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Simulation, Sensitivity Analysis and Optimization of a Commercial Continuous Catalytic Naphtha Reformer

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Abstract: In this study, a 20-lumped kinetics model for naphtha catalytic reforming reactions is used to simulate an industrial Continuous Catalytic Reforming (CCR) process. Fair agreement between the calculated and operating data is obtained. The key process variables affecting the aromatics yield are analyzed in detail to guide the selections of operating conditions. Based on the kinetics model and the process variable analyses, process optimization is also studied and the optimization project is then tested in the actual industrial unit about one month. The testing results validate that the aromatics yield increases about 0.49 percent in weight averagely, which is close to the calculated value by process optimization. The optimization project obtained by mathematic computation is proved to be believable and can bring great profits of more than 5,000,000 yuan annually.

Key words: Catalytic reforming, kinetic model, computer simulation, sensitivity analysis, process optimization

INTRODUCTION

Catalytic naphtha reforming is a very important process for producing high octane gasoline and aromatics feedstock in petrochemical industry (Li *et al*., 2010). Hydrogen and lighter hydrocarbons are also obtained as byproducts. The process flow diagram of the reformer modeled in this work is shown in Fig. 1. At the core of this Continuous Catalytic Reforming (CCR) process, which aims to produce BTX (benzene, toluene, xylene), are 3 or 4 adiabatic reactors in series that conduct the solid catalyzed vapor-phase reforming reactions. For the major reactions in the reactors are endothermic, catalytic reformers are designed with multiple reactors and with heaters between the reactors to maintain reaction temperature at operable levels. The effluent from the last reactor enters the flash separator. The most flash vapor circulates to join the naphtha charge as recycle gas. Excess vapor and the separator liquid are then sent to the product separation system, from which hydrogen, Liquefied Petroleum Gas (LPG) and BTX products are obtained.

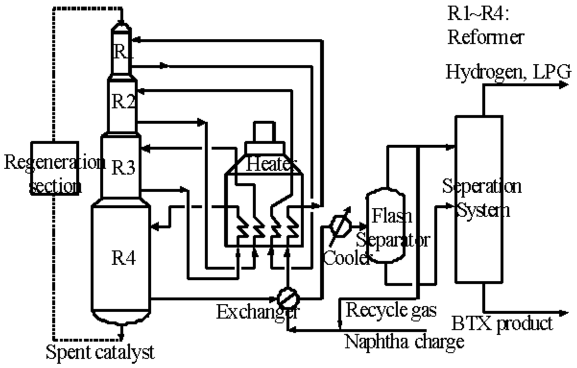

Fig. 1: A process flow diagram of CCR reforming

The naphtha used as catalytic reforming feedstock is very complex usually consisting of about three hundred hydrocarbons with the carbon number range from one to twelve and each of them undergoes various reactions. So, a detailed kinetics model considering all the components and reactions is more complex. By this reason, attempts have been made to model naphtha by considering groups of components (i.e., kinetics lumps) taking part in reforming reactions. Accordingly, various lumped kinetics models to represent catalytic reforming reactions have been reported in the literature, which have different levels of sophistication (Smith, 1959; Ramage *et al*., 1980; Vathi and Chaudhuri, 1997; Taskar and Riggs, 1997; Rahimpour *et al*., 2003; Rodriguez and Ancheyta, 2011; Weng *et al*., 1994; Xie *et al*., 1995; Zhou *et al*., 2004; Hou *et al*., 2007; Wang *et al*., 2012).

In a previous work, we reported a 20-lumped kinetics model for catalytic reforming (Hou *et al*., 2006). In this study, the 20-lumped kinetics model is applied to simulate the commercial continuous catalytic reformer as shown in Fig. 1. Subsequently, the sensitivity analyses of key process variables having great impact on aromatics yield

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are presented. Finally, The process optimization based on the model is also studied and the optimization result is validated in the industrial catalytic reformer.

20-LUMPED KINETICS MODEL

In the reported 20-lumped model, the reforming reaction network undergone by all the 20 lumps is shown in Fig. 2. In this reaction network, except for isomerization, all the main reactions, such as dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins to naphthenes, hydrocracking of paraffins and hydrodealkylation of aromatics, are included as listed in the first column of Table 1.

All the rate equations shown in the second column of Table 1 are nonlinear pseudomono-molecular in nature. Corresponding rate equations are presented below:

$$r_j = dY_j / dt = k_j \cdot Y_j, (\text{Irreversible}) \quad j = 1 \sim 9 \tag{1}$$

$$r_j = dY_j / dt = k_j (Y_j - Y_j / K_{epj}), (\text{Reversible}) \quad j = 10 \sim 31 \tag{2}$$

The reaction rate coefficients of Eq. 1~2 obeying the Arrhenius law can be written as:

$$k_j = k_{0j} \cdot \exp(-E_j / RT) \cdot P_h^{\theta_j} \cdot \varphi \quad 0 < \varphi \le 1, j = 1 \sim 31 \tag{3}$$

where, ϕ is the catalyst deactivation function, which varies between 0 and 1 and is used to multiply the rates of the main reforming reactions calculated without deactivation.

The reaction equilibrium constant K_{epj} in (1) is calculated by the following thermodynamic equation:

$$K_{epj} = \exp(-\Delta G_j / RT), j = 1 \sim 9 \tag{4}$$

Under normal reformer operating conditions, radial and axial dispersion effects were found to be negligible (Hou *et al*., 2006). For the radial flow reactors, the global material and enthalpy balance equations can be described as follows:

$$d\vec{Y} \big/ dR = 2\pi R \cdot H \big/ (LHSV \cdot V_c) \cdot K_r \cdot \vec{Y} \tag{5}$$

$$dT \big/ dR = 2\pi R \cdot H \big/ (LHSV \cdot V_c) \cdot \sum_{j=1}^{17} (r_j \cdot \Delta H_j) / (\vec{C}_p \cdot \vec{Y}) \tag{6}$$

Table 1: Reactions of the 20-lumped kinetics model

Reactions	This work
Dehydrogenation	$N_i \leftrightarrow A_i$, i = 6, 7, 9+$N_8 \leftrightarrow$PX+OX+MX $N_8 \leftrightarrow$EB
Dehydrocyclization	$P_i \leftrightarrow N_i$, i = 6, 7, 8, 9+
Hydrodealkylation	$A_7 \leftrightarrow A_6$ PX+OX+MX$\leftrightarrow A_7$ EB$\leftrightarrow A_7$
	$A_{9+} \leftrightarrow$PX+OX+MX, $A_{9+} \leftrightarrow$EB $A_9 \leftrightarrow A_7$
Hydrocracking	$P_5 \rightarrow P_I + P_{5-i}$ i = 1, 2, $P_6 \rightarrow P_I + P_{6-i}$ i = 1, 2, 3, $P_7 \rightarrow P_I + P_{7-i}$
	i = 1, 2, 3, $P_8 \rightarrow P_i + P_{8-i}$, i = 1, 2, 3, 4, $P_{9+} \rightarrow P_i + P_{9-1}$
	i = 1, 2, 3 ,4

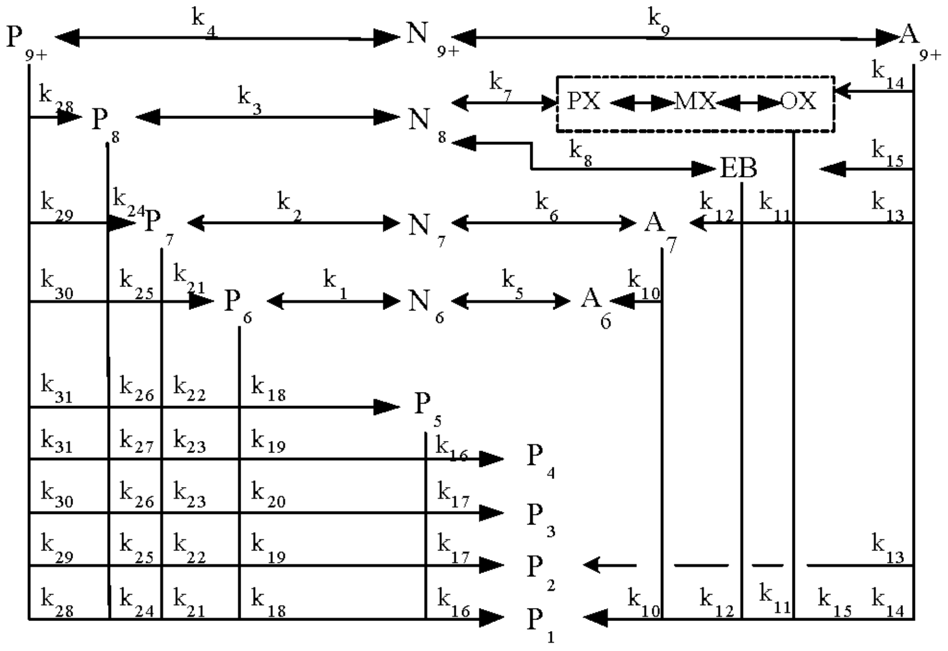

Fig. 2: Reaction scheme for naphtha reforming

where $\bar{Y}$ is the vector of molar flow rates including 20 lumps and H_2. Equation 5 and 6 are solved by a mixed numerical algorithm of fourth order Runge-Kutta and Gear. The thermochemical properties of each lump are computed by taking an arithmetic average of the properties of the corresponding pure chemical components constituting the lump.

The flash seperator is modeled as an isothermal flash operation. This invloved solving a set of materail-balance and vapor/liquid equilibrium equa- tions simutaneously. The formulation of these equations is fairly staightforword and is illustrated in standard texts (Chen and Gu, 1996). The sequential modular approach is implemented for this flow-sheet computation. An iterative solution is required for the recylce presented in the process.

PARAMETER ESTIMATION AND MODEL VALIDATION

The estimation of kinetic parameters for the rate constants k in (3) is a very important step to simulate this commercial CCR process. To decrease the difficulty of parameter estimation, we take activation energies (E), pressure exponents (θ) from the literature[11] and only estimate the 31 frequency factors (k_0) considering the estimation difference of parameters E, θ and un-modeling kinetics. The procedure of parameter estimation is solved by an unstrained optimization problem and the objective function is:

$$\min J(k_0) = \frac{1}{S}\sum_{k=1}^{S}\left(\sum_{j=1}^{m}(y_{k,j}^{cal} - y_{k,j})^2 + \sum_{i=1}^{4}(T_{k,i}^{cal} - T_{k,i})^2\right) \quad (7)$$

where, S, m are the number of samples and focused components, respectively.

The operating and assay data of the CCR process, in which the input and output values are firstly revised by material balance, are applied to estimate the 31 kinetics parameters k_0 by Marquardt optimization algorithm.

The operating conditions and simulation results are summarized in Table 2. It shows that, within broad operating conditions and for different naphtha feedstock, the reformate components in the exit of the last reactor, is predicted accurately by the 20-lumped model. The

Table 2: Prediction precision of the 20-lumped kinetics model

	No	1		2
Operation conditions	Feed (kg·h^{-1})	174544.3275		130190.1426
	Latent aromatics (wt%)	50.15		54.83
	LHSV (h^{-1})	1.03		0.77
	HC (mol moL^{-1})	3.41		5.47
	Reaction pressure (Mpa)	0.88		0.85
	WAIT (°C)	520		505
Components in the exit of the last reactor (wt%)	Prediction values	Actual values	Prediction values	Actual values
Hydrogen: H_2	7.97	8.28	10.38	11.07
Cracking products: P_1	2.38	2.43	2.64	2.80
P_2	4.74	4.76	5.22	5.32
P_3	8.66	8.40	9.42	9.41
P_4	9.04	8.74	9.55	9.18
P_5	5.37	5.75	4.59	5.08
In total	30.19	30.08	31.42	31.79
Reformate P_6	3.71	3.47	4.06	4.11
P_7	3.75	3.39	3.79	3.74
P_8	0.16	0.47	0.74	0.71
P_{9+}	0.00	0.00	0.00	0.00
In total	7.62	7.33	8.59	8.56
N_6	0.43	0.15	0.56	0.10
N_7	0.10	0.21	0.08	0.10
N_8	0.01	0.03	0.02	0.02
N_{9+}	0.00	0.00	0.00	0.00
In total	0.54	0.39	0.66	0.22
A_6	4.11	3.52	5.40	4.62
A_7	13.76	13.78	12.73	12.34
PX	3.53	3.50	2.97	3.02
MX	7.79	7.55	6.55	6.52
OX	4.02	4.40	3.39	3.77
EB	2.85	2.21	2.48	1.97
PX+MX+OX+EB	18.19	17.66	15.39	15.28
A_{9+}	17.62	18.96	15.43	16.12
In total	53.68	53.92	48.95	48.36
Liquid yield	79.34	78.58	81.59	80.10
Aromatics yield	66.73	67.03	67.59	66.78
Octane number of reformate (RON)^b	104.37	104.54	104.48	104.02

RON is calculated by regressive model of quadratic polynomial calculated values of several important operating points, such as liquid yield, aromatics yield and RON, are also close to the operating data.

PROCESS VARIABLE ANALYSIS

The kinetic model is very useful in the sensitivity analyses of process variables to guide selecting the optimal scopes of operating conditions, which is also important for process optimization. Here the above 20-lumped kinetics model is applied to study the effect of the four reactor inlet temperatures (T_1~T_4), reaction pressure and hydrogen-to-oil molar ratio (HC) on process performance such as aromatics yield, catalyst coking content, or energy cost.

In most studies, the four reactor inlet temperatures are supposed to be approximately equal and Weighted Average Inlet Temperature (WAIT) is used as an indicator of the reaction temperature. For this study the four inlet temperatures have been changed independently. This means that when one inlet temperature is altered, the other three tempera-tures are fixed at the plant conditions. The effect of variation in inlet temperature, from the plant operat- ing temperature, on the resulting aromatics yield has been plotted in Fig. 3. The four plant temperatures are 522, 521, 518 and 524°C. It is found that the aromatics yield slowly decreases when the first or second reactor inlet temperature increases over 515°C, but it even increases rapidly when the fourth reactor inlet temperature closes to 530°C. It also can be obtained that the higher temperature is unfavorable to catalyst coking and energy cost, but favorable to hydrogen yield. On the basis of these analyses, the optimal scopes of the four inlet temperatures is selected as 518~523, 518~523, 515~525, 523~528°C, respectively.

Decreasing pressure increases both dehydro-genation of naphthenes and dehydrocyclization of paraffins, favoring an increase in the aromatics yield. However, the reduction in pressure can unluckily increases catalyst coking too. The effect of pressure on aromatics yield and catalyst coking is shown in Fig. 4. It can be found that the aromatics yield increases about 4 wt.% of charge per 0.5 MPa decrease in pressure, while the catalyst coke content also increases about 1.6 times when pressure changes as above. It is careful to decrease the operating pressure due to the given regeneration capacity.

Generally the hydrogen-to-oil molar ratio has little affect on the aromatics yield. The main purposes of hydrogen recycle are as heat carrier and to increase hydrogen partial pressure in the reformers protecting the catalyst from rapid coking. Figure 5 gives the effect of HC on catalyst coking and energy cost. Reducing HC can reduce energy cost, bur also increase catalyst coking. Hence HC exists a low limit to avoid severe coke deposition on catalyst.

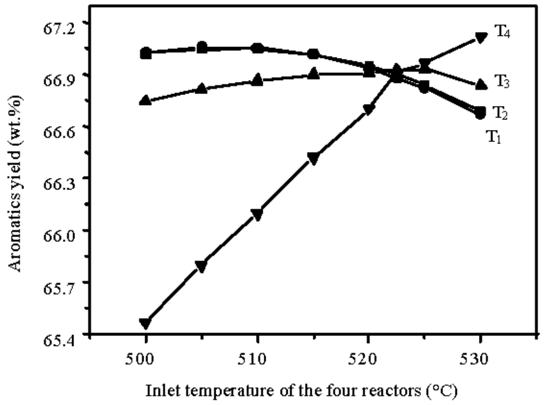

Fig. 3: Effect of the four reactor inlet temper- atures on aromatics yield

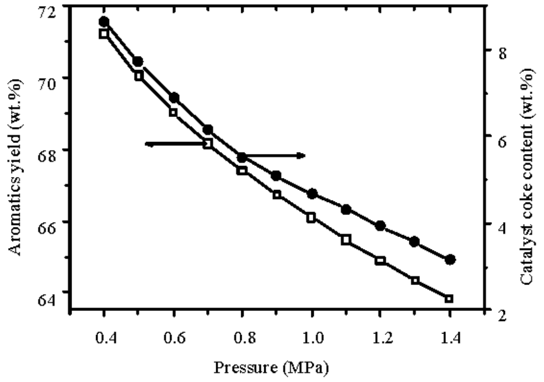

Fig. 4: Effect of reaction pressure on aromatics yield and catalyst coking

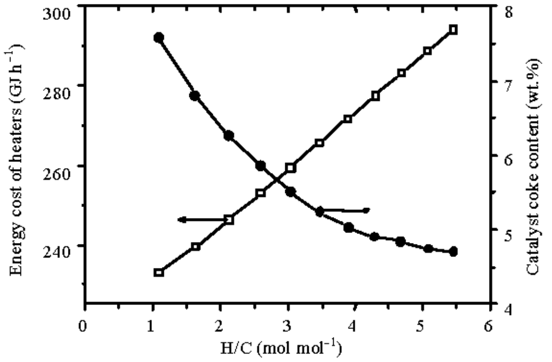

Fig. 5: Effect of hydrogen-to-oil molar ratio on energy cost and catalyst coking

Table 3: Calculated optimization results for key process variables

Process variable	Constraint value	Current value	Optimal value	Increase
(°C)	$518 \le T_1 \le 523$	522.10	521.20	-0.90
T_2 (°C)	$518 \le T_2 \le 523$	521.30	520.50	-0.80
T_3 (°C)	$515 \le T_3 \le 528$	517.50	517.50	0.00
T_4 (°C)	$523 \le T_4 \le 528$	523.90	526.10	2.20
HC (mol mol^{-1})	≤4.0	3.29	3.27	-0.02
CIK (wt.%)	≤6.5	5.28	5.32	0.04
EC (GJ h^{-1})	≤275	263.20	263.50	0.30
Calculated AY (wt.%)		66.91	67.23	0.32

Catalyst distribution (wt%): R1: R2: R3: R4 = 10: 15: 25: 50, Naphtha feed (kg h^{-1}): 171793, LHSV (1 h^{-1}): 1.02, Latent aromatics (wt%): 51.9, Catalyst type: Pt-Sn/Al_2O_3

Table 4: Actual testing results of the optimization project

Process variable	Averaged values of 22 samples before testing	Averaged values of 20 samples after tesing	Increase
T_1 (°C)	521.90	521.30	-0.60
T_2 (°C)	521.30	520.30	-1.00
T_3 (°C)	517.60	517.80	0.20
T_4 (°C)	523.70	525.80	2.10
LHSV (1 h^{-1})	1.02	1.02	0.00
Latent aromatics (wt.%)	53.20	53.10	-0.10
HC (mol mol^{-1})	3.57	3.58	0.01
CK (wt.%)	5.96	6.01	0.05
EC (GJ h^{-1})	266.00	266.40	0.40
Actual AY (wt.%)	67.36	67.85	0.49

PROCESS OPTIMIZATION

Based on the kinetics model and the process variable analyses, process optimization can be realized to improve the process performance and maximize process profitability. After plentiful sensitivity analyses as shown in section 4, the four reactor inlet temperatures and the reaction pressure are considered as key variables to influence aromatics yield. For the reaction pressure can not be changed obviously due to the given process technology, the four reactor inlet temperatures are then selected as decision variables to maximize Aromatics Yield (AY) in this study. The optimization problem with process constraints is described below:

$$
\begin{aligned}
&\max_{T_1,T_2,T_3,T_4} AY \\
&\text{s.t. Equations of } (1) \sim (6) \\
&T_i^L \le T_i \le T_i^U \quad i=1,2,3,4 \\
&CK^L \le CK \le CK^U \\
&HC^L \le HC \le HC^U \\
&EC^L \le EC \le EC^U
\end{aligned}
\tag{4}
$$

The upper and lower limits of the four reactor inlet temperatures (T^L, T^U) are obtained by sensitivity analyses. Process constraints are mainly catalyst coking content (CK), hydrogen-to-oil molar ratio (HC) and Energy Cost (EC). The SQP (Sequential Quadratic Programming) method is selected to solve this NLP (Non-Linear Programming) problem. Table 3 gives the optimization results of key operation conditions to maximize the aromatics yield under specific naphtha feedstock.

As shown in Table 3, the optimized process variables can bring a potential increase of aromatics yield by 0.32 wt.%. Furthermore, the optimization project, which is close with the fourth column of Table 3, is tested in the actual industrial continuous catalytic reforming unit for about one month. The testing results are presented in Table 4. The aromatics yield increases about 0.49 wt% averagely, which is close to the calculated value listed in Table 4. Obviously, the optimization project obtained by process simulation and optimization computation is believable. The benefit acquired by only changing the four reactor inlet temperatures a little will reach more than 5,000,000 yuan annually.

CONCLUSION

A 20-lumped kinetics model for naphtha catalytic reforming reactions is used to simulate an industrial Continuous Catalytic Reforming (CCR) process. Fair agreement between the calculated and operating data is obtained. The key process variables affecting the aromatics yield are analyzed in detail to guide the selections of operating conditions.

Based on the kinetics model and plentiful sensitivity analyses, process optimization is also studied. Unlike most studies, the optimization result and project is not just presented. The optimization project is also tested in the actual industrial unit about one month. The testing optimization result is close to the calculated one by process optimization. Hence, the 20-lumped kinetics model and the optimization strategy are reasonable and believable.

NOMENCLATURE

AY = Aromatics yield, wt%
C_p = Specific heat, kJ·kmol^{-1}·K^{-1}
CK = Catalyst coke content, wt%
E = Activation energy, kJ·mol^{-1}
EC = Energy cost of four heaters, GJ·h^{-1}
ΔG = Reaction heat, kJ·mol^{-1}
H = Height of the catalyst bed, m
ΔH = Heat of reaction, kJ·kmol^{-1}
HC = Hydrogen-to-oil molar ratio
K = Teaction rate coefficient, h^{-1}
k_0 = Frequency factor, s^{-1}·MPa$^{-è}$
K_r = Matrix for reaction rate coefficients
K_{ep} = Reaction equilibrium constant
LHSV = Liquid hourly space velocity, h^{-1}
M = Number of focused components
P, N, A = Paraffins, naphthenes, aromatics
P_h = Partial pressure of hydrogen, MPa
PX, MX, OX, EB = Para-xylene, meta-xylene, ortho-xylene and ethyl-benzene
R = Reaction rate, kmol·s^{-1}
R = Radius of catalyst bed, m or gas contant
S = Number of samples
T = Time on stream, h
T = Reaction temperature, reactor import or export temperature, K
V_c = Catalyst volume, m^3
y = Molar content, mol%
Y = Molar flow rate, kmol/h
WAIT = Weighted average inlet temperature, K

Superscripts

θ = Pressure exponent
L, U = Upper and lower limits of variables

Subscripts

I = Carbon atom number
j = Reaction number or latent variable number
k = Sample number

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