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7-lump kinetic model for residual oil catalytic cracking*

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Abstract: In this paper a novel 7-lump kinetic model is proposed to describe residual oil catalytic cracking, in which coke is lumped separately for accurate prediction. The reactor block is modeled as a combination of an ideal pipe flow reactor (PFR) and a continuously stirred tank reactor (CSTR). Unit factors are designed to correct the deviation between model predictions and practical plant data and tuned by modified Levenberg-Marquardt algorithm. The parameters estimated are reliable and good agreement between the model predictions and plant observations is observed. The model helps us get good insight into the performance of an industrial riser reactor that would be useful for optimization of residual oil catalytic cracking.

Key words: Residua catalytic cracking (RCC), 7-lump kinetic model, Unit factor
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INTRODUCTION

Residua catalytic cracking (RCC) is a process in which crude oil fractions are cracked into more valuable lighter products in a riser reactor with fluidized catalyst. The complexity of charge stocks make it extremely infeasible to characterize and describe at a molecular level, so attempts have been made to lump large numbers of chemical compounds into a kinetic species to describe the complex reactions in the process (Wei and Kuo, 1969; Kuo and Wei, 1969).

Some early works on kinetics and gas oil conversion were published by Voorhies (1945) and Blanding (1953), then many notable kinetic models were developed and the parameter estimation strategies were presented for gas oil catalytic cracking in past decades (Weekman, 1968; 1969; Weekman and Nace, 1970; Jacob and Gross, 1976; Lee *et al*., 1989; Ancheyta-Juárez *et al*., 1997; 1999; Ng *et al*., 2002; Dupain *et al*., 2003; Corma *et al*., 2005). With the present trends towards the use of heavy crude oils coupled with increasing demand for light products, considerable researches were currently underway on the development of kinetic models for residual oil catalytic cracking (Ren, 1992; Takatsuka and Sato, 1987; Den *et al*., 1994; Mu *et al*., 2005). Most models were studied with a 1D hydrodynamic model and pseudo-homogeneous kinetics, while Theologos *et al*.(1999) and Nayak *et al*.(2005) incorporated heat transfer into the model. Heavy products were lumped together in some models (Weekmam, 1968; Lee *et al*., 1989; Corella and Frances, 1991), while in others they were separated into many lumps by chemical type (Jacob and Gross, 1976; Mao *et al*., 1985; Wang *et al*., 1988; Weng *et al*., 1995a; Den *et al*., 1994). However, most developed kinetic models involved gaseous products as a lump and in some cases the gases were also lumped together with the coke. At the same time, a splitting of the lump (gas+coke) into three other lumps was proposed in a few models (Oliveira and Biscaia, 1989; Ancheyta-Juárez *et al*., 1999; Abul-Hamayel, 2003). While John and Wojciechowsky (1975) proposed a kinetic model for the

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gas oil catalytic cracking in which the gas compositions was considered in detail. And recently a model for catalytically cracked gasoline was studied on the secondary reactions (Wang *et al.*, 2005).

The coke formation cannot be predicted independently except in few models (Takatsuka and Sato, 1987; Lee *et al.*, 1989; Wang *et al.*, 2005). However, an accurate prediction of coke for the process is important for conducting heat integration studies and for designing and simulating air blowers and the RCC reactor as well as regenerator. And its combustion provides the necessary heat for feedstock vaporization and for the endothermic cracking reactions. As a result, the prediction of catalytic coke formation is an indispensable part of a simulation model for an industrial riser-reactor for catalytic cracking (Quintana-Solórzano *et al.*, 2005). Recently kinetics was developed accounting for coke formation leading to catalyst deactivation (Froment, 2001; Quintana-Solórzano *et al.*, 2005). In the present work we proposed a 7-lump kinetic model for commercial unit in which coke, dry gas and LPG were lumped separately.

GENERAL KINETIC SCHEME

Process description of reactor block

A schematic of a typical RCC unit is shown in Fig.1, where the preheated feedstock is fed into the bottom of the riser, where it becomes tiny oil droplets and contacts hot reactivated catalyst which provides the sensible heat. The reactions take place immediately in the riser and gas volume increases drastically. The gas phase containing reactant and product, and carrying catalyst particles flows upward to the top where the reactions are completed. The product gas and catalyst are then fed to the cyclone and separated. And at the same time, coke deposition takes place, blocking the internal and external surface and resulting in a substantial reduction in the catalyst's activity. The spent catalyst is fed to the regenerator with enriched air for reactivation and ready for another cracking cycle. The other oil fractions are passed to fractionator for physical separation. The catalyst is made up regularly due to the losses by friction and attrition of catalyst particles.

Kinetic scheme

Generally speaking, detailed models are theoretically sound. But the more lumps a model includes, intrinsically more kinetic parameters need to be estimated. So it is hard for commercial use because of complex parameters estimation and limited feedstock analysis in the factory.

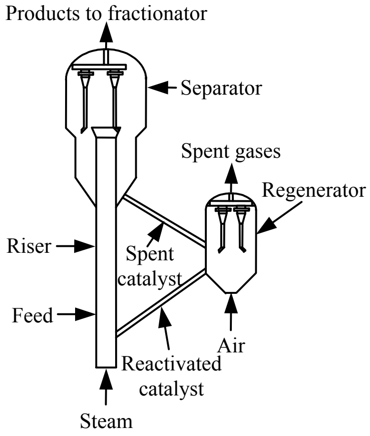

Fig.1 Schematic diagram of a typical RCC unit

To maintain a good balance between kinetics and applicability of the model, we proposed a model with seven lumps for predicting the behavior of the commercial RCC units. Depending on the type of crude oils and its pretreatment, the feedstock is divided into VR (vacuum residue, >500 °C) and VGO (vacuum gas oil, 350~500 °C). And the cracking products are divided into heavy products including CSO (cycled slurry oil, >500 °C) and HFO (heavy fuel oil, 350~500 °C) and light products including LFO (light fuel oil, 200~350 °C), G (gasoline, C_5~200 °C) according to their distillation ranges.

With the introduction of residual oils to RCC process, more amounts of coke and dry gas is formed. Heat integration considerations need an accurate estimation of coke yield and the accurate prediction of dry gas is very important for designing and simulating the gas compressor and air blower. The gases+coke lump in former models is separated into gas1 (liquified petroleum gas (LPG), C_3~C_4), gas2 (dry gas, C_2 and lighter) and C (coke) in the present model.

Two heavy products are treated as the unreacted products and combined with VR and VGO respectively as RFO (residual fuel oil) and HFO in the kinetic scheme. After investigations of hydrocarbons catalytic cracking, some authors observed that the probability of the cracking reaction from gasoline to coke (Oliveira and Biscaia, 1989) and gases to coke

(Pitault *et al.*, 1995) can be neglected since the kinetic constants for these reactions are many orders of magnitude smaller than that for the others, which simplifies the kinetic parameters determination. So the reaction scheme for residua catalytic cracking is put forward and shown in Fig.2.

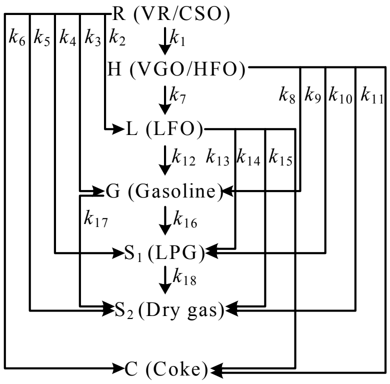

Fig.2 7-lump reaction scheme for residual oil catalytic cracking

The characteristics of the proposed model can be described as follows:

(1) According to the "principle of invariant response", lumps are formed by their boiling ranges having "similar" behavior. The lumping strategy was verified in other models (Weekman, 1968; Jacob and Gross, 1976; Takatsuka and Sato, 1987);

(2) Three main products (LPG, dry gas and coke) can be predicted independently from other lumps with the developed model, that is good for compressor and air blower design and simulation and heat considerations;

(3) The model lumps separated are fit for domestic limit charge stock analysis in the factory and lumping LPG and dry gas separately is to match commercial application;

(4) The limitation of the model is that lumps proposed are not separated by chemical type with the parameters depending on feedstock and catalyst properties.

RESIDUAL OIL CATALYTIC CRACKING KINETICS

Kinetic expression

Heavy oil was considered as a second order reaction and light products as first order in the reported models (Weekman, 1968; Lee *et al.*, 1989; Jacob and Gross, 1976). But a model proposed for residual oil catalytic cracking (Mu *et al.*, 2005) assumed all kind of reactions as first order. An irreversible peseudo-first order reaction was accepted for all reactions in the present work. The reaction rate of a peseudo-species j is assumed to be a function of the molar concentration of species $j(\rho a_j)$, the mass density of catalyst relative to the gas volume (ρ_c/ε) and reaction constant (k'_j), then a kinetic expression of species $j(r_j)$ could be written as

$$r_j = -k'_j \rho_c (\rho a_j)/\varepsilon, \tag{1}$$

where ρ_c is the catalyst density (g/cm^3), ε is void fraction, ρ is gas mixture density (g/cm^3) and a_j is concentration of lump j (moles j/g gas).

As mentioned in (Weekman, 1968; Jacob and Gross, 1976), k'_j decayed with time. Considerable researches have been done on the effects of aromatics adsorption, coke deposit and basic nitrogen poisoning on the catalyst activity that are assumed to be nonselective for all products cracking in the process. Hence the reaction constant can be expressed as

$$k'_j = k_j f(C_{\mathrm{Arh}}) \phi(t_c) f(N), \tag{2}$$

where k_j is an invariant rate constant, $\phi(t_c)$ is the catalyst decay as a function of catalyst residence time, $f(N)$ is the basic nitrogen adsorption function and $f(C_{\mathrm{Arh}})$ a heavy, inert aromatics adsorption function described by

$$f(C_{\mathrm{Arh}}) = 1/(1 + K_h C_{\mathrm{Arh}}), \tag{3}$$

where C_{Arh} represents wt.% of aromatics in residual oil, and K_h the heavy aromatic ring adsorption coefficient, (wt.% C_{Arh})$^{-1}$, K_h=0.128 (Mu *et al.*, 2005).

Hyperbolic function based on time-on-stream (Jacob *et al.*, 1976) and exponential function dependent on time-on-stream (Lee *et al.*, 1989) or coke content (van Landeghem *et al.*, 1996) were studied in the reported models. And a new function concerning feed properties and operating conditions was presented for the heavy oil catalytic pyrolysis process (Meng *et al.*, 2006). In the present work catalyst deactivation was accounted for by a hyperbolic function $\phi(t_\mathrm{c})$ as

$$\phi(t_\mathrm{c}) = 1/(1+\beta t_\mathrm{c}^{\gamma}), \tag{4}$$

where t_c represents time-on-stream, and catalyst deactivation constants β=162.15, γ=0.76 reported by Jacob and Gross (1976).

$f(N)$ is a nitrogen poisoning function as follows

$$f(N) = \frac{1}{1+K_\mathrm{n}N}, \tag{5}$$

where N is grams of basic nitrogen to the catalyst; K_n denotes basic nitrogen poisoning adsorption coefficient, (g basic N/g catalyst)$^{-1}$. With regard to high catalyst to oil ratio, the nitrogen poisoning deactivation can be neglected because of its insignificance.

With the ideal gas assumption

$$\rho = P\overline{MW}/RT, \tag{6}$$

where P is the absolute pressure, R is the gas constant (8.314 J/(mol·K)), T is temperature (K) and $\overline{MW}$ is average molecular weight of all lumps, changing with distance from inlet of the reactor along the riser. Note that

$$\overline{MW} = 1\Big/\sum a_j\,. \tag{7}$$

So the reaction rate in matrix notation can be expressed by

$$\boldsymbol{R} = f(A_\mathrm{rh})\phi(t_\mathrm{c})f(N)\frac{\rho_\mathrm{c}}{\varepsilon}\frac{P}{RT}\frac{1}{\sum a_j}\boldsymbol{Ka}, \tag{8}$$

where $\boldsymbol{R} = \left[\frac{\mathrm{d}a_1}{\mathrm{d}t}\ \frac{\mathrm{d}a_2}{\mathrm{d}t}\ \frac{\mathrm{d}a_3}{\mathrm{d}t}\ \frac{\mathrm{d}a_4}{\mathrm{d}t}\ \frac{\mathrm{d}a_5}{\mathrm{d}t}\ \frac{\mathrm{d}a_6}{\mathrm{d}t}\ \frac{\mathrm{d}a_7}{\mathrm{d}t}\right]^\mathrm{T}$, denotes reaction rate vector consisting of j lumped species; $\boldsymbol{a}$=[a_1 a_2 a_3 a_4 a_5 a_6 a_7], represents composition vector consisting of j lumped species; $\boldsymbol{K}$ represents rate constant matrix, as shown as follows:

$$\boldsymbol{K} = \begin{bmatrix} -(k_1+k_2+k_3+k_4+k_5+k_6) & 0 & 0 & 0 & 0 & 0 & 0 \\ \nu_\mathrm{rh}k_1 & -(k_7+k_8+k_9+k_{10}+k_{11}) & 0 & 0 & 0 & 0 & 0 \\ \nu_\mathrm{rl}k_2 & \nu_\mathrm{hl}k_7 & -(k_{12}+k_{13}+k_{14}+k_{15}) & 0 & 0 & 0 & 0 \\ \nu_\mathrm{rg}k_3 & \nu_\mathrm{hg}k_8 & \nu_\mathrm{lg}k_{12} & -(k_{16}+k_{17}) & 0 & 0 & 0 \\ \nu_\mathrm{rs1}k_4 & \nu_\mathrm{hs1}k_9 & \nu_\mathrm{ls1}k_{13} & \nu_\mathrm{gs1}k_{16} & -k_{18} & 0 & 0 \\ \nu_\mathrm{rs2}k_5 & \nu_\mathrm{hs2}k_{10} & \nu_\mathrm{ls2}k_{14} & \nu_\mathrm{gs2}k_{17} & \nu_\mathrm{s1s2}k_{18} & 0 & 0 \\ \nu_\mathrm{rc}k_6 & \nu_\mathrm{hc}k_{11} & \nu_\mathrm{lc}k_{15} & 0 & 0 & 0 & 0 \end{bmatrix},$$

where ν_{ij} are stoichiometric coefficients calculated as average molecular weights of the lumps:

$\nu_\mathrm{rh}=MW_\mathrm{r}/MW_\mathrm{h}$, $\nu_\mathrm{ri}=MW_\mathrm{r}/MW_\mathrm{i}$, $\nu_\mathrm{rg}=MW_\mathrm{r}/MW_\mathrm{g}$, $\nu_\mathrm{rs1}=MW_\mathrm{r}/MW_\mathrm{s1}$, $\nu_\mathrm{rs2}=MW_\mathrm{r}/MW_\mathrm{s2}$, $\nu_\mathrm{rc}=MW_\mathrm{r}/MW_\mathrm{c}$, $\nu_\mathrm{hl}=MW_\mathrm{h}/MW_\mathrm{l}$, $\nu_\mathrm{hg}=MW_\mathrm{h}/MW_\mathrm{g}$, $\nu_\mathrm{hs1}=MW_\mathrm{h}/MW_\mathrm{s1}$, $\nu_\mathrm{hs2}=MW_\mathrm{h}/MW_\mathrm{s2}$, $\nu_\mathrm{hc}=MW_\mathrm{h}/MW_\mathrm{c}$, $\nu_\mathrm{lg}=MW_\mathrm{l}/MW_\mathrm{g}$, $\nu_\mathrm{ls1}=MW_\mathrm{l}/MW_\mathrm{s1}$, $\nu_\mathrm{ls2}=MW_\mathrm{l}/MW_\mathrm{s2}$, $\nu_\mathrm{lc}=MW_\mathrm{l}/MW_\mathrm{c}$, $\nu_\mathrm{gs1}=MW_\mathrm{g}/MW_\mathrm{s1}$, $\nu_\mathrm{gs2}=MW_\mathrm{g}/MW_\mathrm{s2}$, $\nu_\mathrm{s1s2}=MW_\mathrm{s1}/MW_\mathrm{s2}$.

Their values depend on the basic lumps used.

The average molecular weights of lumps in 7-lump model are given in Table 1.

Table 1 Average molecular weight of 7 lumps

Lumps	Average molecular weight
Residual lump	MW_r=950*
Heavy lump	MW_h=386*
Light lump	MW_l=229*
Gasoline lump	MW_g=117.8**
LPG lump	MW_s1=46.7**
Dry gas lump	MW_s2=18.4**
Coke lump	MW_c=400**

*Molecular weight from Ren *et al.*(1993); **Molecular weight from Peixoto and Medeiros (2001), two gas average molecular weights are almost the same as the data from commercial unit

Ideal plug-flow riser

Most of models reported were assumed to be an ideal plug-flow reactor (Jacob and Gross, 1976; Weng *et al.*, 1995a). Takatsuka and Sato (1987) modeled the reactor as a multistage CSTR because of backmixing presentation. The reactor block is considered as a combination of two different reactors by Sugungun and Kolesnikov (1998) and Mu *et al.*(2005) according to its hydrodynamic regime, the riser is a near ideal plug-flow displacement of the catalyst and reaction mixture, while the main vessel (separator) is an ideal mixing CSTR. In the paper the reactor block was also treated as two kinds as mentioned above.

The reaction mixture of oil fractions and catalyst in the riser section is close to an ideal pipe flow. Then the kinetic model is incorporated into an isothermal plug flow reactor model by the continuity equation, with interparticle diffusion and axial dispersion neglected; the equation can be given by

$$\frac{\partial(\rho a_j)}{\partial t}+G_v\frac{\partial(a_j)}{\partial x}=r_j, \tag{9}$$

where G_v is the superficial mass flow rate of gas mixture (g/(cm^2·h)).

As to static riser reactor, $\partial(\rho a_j)/\partial t=0$, and Eq.(10) can be derived from Eq.(9) as

$$G_v\frac{\mathrm{d}(a_j)}{\mathrm{d}x}=r_j, \tag{10}$$

where x is the length of riser (m).

Combining Eq.(8) and Eq.(10), we get

$$\frac{\mathrm{d}\boldsymbol{a}}{\mathrm{d}X}=\frac{1}{1+K_\mathrm{h}C_\mathrm{Arh}}\frac{1}{1+\beta t_\mathrm{c}^{\gamma}}\frac{P}{S_\mathrm{wh}RT}\frac{1}{\sum a_j}\boldsymbol{Ka}, \tag{11}$$

where $X=l/L$, represents dimensionless distance of the riser; $S_\mathrm{wh}=G_v\varepsilon/(\rho_\mathrm{c}L)$, represents true weight hourly space velocity.

Eq.(11) can be solved by the four fold Runge-Kutta method.

CSTR reactor

The mixture of products and catalyst from riser outlet to settler is considered well mixed. A CSTR is selected to describe the settler. Components continuity equations of an ideally mixed heterogeneous catalytic chemical process can be written as

$$a_j^0-a_j+r_j\tau=0, \tag{12}$$

while

$$\tau=\frac{l_1}{u}=\rho\frac{l_1}{L}\frac{1}{S_\mathrm{wh}}\frac{\varepsilon}{\rho_\mathrm{c}}, \tag{13}$$

where τ denotes products residence time in separator; l_1 total length of separator and L total length of riser.

Then Eq.(12) can be rearranged with Eq.(13) in matrix as

$$\begin{aligned}&\boldsymbol{a}^0-\boldsymbol{a}+\frac{l_1}{L}\frac{1}{1+K_\mathrm{h}C_\mathrm{Arh}}\frac{1}{1+\beta t_\mathrm{c}^{\gamma}}f(N)\frac{\rho_\mathrm{c}}{\varepsilon}\frac{1}{S_\mathrm{wh}}\\&\cdot\left(\frac{P}{RT}\frac{1}{\sum a_j}\right)^2\boldsymbol{Ka}=0,\end{aligned} \tag{14}$$

where $\boldsymbol{a}^0=[a_1^0\ \ a_2^0\ \ a_3^0\ \ a_4^0\ \ a_5^0\ \ a_6^0\ \ a_7^0]^\mathrm{T}$, represents components concentration at outlet of the riser, serving as input data for separator.

COMMERCIAL SIMULATION AND DISCUSSION

Kinetic parameters of the model need to be determined before the model's commercial use. The 11-lump kinetic model on residual oil catalytic cracking was studied using diesel-increasing catalyst MLC-500 in (Yi, 2002) and corresponding kinetic parameters of the catalyst were acquired by the experiments in the lab unit. So it is useful for our model establishing because the hybrid catalyst with majority of MLC-500 was used in the commercial unit. All reaction rate constants (k_j) obeying the Arrhenius law can be represented as

$$k_j=k_{0j}\exp(-E_j/RT). \tag{15}$$

We divided the activation energies into several groups as proposed by Jacob and Gross (1976):

(1) G lump formation reactions from HFO and LFO lumps;

(2) S_1, S_2 and C lumps formation reactions from HFO and LFO lumps;

(3) HFO and LFO lumps formation reactions from RFO lump and LFO and G lumps formation from HFO lump;

(4) S_1, S_2 and C lumps formation reactions from RFO lump;

(5) S_1, S_2 and C lumps formation reactions from G lump;

(6) S_2 lump formation reactions from S_1 lump.

As there are no group components separated in heavy oil, a strategy for activation energies is adapted as follows

$$E_j = \sum (w_i E_{0i}), \tag{16}$$

where E_j is activation energy; w_i mass fraction of group components in feed oil; E_{0i} activation energy from (Yi, 2002).

Hence the error introduced from activation energy accumulates to the corresponding frequency factor. The frequency factors were determined by minimizing the deviation between predictions and plant data. The estimated kinetic parameters were given in Table 2.

Table 2 Kinetic parameters of 7 lumps on hybrid catalyst at 500 °C

Reaction	Rate constant (k_j) (m^3/(kg cat·h))	Frequency factor (k_{0j}) (m^3/(kg cat·h))	Activation energy (E_j) (kJ/mol)
RFO→HFO	k_1: 14.9388	35520	50.727
RFO→LFO	k_2: 5.7829	13750	50.727
RFO→G	k_3: 11.6920	2780	50.727
RFO→S_1	k_4: 3.5921	42.68	16.150
RFO→S_2	k_5: 0.3592	4.268	16.150
RFO→C	k_6: 11.5558	137.3	16.150
HFO→LFO	k_7: 5.7829	13750	50.727
HFO→G	k_8: 0.9453	1130	46.240
HFO→S_1	k_9: 0.1355	1284	59.750
HFO→S_2	k_{10}: 0.0135	128.4	59.750
HFO→C	k_{11}: 0.3272	3101	59.750
LFO→G	k_{12}: 0.5742	686.4	46.240
LFO→S_1	k_{13}: 0.0086	81.22	59.750
LFO→S_2	k_{14}: 0.0009	8.122	59.750
LFO→C	k_{15}: 0.0596	564.6	59.750
G→S_1	k_{16}: 0.0003	43.66	78.490
G→S_2	k_{17}: 0.0001	21.83	78.490
S_1→S_2	k_{18}: 0.0033	31.74	59.750

Although many key factors greatly affecting oil fractions cracking have been considered in the established kinetic model, the real oil catalytic cracking performance is not totally described by the model with ideal assumptions. Fortunately the estimation of frequency factors with commercial data undergoes full considerations of uncertain factors. However the conditions operated in commercial RCCUS change a lot as time goes on. So the behaviors of products will be different. The traditional method to solve the problem is to set unit factors to adjust deviations between the predicted yields by model and the real yields from commercial process (Weng *et al.*, 1995b). Seven unit factors are proposed to regulate reaction constants (Yi, 2002) and they are:

(1) FU(1): adjusting all reaction constants k_1~k_{18};

(2) FU(2): adjusting HFO, LFO and G lumps formation reaction constants from RFO k_1, k_2, k_3 and LFO formation reaction constant from HFO k_7;

(3) FU(3): adjusting S_1, S_2 and C lumps formation reaction constants from RFO k_4, k_5, k_6;

(4) FU(4): adjusting G formation reaction constants from HFO and LFO k_8, k_{12};

(5) FU(5): adjusting S_1 and S_2 formation reaction constants from HFO and LFO k_9, k_{10} and k_{13}, k_{14};

(6) FU(6): adjusting C formation reaction constants from HFO and LFO k_{11}, k_{15};

(7) FU(7): adjusting S_1 and S_2 formation reaction constants from G k_{16}, $k_{17;}$

(8) FU(8): adjusting S_2 formation reaction constant form S_1 k_{18}.

All the unit factors were regressed by the modified Levenberg-Marquardt algorithm with two sets of plant data (No. 1 and No. 2). The operating conditions and balanced plant data of RCCUS are shown in Table 3, and the estimated unit factors are presented in Table 4. We made sure that they are at reasonable ranges from Table 4.

As all kinetic parameters had been obtained, we can simulate a commercial RCCUS with different feedstock under different operation conditions (No. 3, No. 4 and No. 5). The comparison between model prediction and plant observation is presented in Fig.3. And the deviation and relative error were introduced for elucidating the precision of the proposed model as shown in Table 5. The symbol '−' in the table means that plant observation is smaller than the prediction.

Table 3 Operating conditions and balanced plant data of RCCUS

		No. 1	No. 2	No. 3	No. 4	No. 5
Operating conditions	Reaction temperature (°C)	511.71	511.75	512.93	511.25	513.11
	Reaction pressure (kPa)	150.02	143.42	151.14	154.03	152.14
	Feed (*t*·*h*−1)	144.2	142.94	141.38	142.01	140.77
	Ratio of catalyst to feed	3.576	3.6442	3.8596	3.6777	3.8967
	Ratio of recycle oil to fresh feed	0	0	0	0.030315	0
Components in feed (%(w))	Wax oil	73.44	74.54	76.07	54.17	53.24
	Vacuum heavy oil	18.66	17.44	15.88	35.33	38.74
	Recycled gasoline	7.90	8.02	8.05	7.74	8.02
	Recycled heavy oil	0	0	0	2.76	0
	Total	100	100	100	100	100
Components in reactant (%(w))	RHFO	4.75	5.36	4.42	5.17	5.02
	LFO	27.91	27.75	28.41	25.29	27.13
	G	36.98	35.42	41.37	40.96	37.37
	S1	18.10	19.49	15.53	17.73	18.97
	S2	4.14	4.52	3.78	3.84	3.97
	C	8.13	7.47	6.50	7.02	7.55
	Total	100	100	100	100	100

%(w): mass fraction

Table 4 Unit factors obtained from RCCUS data

FU(1)	FU(2)	FU(3)	FU(4)	FU(5)	FU(6)	FU(7)	FU(8)
1.508	0.5239	0.2225	0.4015	1.676	2.267	0.9756	0.8245

Table 5 Deviation and relative error of model prediction and plant observation

Product	No. 3		No. 4		No. 5	
	Deviation (%)	Relative error (%)	Deviation (%)	Relative error (%)	Deviation (%)	Relative error (%)
RHFO	−2.01	−45.5	−0.80	−15.38	−1.08	−21.51
LFO	1.71	6.02	−1.25	−4.93	0.57	2.11
G	3.62	8.76	2.88	7.04	−0.70	−1.88
S_1	−2.03	−13.10	0.01	0.06	1.33	7.01
S_2	−0.73	−19.28	−0.71	−18.49	−0.56	−14.21
C	−0.56	−8.63	−0.14	−2.00	0.44	5.86

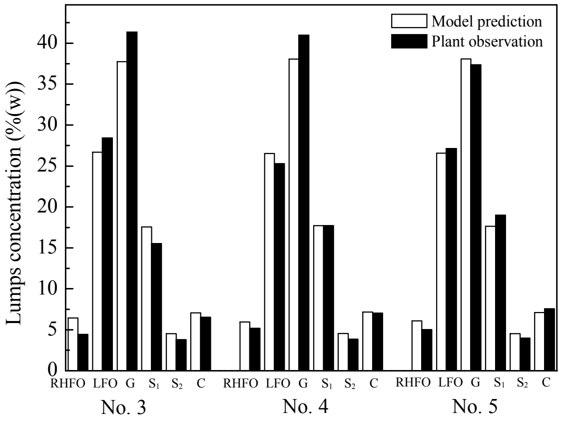

Fig.3 Comparison of model prediction and plant observation

We can draw a conclusion that there is good consistency between the predictions and observations from Fig.3, which proves that the kinetic parameters suggested and the unit factors estimated are reliable. As shown in Table 5, the proposed kinetic model gives accurate predictions of product yields with the maximal deviation of 3.62% with different feedstock under different operating conditions. Therefore we are sure of the credibility and extrapolability of the kinetic model. The light products (S_1+S_2+C) yield predicted is a little higher on the condition the feedstock is composed of more heavy fuel oil, which accords with the fact and illustrates the value of the model on the beam. And we conclude from the table that the relative error of lumps RHFO and S_2 are high because of their relatively low yields. But with respect to C lump, the prediction is more precise than those of RHFO and S_2 owning to its sole lump.

As reaction center of the products and heat carrier in the process, catalyst should be paid more attention to, especially the catalyst circulation between reactor and regenerator. Heat balance in the RCCUS associating all the operation parameters and the heat between reactor and regenerator should be kept in balance, or the operation will be out of control. A majority of heat required for feedstock vaporization and endothermic reactions in the RCC process comes from burning the deposited coke on the spent catalyst surface. Too much heat produced should be removed and too little for reactions should be enhanced under conditions of thermal balance. On the other hand, the capacity of air for coke burning will be quantitative because of veracious coke quantity, which exactly affects regeneration air-blowing system. And the more coke produced in the process, the more steam should be needed for spent catalyst hydrocarbon stripping. Hence precise coke formation prediction is crucial. The separated lump of coke in the model ensures precise prediction of coke. Pressure balance in the RCCUS is another key factor for stable operation of the unit and should also be kept for catalyst circulation. At the point of gas compression, the accurate estimation of lumps by the model gives us guidance to design gas compressor. All of abovementioned conditions demonstrate the significance of lump separation during the model establishment.

The simulation of all five sets of commercial data is illustrated in Fig.4. The yields can be seen to be steady from the figure although the feedstock and the operation conditions are dissimilar.

Component concentration profiles along the riser reactor can be easily described by the model. The typical profiles are shown in Fig.5. The performance of two regimes is distinctly notable, and it is observed that most of the oil cracking occurs in the vicinity of the feed injection zone from the figure, which means that oil fraction cracking is an instantaneous reaction. Moreover, further reactions are found in the separator, which convinces us the importance of combining the two types of reactor. Primary products and secondary products exist in the reactor. Though there are some uncertainties and adjustable parameters in the kinetic model, the overall framework and the developed model can be used to simulate industrial reactors as well as to get an insight into the performance of RCCUS, which helps us a lot during commercial operation.

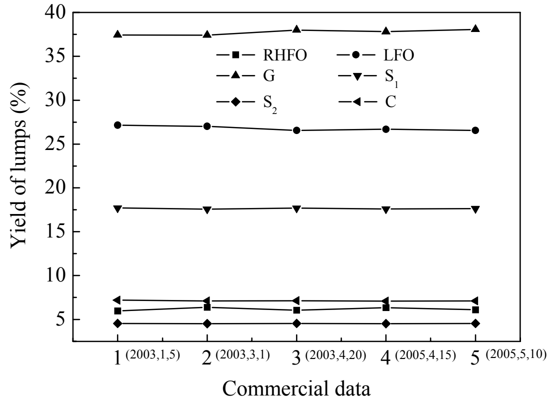

Fig.4 Lumps yield distribution with time

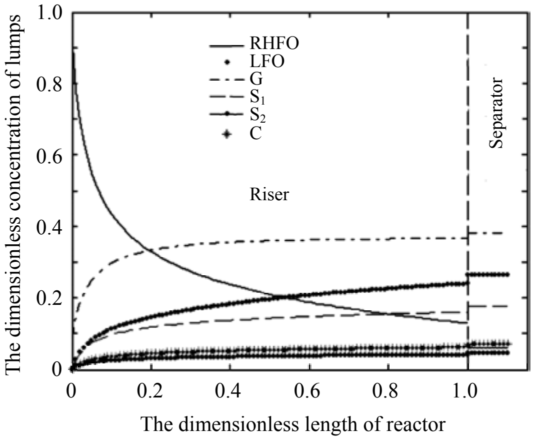

Fig.5 Component concentration profiles along the reactor

CONCLUSION

A novel 7-lump kinetic model for residual oil catalytic cracking including RFO, HFO, LFO, gasoline, LPG, dry gas and coke lumps is proposed. The activation energies are taken from the reported paper and the unit factors are estimated for each involved reaction with commercial data. The products yields predicted by the proposed model are consistent with the collected data from an industrial RCCUS.

The advantage of the model is the ability to predict LPG, dry gas and coke yields separately which satisfies the users' demand and is fit for commercial use. Most of all, it provides guidance for us to analyze whether the RCC units' capacity satisfies the process or not.

The proposed model is suitable for off-line process simulation as well as on-line soft sensor application, which is the basis of process optimization and advanced process control.

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