocracking by Stangeland. A major advantage to this kinetic model is that its establishment and application don't need the complete distillation data of residua and products. The results predicted by this model agree satisfactorily with the experimental observation.

INTRODUCTION

The hydrocracking of residuum is a very complex reaction system in which thousands of organic species participate in a highly coupled mode. For this reaction system, it is not possible to establish kinetic equation for every reaction species by the conventional method used in reaction kinetics studies. Such a complex reaction system must be simplified so that the kinetics characteristics of residuum hydrocracking could be elucidated with mathematical equation, that is to say, the lumping method would be used. Lumping method for reaction kinetics is to build a lumping kinetic model in which the innumerable chemical compounds in reaction system is classified as a number of lumps by means of the kinetic characteristics of molecule reaction. The strategy of modeling a given reaction system usually varies with the specific goal to be attained. For example, a large number of chemical compound could be lumped by the total content of a component or a kind of component, by the boiling point range (compounds having similar boiling point grouped into a lump), by the chemical structure (compound having similar chemical structure as a lump), or sometimes by the combination of boiling point range and the chemical structure similarity.

Considerable effort has been focused worldwide on investigating the hydrocracking kinetics of distillates^[1] and a better narrow-boiling point lumping model has been proposed by Stangeland (1974)^[2] which can be used to predict the product distribution for distillate hydrocracking. There are a few studies on the kinetic model of residuum hydrocracking, and most of them were product lumping models which is not flexible enough to cope with various operation conditions and product scheme, although some investigators have tried to apply such model to commercial operation. Once the product scheme is subject to change, the parameters of product lumping model should be recalculated so as to approach the new product scheme.

Most of studies on the narrow-boiling point lumping model are based on the Stangeland model developed for distillate hydrocracking which requires the complete distillation data of feed and product and characterizes each lump by its final boiling point. These models have not been applied successfully to residuum hydrocracking for lack of the complete distillation curve of heavy oil feed and product. The prediction results is greatly different from the experimental observation in high boiling point range, even if these model are applied to heavier distillate hydrocracking^[3].

In the present study, based on the flexibility of the rate distribution and production distribution functions in the Stangeland narrow-boiling point lumping model, a lumping kinetic model suitable for residuum hydrocracking was proposed by combination of the correlation results on SFEF (Super Fluid Extraction Fractionation) fraction hydrocracking ^[1].

EXPERIMENTAL

The Gudao Vacuum residuum was hydrocracked in a 100mL autoclave with crushed ICR-130H Catalyst of 0.35mm average diameter at the initial hydrogen pressure 8.5 MPa, with agitation speed at 850rpm and in the temperature range of 390-420°C. After hydrocracking, gas, liquid and coke were separated and analyzed. The yield of gas, liquid and coke were determined and the simulated distillation data of feed and liquid product were obtained.

KINETIC MODEL

The kinetic model is based on the concept of pseudo-components (narrow fractions) and is similar to one proposed by Stangeland (1974). Assumptions in the present model are as follows:

- (1) The feed and products are represented by a series of continuous mixture which are pseudo-components of boiling range of 28°C and could be characterized by its final boiling point. The lightest pseudo-component is gas lump of boiling point below 10°C. The residual part of boiling point above 537.8°C. was treated as a lump, the heaviest pseudo-component, and characterized by a pseudo-boiling point (TBP_i).
- (2) Each pseudo-component is assumed to undergo a first order irreversible reaction. Polymerization reaction is neglected and no coking reaction is supposed.
- (3) The rate constant of hydrocracking of any lump is assumed to be relative to the heaviest lump in the model.
- (4) A lump can be hydrocracked into any lighter lump, but no conversion occurs among the lightest four lumps.

The reaction kinetic model of residuum hydrocracking is given by the following differential equations:

$$\frac{dF_i}{dt} = -k_i F_i + \sum_{j=i+1}^n k_j p_{ij} F_j \quad i=1,2, \dots, n$$

where k_i is the constant of lump i hydrocracking (hr^{-1}), t is reaction time (hr), and p_{ij} is the fraction of the cracked products from a heavier component, j , that become a lighter component i .

The calculation methods of k_i and p_{ij} have a great influence on the validity of the model. It is too difficult to derive a mathematical model if the number of model parameter is too great. But if the model parameters are not sufficient, the model would be lack of flexibility in application. Equations for calculating k_i was selected as follows:

$$k_i = k_0 \exp\left(-\frac{E}{RT_i}\right) \cdot \left[T_i + A(T_i^3 - T_i)\right] \quad T_i = \frac{TBP_i}{TBP_f}$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), T_i is the temperature (K), T_i is the temperature parameter of lump i , TBP_i is the final boiling point of lump i (°F) and TBP_f is the pseudo-boiling point of the heaviest component (°F). k_0 is frequency factor (hr^{-1}) and E represents the apparent activation energy. Li (1994) proved that the relative deviation of

$k_0 \exp\left(-\frac{E}{RT_r}\right)$ is not greater than 3% when k_0 and E vary in a reasonable range. So the apparent activation energy was set to a constant value ($E=108\text{KJ/mol}$)^[4].

Because there is a strong decreases in cracking rate as the boiling point of hydrocarbon is less than 250°F and the heaviest lumping in residuum hydrocracking has a dominant amount, the rate constant k_i was modified in terms of the following relations:

$$k_i = \begin{cases} 0.0 & TBP_i \leq 250 \\ 0.33k_i & TBP_i = 300 \\ 0.78k_i & TBP_i = 350 \\ 3.0k_i & TBP_i = TBP_j \end{cases}$$

and the product distribution function was represented by the equations as follows:

$$p_{ij} = \begin{cases} 0.0 & i \leq j \\ C \cdot \exp[-0.00693 \cdot (TBP_j - 250)] & i = n, j \leq i - 1 \\ P(Y_{ij}) - P(Y_{i+1,j}) & i < n, j \leq i - 1 \end{cases} \quad P(Y_{ij}) = [Y_{ij}^2 + B(Y_{ij}^3 - Y_{ij}^2)](1 - p_{ij})$$

$$Y_{ij} = \frac{TBP_i - 50}{TBP_j - 100}$$

So, kinetic parameters (k_i and p_{ij}) in residuum hydrocracking reaction can be represented by five model parameters (k_0, A, B, C, TBP_p). The distinction of this model and Stangeland model lies in:

- (1) Suitable for the cases lacking complete TBP distillation data of feed and product.
- (2) The pseudo-boiling point (TBP_p) is proposed to characterize the heaviest lump and the rate constant distribution function is modified.
- (3) Any lump may be hydrocracked into any lighter lump. this is especially important when the heaviest lump accounts for a dominant amount.
- (4) The pseudo-boiling point, TBP_p , was set by the correlation of SFEF fraction hydrocracking.

Estimation of model parameters is done by algorithm according to Herbest (1968)^[5]. The objective function is defined as the sum of the squares of the differences between the observed and calculated composition of the pseudo-component.

DISCUSSION

Through the estimation of model parameters, TBP_p at different reaction temperature were found approximately the same value, 1100°F . It could be thought that the properties of feed at the zero reaction time are similar no matter what reaction temperature was set, although the cracking reaction may occur already to a certain extent. Thus, TBP_p was fixed invariably to be equal to 1100°F , the deviation due to this decision can be compensated by adjusting other parameters. The relations of other model parameters and reaction temperature are given as follows,

$$\left. \begin{aligned} A &= 11881.8 - 88.0901\text{Tr} + 0.217577\text{Tr}^2 - 0.000179023\text{Tr}^3 \\ B &= 2329.12 - 17.6345\text{Tr} + 0.0445643\text{Tr}^2 - 3.75908\text{E} - 005\text{Tr}^3 \\ C &= 28180.1 - 210.262\text{Tr} + 0.522687\text{Tr}^2 - 0.000432817\text{Tr} \\ k_0 &= 11960.5 - 88.8419\text{Tr} + 0.219754\text{Tr}^2 - 0.000180983\text{Tr}^3 \end{aligned} \right\}$$

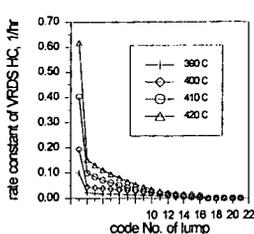


Fig. 1 Rate constant of each lump hydrocracking

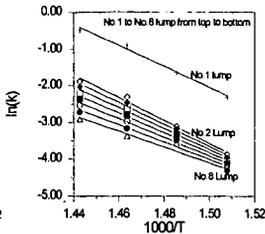


Fig 2 Rate constant of lumps v.s. temperature

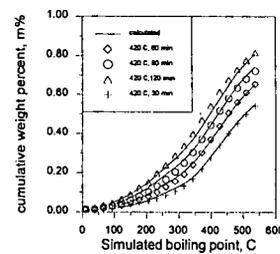
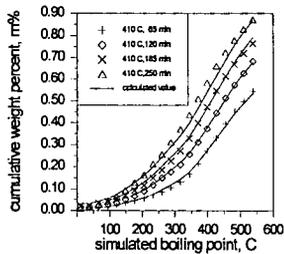
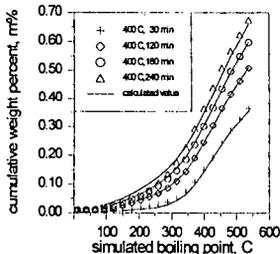
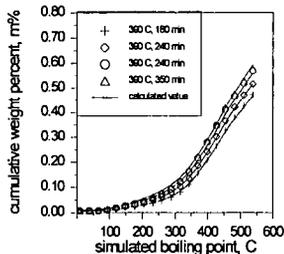


Fig. 3 Comparison of calculated and observation distillation curves

The rate constants of each lump hydrocracking were illustrated in Figure 1. The rate constant of the heaviest lump is far larger than those of any other lumps. At the same temperature, hydrocracking rate decreases gradually with the lowering of boiling point of lump component. The rate constant of the heaviest pseudo-component is 3.6-4.1 times as large as that of the next lump and 3-4 orders of magnitude larger than that of the lightest pseudo-component which is supposed to have been undergone hydrocracking. The methods chosen for calculating the cracking rate and product distribution of 1 to 8 lumps pave the way to the success of the model.

The cracking rate constants of the lump with higher boiling point are presented in Arrhenius plots in Figure 2. For each lump a straight line was obtained, especially for the heaviest four lumps. This suggests that the present model represents adequately the kinetic characteristics of GDVR hydrocracking.

The observed and calculated product yields at different reaction conditions are summarized in Table 1. The relative deviation between observed and predicted yields of the distillate products are not greater than 1.5% which is just the same as the permitted error of simulated distillation except for reaction condition at 410°C and 120 min.^[6] As shown in figure 3, the predicted yields based upon those model parameters mentioned above are represented as solid lines and the discrete observed data as points of different form. In general, the agreement is quite good and

probably closed to experimental error, which shows that it is feasible to characterize residuum-hydrocracking reaction by this narrow-boiling point lumping model.

CONCLUSION

A lumping model suitable for residuum hydrocracking was proposed by modifying the Stangeland model, and the agreement of the calculated yields with the observed ones is quite good. But there is much work to be done in order to check the suitability of this model for different hydrocracking feedstocks and various reaction conditions.

Table 1 The observed and calculated distillate product yield at different reaction conditions (m%)

Temperature, Time	390°C, 180min			390°C, 240min			390°C, 300min		
	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..
gas	0.73	0.43	0.30	0.71	0.39	0.12	0.82	0.76	0.06
38—204°C	2.34	2.64	-0.30	3.11	3.41	-0.30	3.73	4.13	-0.40
204—343°C	8.20	8.25	-0.05	9.85	9.69	-0.16	11.62	11.02	0.60
343—537°C	36.08	35.53	0.55	37.93	37.95	-0.02	40.74	40.08	0.66
>537°C	52.65	53.14	-0.49	48.40	48.36	0.04	43.09	44.0	-0.91
Temperature, Time	390°C, 350min			400°C, 30min			400°C, 120min		
	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..
gas	0.71	0.90	-0.19	0.70	0.95	-0.25	0.91	0.66	0.25
38—204°C	4.04	4.71	-0.67	1.06	1.05	0.01	3.43	3.81	-0.38
204—343°C	12.11	12.05	0.06	5.49	5.05	0.34	9.91	9.79	0.12
343—537°C	40.90	41.66	-0.76	29.17	28.68	0.49	36.46	36.83	-0.37
>537°C	42.23	40.68	1.55	63.58	64.36	-0.78	49.29	48.91	0.38
Temperature, Time	400°C, 120min			400°C, 240min			410°C, 65min		
	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..
gas	1.02	1.08	-0.06	1.12	1.46	-0.34	0.91	0.73	0.18
38—204°C	4.92	5.50	-0.58	5.48	6.76	-1.28	4.61	5.03	-0.42
204—343°C	12.52	12.60	-0.08	16.14	14.65	1.49	11.18	11.89	-0.71
343—537°C	41.25	40.70	0.55	44.76	43.21	1.55	37.66	35.85	1.84
>537°C	40.29	40.12	0.17	32.30	33.92	-1.42	45.64	46.53	-0.89
Temperature, Time	410°C, 120min			410°C, 185min			410°C, 255min		
	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..
gas	1.22	1.35	-0.13	1.64	2.08	-0.44	2.09	2.86	-0.77
38—204°C	5.70	8.14	-2.44	9.92	10.91	-0.99	14.21	13.17	1.04
204—343°C	14.65	16.68	-2.03	21.21	20.76	0.45	27.31	25.87	1.44
343—537°C	43.57	41.41	2.16	44.56	45.48	-0.92	43.48	45.12	-1.64
>537°C	34.86	32.15	2.71	22.66	20.77	1.89	12.91	12.97	-0.06
Temperature, Time	420°C, 35min			420°C, 60min			420°C, 120min		
	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..	Obs.	Calcd.	Diff..
gas	0.96	0.34	0.42	1.27	0.93	0.34	1.90	1.90	0.00
38—204°C	4.45	5.35	-0.90	6.55	7.19	-0.64	13.42	13.21	0.21
204—343°C	11.59	11.96	-0.37	16.42	16.72	-0.30	24.62	22.99	1.63
343—537°C	37.13	37.38	-0.25	41.17	40.54	0.30	41.81	43.23	-1.42
>537°C	45.87	44.74	1.10	34.59	34.61	-0.02	18.25	18.67	-0.42

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