A study on naphtha catalytic reforming reactor simulation and analysis

LIANG Ke-min (梁克民)[†1], GUO Hai-yan (郭海燕)[1], PAN Shi-wei (潘世伟)[2]

(*[1]School of Petrochemical Engineering, Shenyang University of Technology, Liaoyang 111003, China*)
(*[2]School of Advanced Professional Technology, Shenyang University of Technology, Liaoyang 111003, China*)
[†]E-mail: lks-ly@163.com

Abstract: A naphtha catalytic reforming unit with four reactors in series is analyzed. A physical model is proposed to describe the catalytic reforming radial flow reactor. Kinetics and thermodynamics equations are selected to describe the naphtha catalytic reforming reactions characteristics based on idealizing the complex naphtha mixture by representing the paraffin, naphthene, and aromatic groups by single compounds. The simulation results based above models agree very well with actual operation unit data.

Key words: Naphtha, Catalytic reforming, Kinetics, Simulation and analysis
doi:10.1631/jzus.2005.B0590   **Document code:** A   **CLC number:** TE624.42

INTRODUCTION

Catalytic reforming of naphtha or mixture of naphtha with a certain amount of cracking oil is a process of great interest to the petrochemical industry for the production of aromatic compounds that are raw materials for plastics, elastomers and resins manufacture. Catalytic reforming unit uses naphtha or cracking oil as feedstock to produce rich aromatic compounds and high octane value liquid products through reactions such as aromatization, cyclization, and hydrocracking. At the same time, it produces hydrogen (H) and liquified petroleum gas (LPG) as its by-products. The design or simulation of the catalytic reforming reactor is very difficult because of complicated components of catalytic reforming feedstock, higher operating temperature of the system, and the complicated reactions in the reactor.

Much research (Pontes *et al.*, 1999) on this subject had been carried out. Results have been published on the process, reactions and kinetics. A conventional naphtha catalytic reforming unit consists of 3 or 4 radial flow reactors in series operated under adiabatic conditions. The temperature and the H_2/HC

molar ratio are the most important process variables. A bifunctional catalyst with Pt and a second metal is generally used. In addition, some novel processes (Melnikov and Makarova, 1998; Smith, 1960; Bolz *et al.*, 1999) of catalytic reforming had been developed.

The kinetics of catalytic reforming has been attracting the attentions of many researchers. A successful kinetic analysis proposed by Smith (1959), was based on idealizing the complex naphtha mixture by representing the paraffin, naphthene, and aromatic groups by single compounds. The nature of the reforming reactions in which the number of carbon atoms was the same for the precursor and product justified this procedure. Reaction rates were derived from the assumption of a homogeneous system.

Jorge and Eduardo (2000) proposed a lumped kinetic model for the naphtha catalytic reforming process. The model utilizing lumped mathematical representation of the reactions taking place was in terms of isomers of the same nature. Arrhenius-type variation was added to the model in order to include the effect of pressure and temperature on the rate constants. Many other kinetic models (Jerzy, 1999) are not described here.

A catalytic reforming unit with 4 reactors in series was analyzed and simulated in this paper. Kinetics proposed by Smith was adopted to describe the reactions occurring during catalytic reforming. Simulation results were compared with the actual data.

MATHEMATICAL MODEL

Basic assumption

The structure of a catalytic reforming reactor is shown in Fig.1. The following assumptions are proposed on the basis of the features of catalytic reforming reactions, reactor and its operation conditions:

1. The temperature along the axial direction (S) of the radial flow reactor is homogeneous, that is $dT_s=0$.

2. The concentration along the axial direction of the radial flow reactor is homogenous, that is $dN_s=0$.

3. Reactions are in homogenous phase.

Based on the above hypothesis, the temperature and concentration gradients along the axial direction can be neglected and only radial direction variables are considered. In fact, the fixed bed reactor is considered as a homogeneous reactor.
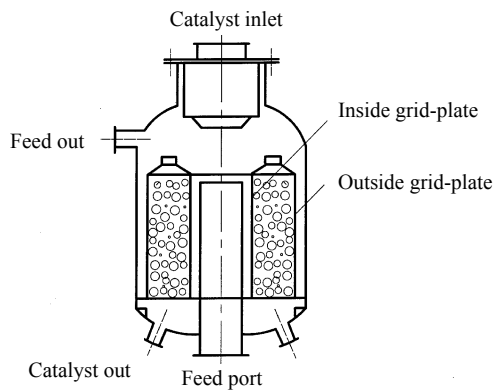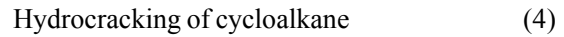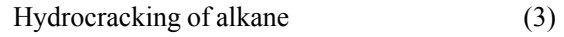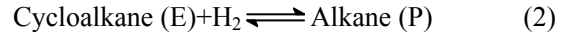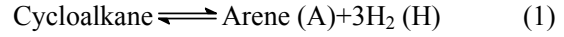

Fig.1 Structure of catalytic reforming radial flow reactor
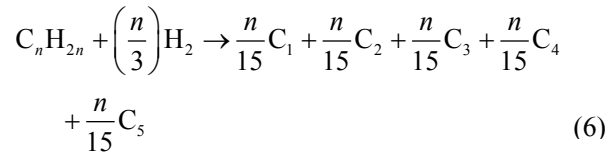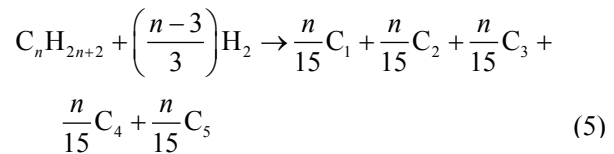
Dynamics

If some pseudo ingredients (i) are appropriately used to simplify the feedstock of naphtha catalytic reforming, four dominant idealized reactions (Smith, 1959) can be used to describe the catalytic reforming process so that the catalytic reforming system can be simplified significantly. These four reactions are called model reactions. The chemical reaction equations are as follows

$$\text{Cycloalkane} \rightleftharpoons \text{Arene (A)} + 3\text{H}_2 \text{ (H)} \tag{1}$$
$$\text{Cycloalkane (E)} + \text{H}_2 \rightleftharpoons \text{Alkane (P)} \tag{2}$$
$$\text{Hydrocracking of alkane} \tag{3}$$
$$\text{Hydrocracking of cycloalkane} \tag{4}$$

According to Smith (1959), hydrocracking produces nearly the same amounts of moles of $C_1 \sim C_6$ cuts. Therefore, the model reaction Eq.(3) and Eq.(4) can be represented by the following formula:

$$C_nH_{2n+2} + \left(\frac{n-3}{3}\right)H_2 \rightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5 \tag{5}$$

$$C_nH_{2n} + \left(\frac{n}{3}\right)H_2 \rightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5 \tag{6}$$

where, n is the number of carbon atoms. For a certain reforming feedstock, the n value can be obtained through the average mole weight M_f (kg/kmol) of the feedstock and the family of component x_P, x_E, x_A. Their relation is

$$n = M_f - 2x_p + 6x_A \tag{7}$$

where, $x_p + x_E + x_A = 1$ and x_P, x_E, x_A are mole fractions of alkane, cycloalkane, and aromatics, respectively.

The corresponding empirical reaction rate equations (Rase, 1977) are based on model reaction Eqs.(1)~(4).

Cycloalkane transformed into arene:

$$r_1 = \eta k_{p1}(P_E - P_A P_H^3 / K_{p1}) \tag{8}$$
$$k_{p1} = 9.87\exp(23.21 - 34750/1.8T) \tag{9}$$

Cycloalkane transformed into alkane:

$$r_2 = \eta k_{p2}(P_E P_H - P_P / K_{p2}) \tag{10}$$
$$k_{p2} = 9.87\exp(35.98 - 59600/1.8T) \tag{11}$$

Hydrocracking of alkane:

$$r_3 = \eta k_{p3} P_P / P \tag{12}$$

$$k_{p3}=\exp(42.97-62300/1.8T) \qquad (13)$$

Hydrocracking of cycloalkane:

$$r_4=\eta k_{p4}P_E/P \qquad (14)$$
$$k_{p4}=\exp(42.97-62300/1.8T) \qquad (15)$$

where, η is corrective coefficient of catalyst; k_{p1} is reaction rate constant corresponding to r_1, kmol/(h·kg cat·MPa); k_{p2} is reaction rate constant corresponding to r_2, kmol/(h·kg cat·MPa^2); k_{p3} is reaction rate constant corresponding to r_3, kmol/(h·kg cat); k_{p4} is reaction rate constant corresponding to r_4, kmol/(h·kg cat); K_{p1} is equilibrium constant of cycloalkane transformed into arene, (MPa)^3; K_{p2} is equilibrium constant of cycloalkane transformed into alkane, MPa^{-1}; P is pressure of system or component fractional pressure, MPa; r_1 is reaction rate of cycloalkane transformed into arene, kmol/(h·kg cat); r_2 is reaction rate of cycloalkane transformed into alkane, kmol/(h·kg cat); r_3 is reaction rate of hydrocracking of alkane, kmol/(h·kg cat); r_4 is reaction rate of hydrocracking of cycloalkane, kmol/(h·kg cat).

Occurrence of hydrocracking reaction occurring in the catalytic reforming process is the main causative factor catalyst deactivation. For different periods of catalytic activity, the carbon accumulation extent are not the same. Therefore, the values η are different from each other. For new catalyst, $\eta=1$ and in other conditions, $0<\eta<1$. The value of η can be calculated based on working conditions and time span of the catalytic activity.

Thermodynamics

The most important reaction in the catalytic reforming is the transformation of cycloalkane into aromatics. It is a rapid reaction which approaches to equilibrium in very short time. For reactions of cycloalkane transformation into aromatics and alkane, their reaction equilibrium constants are as follows (Smith, 1959):

$$K_{p1}=P_A P_H^3/P_E=1.04\times10^{-3}\exp(46.15-46045/1.8T) \quad (16)$$
$$K_{p2}=P_P/(P_E\cdot P_H)=9.87\exp(8000/1.8T-7.12) \qquad (17)$$

For the above four model reactions, considering the reaction enthalpy and the number of moles of hydrogen consumed or released during the reaction, the reaction enthalpies based on the number of moles of hydrogen (ΔH_1 reaction enthalpy of model reaction (1), kJ/(kmol H$_2$); ΔH_2 reaction enthalpy of model reaction (2), kJ/(kmol H$_2$); ΔH_3 reaction enthalpy of model reaction (3), kJ/(kmol H$_2$); ΔH_4 reaction enthalpy of model reaction (4), kJ/(kmol H$_2$) are as follows:

$$\Delta H_1=71038.06 \text{ kJ/(kmol H}_2) \quad \text{(endothermic)}$$
$$\Delta H_2=-36953.33 \text{ kJ/(kmol H}_2) \quad \text{(exothermic)}$$
$$\Delta H_3=-56597.54 \text{ kJ/(kmol H}_2) \quad \text{(exothermic)}$$
$$\Delta H_4=-51939.31 \text{ kJ/(kmol H}_2) \quad \text{(exothermic)}$$

The reactants and products of a catalytic reforming unit can be considered as ideal gases. The relation between its heat capacity (C_p, kJ/(kmol·°C)) and temperature is

$$C_p=4.1868(a+bT+cT^2+dT^3) \qquad (18)$$

where, a, b, c and d can be obtained from physical properties manual and is listed in Table 1 (Lu, 1982; Reid *et al.*, 1977).

Table 1 Coefficients of heat capacity equation of ideal gases

ID	a	$b\times10^3$	$c\times10^6$	$d\times10^9$
H$_2$	6.483	2.215	−3.298	1.826
C$_1$	4.598	12.45	2.680	−2.703
C$_2$	1.292	45.84	−16.57	2.081
C$_3$	−1.009	73.15	−37.89	7.678
C$_4$	2.266	79.13	−26.47	−0.674
C$_5$	−0.866	116.4	−61.63	13.67
P	−1.456	184.2	−100.24	21.15
E	−14.789	187.3	−106.0	22.37
A	−5.817	122.4	−66.05	11.73

Model of reactor

The physical model for catalytic reforming radial flow reactor is shown in Fig.2. The outer radius of the catalyst bed is R_o and the inner radius of the catalyst bed is R_i. For a element dR at (R, R+dR), the inlet material stream into it is N_i and the temperature is T. The outlet material stream is N_i+dN_i and the temperature is T+dT. With mass and enthalpy balances for the element combining kinetic and thermodynamic equations, the concentration and temperature distributions along the reactor radius can be derived as:

$dN_A/dR=2\pi RL\rho_b r_1$ (19)

$dN_E/dR=2\pi RL\rho_b(-r_1-r_2-r_4)$ (20)

$dN_P/dR=2\pi RL\rho_b(r_2-r_3)$ (21)

$dN_H/dR=2\pi RL\rho_b(3r_1-r_2-((n-3)/3)r_3-(n/3)r_4)$ (22)

$dT/dR=(2\pi RL\rho_b)/(\Sigma F_i C_{pi})\times\{3r_1(-\Delta H_1)+r_2(-\Delta H_2)$
$\qquad +[(n-3)/3]r_3(-\Delta H_3)+(n/3)r_4(-\Delta H_4)\}$ (23)

Eq.(19) to Eq.(22) describe changing rates of arene, cycloalkane, alkane, and hydrogen along the bed layer radius. For the adiabatic fixed bed radial flow reactor, its temperature distribution is represented by Eq.(23). F is feedstock, kmol/h; N is flow rate, kmol/h; L is height of catalyst bed in reactor, m; ρ_b is bulk density of catalyst, kg/m^3.
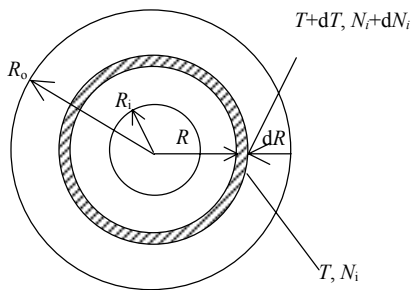

Fig.2   Physical model of catalytic reforming radial flow reactor

SIMULATION OF THE REACTOR

Fig.3 shows a flow diagram with four reactors in series. With conditions at the reactor inlet as boundary conditions, the concentration and temperature distributions can be calculated by solving grouped Eq.(19) to Eq.(23) with fixed step, four order Runge-Kutta method. The computing diagram is shown in Fig.4. Four catalytic reforming radial flow reactors of the Chemical Plant No.1 of the Liaoyang Petrochemical Fiber Company were analyzed and simulated with this model.
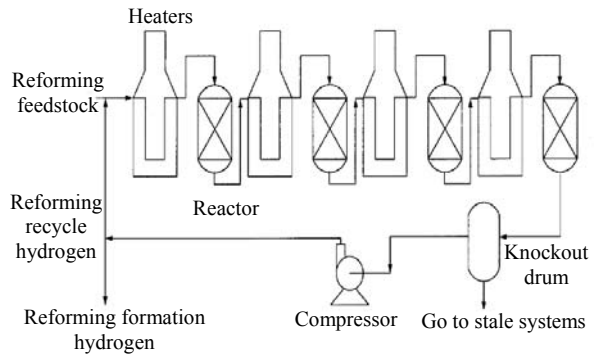

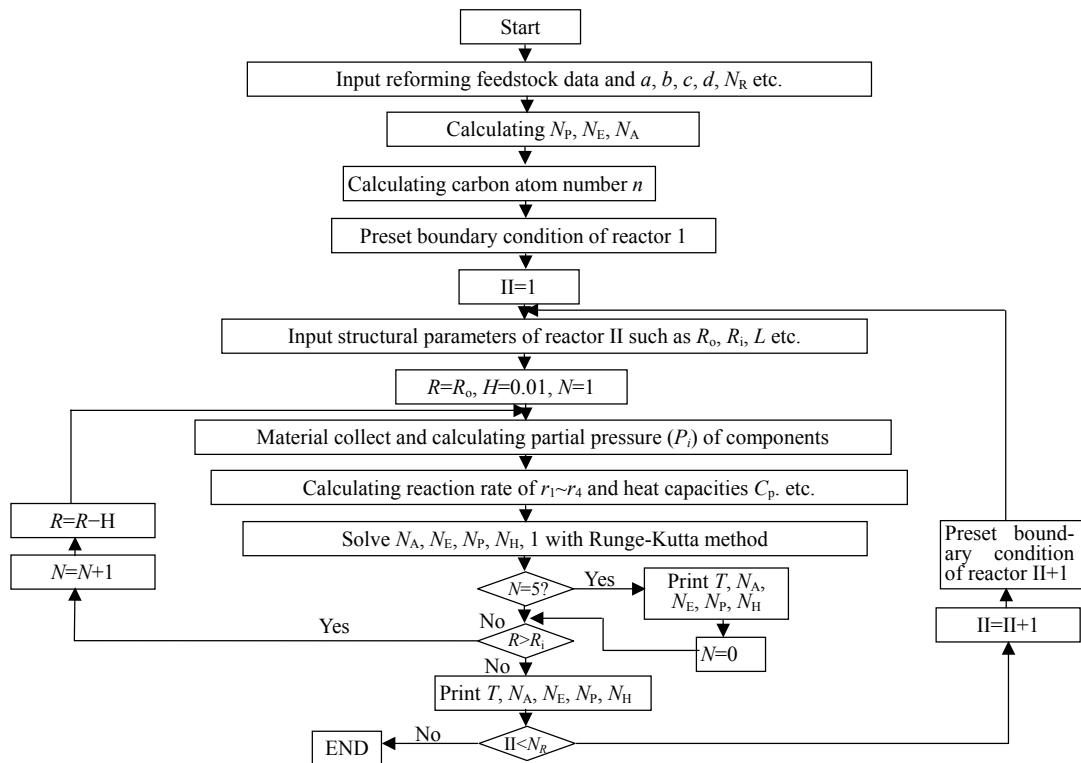**Fig.3   Schematic flow diagram of four reactors in series of catalytic reforming**

Fig.4   Computer simulation program blocks

Basic data

Liaohe straight-run distillation naphtha (Liaohe Petroleum Field, China) was selected as reforming feedstock. Its distillation temperature range is 65 °C~145 °C, d_4^{20}=0.7314. Engler distillation data is listed in Table 2. The feedstock of catalytic reforming reactors and recycle hydrogen content data (Yong, 1995) is shown in Tables 3 and 4. The inlet temperatures of all reactor I, II, III and IV were 521 °C. The operating pressure was 1.730~1.408 MPa and recycling hydrogen flow rate was 3.1372×10⁴ Nm³/h.

Simulation calculation

Simulation calculation was carried out using data listed in Tables 2−4 and the results are listed in Table 5. Because people usually focus on the reactor production ability, conversion rate, hydrogen generated by reforming, temperature of catalyst bed, etc., the temperature, arene, cycloalkane, alkane, and hydrogen varying with the radius of the beds are listed in Table 5. Note that the data used in the simulation calculation is calibration data in the latest operation period. The catalyst correction coefficient η=0.432 at this period.

RESULTS AND DISCUSSIONS

It obvious, from the data listed in Table 4, that in reactor I and II, the main reaction happened is cycloalkane aromatization, is an endothermic reaction and the bed layer temperature drop of these two reactors is larger. In reactor III and IV, alkane dehydrogenization, cyclization, and hydrocracking reactions

Table 2 Engler distillation data

Distillation fraction (%)	IBP	10	50	90	EBP
b.p. (°C)	77	85	114	135	157

Table 3 Recycle hydrogen content of catalytic reforming reactors

ID	Recycle hydrogen content (%, v)
H_2	84.94
C_1	5.85
C_2	3.88
C_3	2.93
C_4	2.17
C_5	0.19
B	0.04

Note: B: Benzene

Table 4 Reforming feedstock content of catalytic reforming reactors

ID	Reforming feedstock content (%, m)
C_4	0.02
C_5	0.15
C_6	4.55
C_7	31.56
C_8	18.65
C_9	4.44
C_{10}^+	1.57
$C_\gamma C_5$	0.24
m-$C_\gamma C_5$	1.03
$C_\gamma C_6$	3.21
$C_\gamma C_7$	20.26
$C_\gamma C_8$	19.12
$C_\gamma C_9$	4.54
$C_\gamma C_{10}^+$	0.02
B	0.49
T	3.54
EB	0.35
PX	0.39
MX	2.03
OX	1.10
C_9^+A	0.74

Note: T: Toluene; EB: Eshylbenzene; PX: Parexylene; MX: Meta-xylene (1,3-dimethylbenzene); OX: Orthoxylene; C_9^+A: Arene of C_9 and over

are dominant there. At the same time, the cycloalkane produced there through cyclization continues to aromatize, but the amount is not large. Furthermore, a large amount of heat was released by cyclization and hydrocracking reactions. Therefore, the bed temperature drop in these two reactors, the last one especially, is smaller.

It should be pointed out that under some suitable conditions the reversal reaction represented by Eq.(10), alkane transformation into cycloalkane becomes more important. On the one hand, aromatic production yield can be increased. On the other hand, non-aromatic content in reforming arene can be decreased and aromatic compounds transformation rate can be increased.

Based on data in Table 5, the temperature distribution curve in the catalyst bed, that is, the temperature variation within the radius of the catalyst bed, is shown in Fig.5 showing that at the inlet side (i.e. higher value of R) of the reactors I and II, the bed temperature varies rapidly and at the outlet side (i.e. smaller R) the bed temperature varies slowly. Because

Table 5 The simulation results

| Reactor ID	Bed Radius (mm)	Bed temperature (°C)	Arene (kmol/h)	Cycloalkane (kmol/h)	Alkane (kmol/h)	Hydrogen (kmol/h)
I	510	521.00	16.180	90.050	76.630	1257.870
	460	496.88	32.979	71.642	76.650	1300.845
	410	486.04	39.943	64.052	76.603	1320.133
	360	479.48	44.096	59.601	76.565	1331.804
	310	475.03	46.879	56.644	76.535	1339.686
	260	471.88	48.843	54.569	76.513	1345.276
	210	469.60	50.254	53.084	76.496	1349.304
	170	468.26	51.084	52.213	76.486	1351.676
II	585	521.00	51.084	52.213	76.486	1351.676
	535	503.79	62.982	39.260	75.398	1382.185
	485	495.27	68.681	33.255	74.850	1397.267
	435	489.94	72.194	29.608	74.500	1406.714
	385	486.27	74.589	27.136	74.251	1413.266
	335	483.60	76.334	25.363	74.066	1417.946
	285	481.62	77.619	24.055	73.926	1421.453
	235	480.14	78.579	23.083	73.818	1424.073
	185	479.04	79.286	22.369	73.737	1426.066
	170	478.78	79.457	22.196	73.717	1426.474
III	760	521.00	79.457	22.196	73.717	1426.474
	710	510.04	87.774	14.685	70.250	1445.538
	660	504.52	91.956	11.158	68.188	1455.138
	610	501.13	94.556	9.090	66.709	1461.024
	560	498.83	96.345	7.744	65.560	1464.998
	510	497.17	97.652	6.811	64.670	1467.839
	460	495.94	98.643	6.138	63.862	1469.948
	410	495.00	99.412	5.640	63.220	1471.551
	360	494.27	100.017	5.262	62.683	1472.787
	310	493.71	100.495	4.979	62.237	1473.748
	260	493.27	100.872	4.762	61.871	1474.491
	210	492.93	101.163	4.599	61.578	1475.058
	170	492.72	101.342	4.501	61.393	1475.404
IV	825	521.00	101.342	4.501	61.393	1475.404
	775	519.26	103.680	4.447	56.750	1477.891
	725	517.69	105.670	4.227	53.094	1480.240
	675	516.33	107.329	3.977	50.175	1482.287
	625	515.19	108.708	3.743	47.756	1484.025
	575	514.24	109.859	3.537	45.767	1485.487
	525	513.44	110.822	3.361	44.105	1486.714
	475	512.77	111.630	3.213	42.708	1487.743
	425	512.20	112.308	3.089	41.533	1488.603
	375	511.74	112.875	2.985	40.547	1489.319
	325	511.35	113.346	2.900	39.726	1489.910
	275	511.03	113.732	2.830	39.050	1490.393
	225	510.78	114.041	2.775	38.507	1490.777
	175	510.59	114.280	2.733	38.085	1491.074
	170	510.57	114.301	2.729	38.049	1491.099
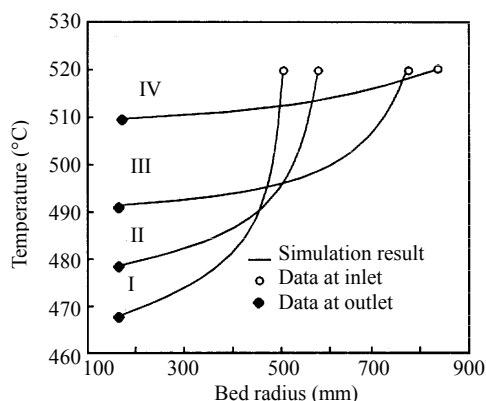
Fig.5 The temperature distribution of reforming radial flow reactor

there was more catalyst in the inlet where the reactants content was higher than that at the outlet. Therefore, more aromatic compounds were generated and more heat was absorbed at the inlet side. The situation at the outlet side was totally opposite. For reactor III and IV in spite of the trend being similar to that of reactors I and II, the temperature varied more gently because the reactions were exothermic.

For comparison, the reactors calibration values are also shown in Fig.5. The simulation results and actual values of the reforming product are shown in Table 6. These results indicate that the model and simulation in the present paper are satisfactory.

Table 6 Comparison between actual values of reforming product and simulation results

Item	Flow rate of products (kg/h)			Productivity of arene (%, m)
	Depentane oil	Arene	Non-arene	
Actual (Yong, 1995)	15585	11185	4399.65	57.96
Simulation	15580.96	11258.49	4322.47	58.33
Error (%)	−0.026	0.657	−1.754	0.638

CONCLUSIONS

1. The three assumptions in the present model are reasonable. The results indicate that the one-dimensional homogenous model is suitable for describing catalytic reforming radial flow reactor.

2. Once pseudo ingredients were selected suitably. The present empirical kinetics model can be well applied to catalytic reforming reactor for simulation and optimization.

3. This method can be used to predict aromatic capacity, yield, transformation rate, bed temperature, and so on for new operation conditions. Therefore, the optimum operating parameters can be obtained to yield maximum profit.

References

Bolz, C.R., Graziani, K.R., Harandi, M.N., Ozawa, Y., Sorensen, C.M., 1999. Radial-Flow Reactors Containing Multiple Catalyst Beds, Especially for Naphtha Reforming and Upgrading. PCT Int. Appl. WO 9920384.

Jerzy, S., 1999. On the kinetics of catalytic reforming with the use of various raw materials. *Energy Fuels*, **13**(1):29-39.

Jorge, A.J., Eduardo, V.M., 2000. Kinetic modeling of naphtha catalytic reforming reactions. *Energy Fuels*, **14**(5): 1032-1037.

Lu, H., 1982. Manual of Petrochemical Industry Fundamental Data. Chemical Industy Press, Beijing (in Chinese).

Melnikov, V.B., Makarova, N.P., 1998. Modification of reforming: Without hydrogen circulation. *Khim. Tekhnol. Topl. Masel.*, **23**(1):9-13.

Pontes, L.A.M., Rangel, M.D.C., Mario, D.J.M., 1999. Catalytic reforming of naphtha. *An Assoc. Bras. Quim.*, **48**(3):169-179.

Rase, H.F., 1977. Chemical Reactor Design for Process Plants. Vol. 2, John Wiley & Sons, Inc.

Reid, R.C., Prausnitz, J.M., Sherwood, T.K., 1977. The Properties of Gases and Liquids. 3rd Ed., McGraw-Hill Co., p.108-109.

Smith, R.B., 1959. Kinetic analysis of naphtha reforming with platinum catalyst. *Chem. Eng. Progr.*, **55**(6):76-80.

Smith, R.B., 1960. Reforming of naphtha in several stages. U.S. 2, 965, 560.

Yong, W., 1995. Calibration of E603 reforming catalyst. *Liaohua Sci. and Tech.*, **16**(4):16-19.