

## Five lumped kinetic models of liquefied petroleum gas under aromatization reaction conditions

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**Abstract**—The aromatization reaction of liquefied petroleum gas has been studied by using three liquefied petroleum gases as raw material and LBO-A as catalyst, and a five lumped kinetics model network has been put forward on the basis of lumped theory and the aromatization reaction mechanism. In the network the aromatization reaction species were firstly lumped into C<sub>4</sub><sup>+</sup>, C<sub>4</sub><sup>0</sup>, propylene, low molecule hydrocarbon, liquid and coke. A mathematical method is first introduced to study the product distribution of liquefied petroleum gas aromatization reaction. The results from experimental data are in accordance with the quantitatively analytical conclusions drawn from the calculated data.

Key words: Five Lumped Kinetics, Liquefied Petroleum Gas, Aromatization Reaction

### INTRODUCTION

In 1994, 1.27 hundred million tons of raw petroleum was processed, more than 2.2 million tons of ethylene was produced, and the resources of liquefied petroleum gas (C<sub>4</sub> fraction and C<sub>5</sub> fraction) reached approximately 3.7 million tons in China [Hongjun and Ping, 2005; Hongjun, 2005]. The resources of liquefied petroleum gas have become more and more abundant in China, and the output of liquefied petroleum gas is more than 300 thousand tons per year [Lihe et al., 2006; Bin et al., 2006]. The resources of liquefied petroleum gas are mainly from three resources in China from oil-gas fields, the refineries and gas cracking [Longyan et al., 2005], respectively.

Nowadays the resources of liquefied petroleum gas are not completely transferred to higher value products, since most resources are burned as fuel [Hongjun, 2006]. Recently, research work has focused mainly on how to use liquefied petroleum gas effectively [Guisnet et al., 1992; Choudhary, 2006]. The effects of reaction conditions on the aromatization reaction of liquefied petroleum gas have been studied, but the lumped kinetics models seldom are.

In this paper, five lumped kinetics models, which can predict aromatization reaction product distribution under various operating conditions and calculate the maximum deviations of the product yield between calculated results and practical values, are established for a confined fluidized bed reactor.

### EXPERIMENT

#### 1. Feedstock

Huabei, Hua'ebin and Qilu liquefied petroleum gas are obtained from an FCC unit of Huabei Petrochemical Company, Hua'ebin Petrochemical Company and Qilu Petrochemical Company, respectively. The components of the three liquefied petroleum gases are shown in Table 1.

Table 1. Components of liquefied petroleum gas, wt%

Name	Huabei	Hua'ebin	Qilu
C <sub>3</sub> H <sub>8</sub>	0.23	0.05	0.07
C <sub>3</sub> H <sub>6</sub>	0.11	0.00	0.00
i-C <sub>4</sub> H <sub>10</sub>	39.71	40.71	6.13
n-C <sub>4</sub> H <sub>10</sub>	9.27	13.01	18.83
t-2-butene	13.56	13.05	28.94
c-2-butene	8.36	7.84	17.70
n-butene-1	11.91	11.07	12.56
i-butene	16.54	13.50	15.42
C <sub>5</sub> <sup>+</sup>	0.31	0.77	0.35
total	100	100	100

Table 2. Properties of LBO-A catalyst

Parameters	Value
Apparent density, g/ml	0.8
Particle size distribution, % (by mass)	
0-45.8 μm	20.6
45.8-111.0 μm	60.3
>111.0 μm	19.1
micro-activity test index (MATI)	56

#### 2. Catalysts

Catalyst (LBO-A) obtained from Lanzhou Petrochemical Institute is researched. LBO-A in a confined fluidized bed reactor was aged with 2 ml/min vapor at temperature 700 °C, 750 °C or 800 °C, respectively. Its properties are presented in Table 2.

The micro-activity test index (MATI) is obtained by using a micro-reactor. The material oil provided by Beijing Petroleum Chemical Institute is light oil for the micro-reactor and its distillation range is from 225 °C to 337 °C. The reaction temperature, time, inflow oil, catalyst weight in the micro-reactor are stable, that is, 460 °C, 70 s, 1.56 g, 5.0030±0.0010 g, respectively. By applying SP 3420 Gas Chromatograph the liquid product of the above reaction is distilled and analyzed. MATI is given as follows:

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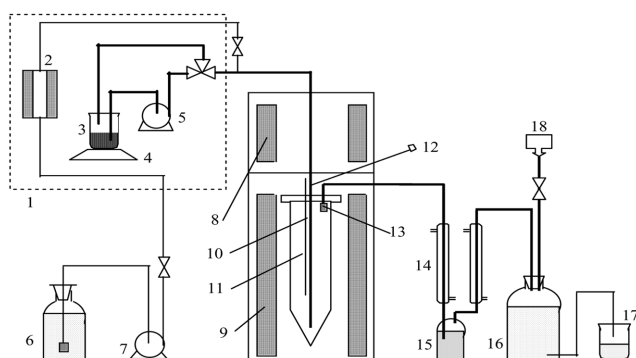


Fig. 1. Schematic drawing of experimental apparatus.

- |                              |                                      |
|------------------------------|--------------------------------------|
| 1. Constant temperature room | 11. Reactor                          |
| 2. Steam furnace             | 12. Catalyst inlet                   |
| 3. Feedstock                 | 13. Filter                           |
| 4. Electronic scale          | 14. Condenser                        |
| 5. LPG pump                  | 15. Liquid product collection bottle |
| 6. Water tank                | 16. Collection gas bottle            |
| 7. Water pump                | 17. Beaker                           |
| 8. Preheated room            | 18. Gas sample bag                   |
| 9. Furnace                   |                                      |
| 10. Thermocouple             |                                      |

$$M = 1 - \frac{(m \cdot W_2)}{m_1} \quad (1)$$

Where  $M$  is MATI, %;  $m$  is liquid product weight, g;  $m_1$  is total inflow oil weight, g;  $W_2$  is the mass fraction of diesel oil in the liquid product.

### 3. Experimental Method

A confined fluidized bed reactor was applied in the aromatization reactions of liquefied petroleum gas and was shown in Fig. 1. It consisted of five parts: LPG pumping system, reaction zone, temperature control, product separation and collection system. Variable amount of distilled water was pumped into the furnace to exchange into steam, and then mixed with liquefied petroleum gas pumped by another pump simultaneously at the outlet of a constant temperature box. The mixture was heated to approximately 420 °C in a preheated room before it entered the reactor.

### 4. Operating Conditions

The operating conditions for the aromatization reactions of liquefied petroleum gas are summarized in Table 3.

### 5. Analytical Method

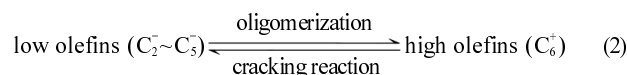
An HP6890 Gas Chromatograph with Chem Station software, which was supplied from America Agilent Technologies Inc, was used to measure the volume percentage of aromatization gas components. These data were converted to mass percentage in the equation of state for ideal gases. The aromatization liquid was analyzed with SP-3420 Chromatograph, which was provided by Beijing Beifen

Tianpu Equipment LTD, to obtain the mass percentage of n-paraffins, i-paraffins, naphthene, olefins and aromatics. The mass percentage of coke on catalyst was measured with KJ-02 Fast and Exact Measuring Coke Equipment, which was obtained from China Petroleum University.

### 6. Experimental Principle (10)

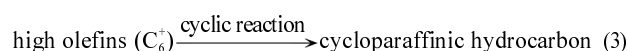
Small ( $C_2 \sim C_5$ ) and long chain olefins can exchange each other with catalyst.

Under the reactor conditions this is a gas-phase reversible reaction. The chemical Eq. (2) is shown as follows:



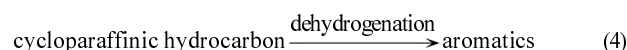
The cyclization takes place when high olefins ( $C_6^+$ ) and catalyst are in contact.

The chemical Eq.(3) is expressed as follows:



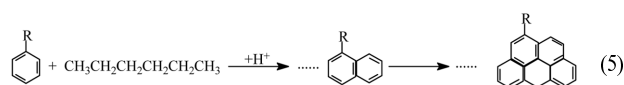
Cycloparaffinic hydrocarbon and Lewis acidity produce aromatics with catalyst.

The chemical Eq. (4) is shown as follows:



The coking reactions take place when aromatics and n-paraffins are in contact.

The chemical Eq. (5) is expressed as follows:



## ESTABLISHING NINE LUMPED KINETICS MODELS

### 1. Five Lumped Kinetic Models Scheme and Reaction Network

According to the guiding principles of the lumped theory and based on the aromatization reaction mechanism, a new complex reaction network with five lumped kinetics models was proposed for the aromatization reaction of liquefied petroleum gas. In the network the aromatization reaction species were firstly lumped into  $C_4^+$ ,  $C_4^0$ , propylene, low molecule hydrocarbon, liquid and coke. Four main type reactions among these lumped components were considered in the aromatization reaction network, such as olefins cyclization and dehydrogenation to aromatics, high olefins cracking to low olefins, low olefins oligomerization to high olefins, aromatics and n-paraffins coking to coke and so on. For the purpose of simplification, some reactions that seldom take place and reactions of less importance were eliminated from the network. The five lump

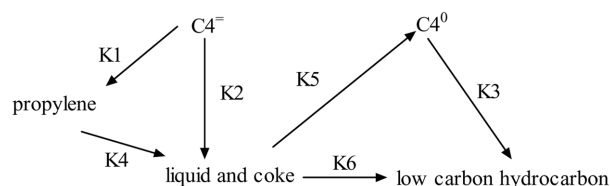


Fig. 2. Five lump web models of liquefied petroleum gas.

Table 3. Operating conditions for liquefied petroleum gas

Parameters	Value
Reaction temperature, °C	450-550
Weight hour space velocity (WHSV), h <sup>-1</sup>	2.0-6.5
Water inflow, ml/min	2
LBO-A, g	60

web model of liquefied petroleum gas studied on its reaction mechanism is shown in Fig. 2.

## 2. Mathematical Models

It is supposed that all reaction equations of five lump reaction web models in the aromatization reaction of liquefied petroleum gas are first-order irreversible reaction. The performance of liquefied petroleum gas and catalyst in a confined fluidized bed reactor is piston flow, non-axial diffusion, non-radial concentration and non-temperature gradient, and its reaction is controlled by the reaction dynamic and the effect of external-diffusion.

Lump I becomes into lump J, and its Eq. (6) is expressed as follows:



Component j is calculated from reactor bed high x to x+dx for a confined fluidized bed reactor.

Liquefied petroleum gas going into infinitesimal is given as:

$$c_j u \Omega dt \quad (7)$$

Liquefied petroleum gas going out infinitesimal is:

$$(c_j + dc_j)(u + du) \Omega dt \quad (8)$$

Material balance is given by:

$$c_j u \Omega dt = (c_j + dc_j)(u + du) \Omega dt + r_j \Omega dx dt \quad (9)$$

Eq. (9) is simplified as follows:

$$u dc_j + c_j du + dc_j du = -r_j dx \quad (10)$$

The infinitesimal liquefied petroleum gas's density remains unchanged based on the above assumption.

Where du is defined as: du=0

Using the above parameter simplifies Eq. (11) as follows:

$$u \frac{dc_j}{dx} = -r_j \quad (11)$$

Feed amount (liquefied petroleum gas and water vapor)  $F_0$  (kg/s) is expressed as follows:

$$F_0 = u \Omega \rho \quad (12)$$

$$\text{and } \rho = \frac{p \overline{MW}}{RT} \quad (13)$$

$$\text{and } u = \frac{F_0}{\Omega} \cdot \frac{RT}{p \overline{MW}} \quad (14)$$

Eq. (11) can be simplified by using the above equation as follows:

$$\frac{dc_j}{dx} = -\frac{\Omega}{F_0} \cdot \frac{p \overline{MW}}{RT} r_j \quad (15)$$

Component j's reaction velocity (12) in the first-order reaction is calculated

$$r_j = -k_j' \rho_{cat} c_j \quad (16)$$

Where  $\rho_{cat}$  is parameter for catalyst, one obtains:

$$\rho_{cat} = \psi_{cat} \rho \quad (17)$$

By introducing Eq. (17) into Eq. (16), it may be given that:

$$r_j = -k_j' \psi_{cat} \rho c_j \quad (18)$$

Introducing Eqs. (12) and (18) into Eq. (15) yields:

$$\frac{dc_j}{dx} = \frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} k_j' c_j \quad (19)$$

It is well known that a catalyst's deactivation is caused by its surface coke. So it is supposed that a catalyst's deactivation is a catalyst's coke yield function and is non-selective and all velocity constants decrease with the same rate condition. The catalyst deactivation function  $\phi$  is a scalar and real velocity constant and  $k_j'$  is given as follows:

$$k_j' = k_j \phi(C_{c4}) \quad (20)$$

$$\phi(C_{c4}) = \exp(-\alpha C_{c4}) \quad (21)$$

By introducing Eqs. (20) and (21) into Eq. (19), it may be shown that:

$$\frac{dc_j}{dx} = \frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} k_j e^{-\alpha C_{c4}} c_j \quad (22)$$

A confined fluidized bed reactor's length is L and dimensionless length is  $X = x/L$ . Eq. (22) is simplified as follows:

$$\frac{dc_j}{dX} = \frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} L k_j e^{-\alpha C_{c4}} c_j \quad (23)$$

$$\frac{dc_1}{dX} = -\frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} L (k_1 + k_2) e^{-\alpha C_{c4}} c_1 \quad (24)$$

$$\frac{dc_2}{dX} = \frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} L [v_{42} k_5 c_4 - k_3 c_2] \cdot e^{-\alpha C_{c4}} \quad (25)$$

$$\frac{dc_3}{dX} = \frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} L (\cdot v_{13} k_1 c_1 - k_4 c_3) \cdot e^{-\alpha C_{c4}} \quad (26)$$

$$\frac{dc_4}{dX} = \frac{p \overline{MW}}{RT} \psi_{cat} \frac{1}{u} L (\cdot v_{23} k_4 c_3 + v_{14} k_2 c_1 - (k_5 + k_6) c_3) \cdot e^{-\alpha C_{c4}} \quad (27)$$

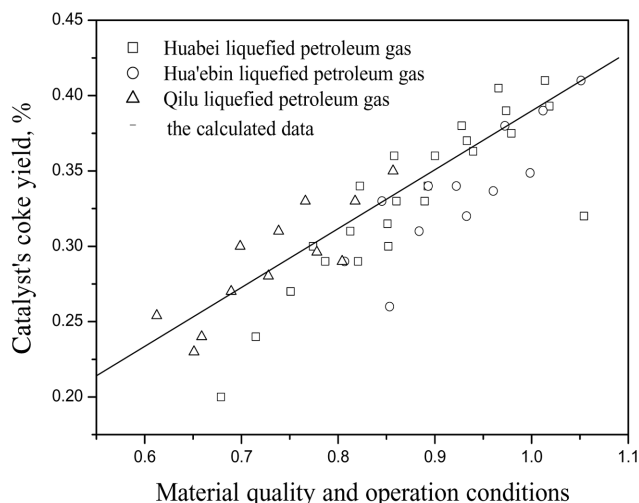
$$c_5 = (1 - c_1 M_1 - c_2 M_2 - c_3 M_3 - c_4 M_4) / M_5 \quad (28)$$

Where  $c_j$  is concentration of component j, kmol/m<sup>3</sup>; u is liquefied petroleum gas linear velocity of a fluidized bed, m/s;  $\Omega$  is lateral section of a fluidized bed, m<sup>2</sup>;  $r_j$  is reaction velocity of Component j, kmol/(s·m<sup>3</sup>);  $\rho$  is liquefied petroleum gas density of a fluidized bed, kg/m<sup>3</sup>; p is reaction pressure, Mpa;  $\overline{MW}$  is mean molecular weight, kg; R is atmosphere constant; T is reaction temperature, K;  $\rho_{cat}$  is catalyst's density, kg/m<sup>3</sup>;  $\psi_{cat}$  is mass ratio catalyst to oil;  $\alpha$  is catalyst's deactivation constant;  $C_{c4}$  is catalyst's coke yield, s; L is reactor's high, m;  $v_{ij}$  is chemistry measuring coefficient of lump I becoming to lump J;  $k_j'$  is velocity constant of lump I becoming to lump J;  $M_i$  is relative molecule quality;  $R_{wo}$  is mass ratio water to oil.

## 3. Measuring Method of Deactivation Function

Using a confined fluidized bed reactor and aromatization catalysts LBO-A, three liquefied petroleum gases (Huabei liquefied petroleum gas, Hua'ebin liquefied petroleum gas and Qilu liquefied petroleum gas) have been studied.

The liquefied petroleum gas material (C4's olefins content), reaction temperature (T), liquefied petroleum gas' detention time (t)



**Fig. 3. The changeable trend of the catalyst's coke yield with material quality and operation conditions.**

and catalyst's detention time ( $t_c$ ) have an influence on the catalyst's coke yield ( $C_{C4}$ ) in the aromatization reaction of C4 liquefied petroleum gas. The experimental data, reaction conditions and C4's olefins content are calculated to regress with the computer. The curve Eq. (29) of relationship between  $C_{C4}$  with C4's olefins content, reaction temperature, liquefied petroleum gas' detention time and catalyst's detention time is expressed as follows:

$$C_{C4} = 38.766 \times [-0.19 - 0.3772 \cdot Z + 0.0024 \cdot T^{0.8771} \cdot t_c^{-0.062}] \cdot t_c^{0.0890} \% \quad (29)$$

From Eq. (29), material quality and operation conditions have an important influence on the catalyst's coke yield. The catalyst's coke yield increases with the increase of C4's olefins content, reaction temperature and catalyst's retention time, but it decreases with the increase of liquefied petroleum gas' retention time.

$[-0.19 - 0.3772 \cdot Z + 0.0024 \cdot T^{0.8771} \cdot t_c^{-0.062}] \cdot t_c^{0.0890}$  is the material quality and operation conditions. The catalyst's coke yield will be calculated with the change of material quality and operation conditions based on the Eq. (29). And the calculated data and the experimental data will be contrasted in Fig. 3. The results from experimental data are in accordance with the quantitative analytical conclusions drawn from the calculated data.

By introducing Eqs. (29) into Eq. (21), it may be shown that:

$$\phi_{C4} = \exp(-\alpha [-0.19 - 0.3772 \cdot Z + 0.0024 \cdot T^{0.8771} \cdot t_c^{-0.062}] \cdot t_c^{0.0890}) \quad (30)$$

It is supposed that the catalyst deactivation constant  $\alpha$  is an unchangeable constant with the increase of reaction temperature. On the other hand, its deactivation function can be applied for different liquefied petroleum gas because of including C4's olefins content.  $\alpha$ 's value will be regressed based on the experimental data. So the liquefied petroleum gas deactivation function equation is obtained as follows:

$$\phi_{C4} = \exp(-0.56 \cdot (-0.19 - 0.3772 \cdot Z + 0.0024 \cdot T^{0.8771} \cdot t_c^{-0.062}) \cdot t_c^{0.0890}) \quad (31)$$

#### 4. Measuring Method of Five Lumped Kinetic Models

The numerical value result of lumped kinetics models are obtained by using modified Marquardt on the basis of Marquardt principle. The lumped kinetics function Eq. (32) is shown as follows:

$$S(k) = \sum [y_{exp} - y_{cal}(t, c(t, k))]^T [y_{exp} - y_{cal}(t, c(t, k))] \quad (32)$$

Where  $k$  is models parameter;  $y$  is variable;  $c$  is concentration;  $T$  is mathematical sign, vector matrix reversal;  $cal$  is calculated value;  $exp$  is experimental value, and where

$$y = (c_1, c_2, \dots, c_n)^T \quad (33)$$

is the concentration function.

$y_{cal}$  is open at  $k^{(0)}$  by using Taylor, and it is supposed that:

$$\frac{\partial S(\Delta k)}{\partial \Delta k} = 0 \quad (34)$$

Eq. (35) is given as follows:

$$\begin{aligned} & \sum \left[ \frac{\partial c}{\partial k} \right]_{k^{(0)}}^T \left[ \frac{\partial y_{cal}}{\partial c} \right]_{k^{(0)}}^T \left[ \frac{\partial y_{cal}}{\partial c} \right]_{k^{(0)}} \left[ \frac{\partial c}{\partial k} \right]_{k^{(0)}} \cdot \Delta k \\ & = \sum \left[ \frac{\partial c}{\partial k} \right]_{k^{(0)}}^T \left[ \frac{\partial y_{cal}}{\partial c} \right]_{k^{(0)}}^T [(y_{exp} - y_{cal}(t, k^{(0)}))] \end{aligned} \quad (35)$$

By definition,  $G = \partial y / \partial a$ ,  $A = \partial a / \partial k$ , may be shown to be:

$$G = \begin{bmatrix} 0 & 1 & 0 & 0 & \dots & 0 \\ 0 & 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 0 & 1 & \dots & 0 \\ M & M & M & M & O & M \\ 0 & 0 & 0 & 0 & \dots & 1 \\ -\frac{M_1}{M_n} & -\frac{M_2}{M_n} & -\frac{M_3}{M_n} & -\frac{M_4}{M_n} & \dots & -\frac{M_{n-1}}{M_n} \end{bmatrix} \quad (36)$$

Every unit of the sensitive matrix can be solved by the difference method. Eq. (37) is shown as follows:

$$A_{ij} = [a(k_1, k_2, \dots, k_j + \Delta k_j, \dots, k_p) - a(k_1, k_2, \dots, k_j - \Delta k_j, \dots, k_p)] / 2\Delta k_j \quad (37)$$

Where  $A$  and  $b$  are defined as follows, respectively:

$$A = \sum A^T G^T G A \quad (38)$$

$$\text{and } b = \sum A^T G^T [y_{exp} - y_{cal}(t, c(t, k^{(0)}))] \quad (39)$$

Using the above parameter simplifies Eq. (35) as follows:

$$A \cdot \Delta k = b \quad (40)$$

**Table 4. Yield of five lumped compounds at 450 °C (wt%)**

No.	WHSV	C4 <sup>-</sup>	C4 <sup>0</sup>	Propylene	Liquid and coke	Low molecule hydrocarbon
1	2.0	22.61	53.04	4.14	19.19	1.02
2	2.5	26.31	52.71	4.13	16.02	0.83
3	3.0	27.85	51.09	4.07	16.30	0.69
4	3.5	29.09	49.70	4.02	16.59	0.61
5	4.0	31.22	49.23	3.71	15.29	0.56
6	4.5	30.62	48.64	4.01	16.25	0.48
7	5.0	34.43	49.07	3.38	12.65	0.48
8	5.5	34.14	48.40	3.26	13.80	0.39
9	6.0	34.41	48.94	3.34	12.87	0.43
10	6.5	36.91	48.94	2.90	10.86	0.40

**Table 5. Yield of five lumped compounds at 500 °C (wt%)**

No.	WHSV	C4 <sup>-</sup>	C4 <sup>0</sup>	Propylene	Liquid and coke	Low molecule hydrocarbon
1	2.0	26.22	53.02	3.96	15.35	1.45
2	2.5	28.68	52.97	4.11	12.91	1.33
3	3.0	28.42	51.56	4.66	14.28	1.07
4	3.5	28.67	50.79	4.53	15.06	0.95
5	4.0	30.42	50.53	4.43	13.71	0.91
6	4.5	33.47	49.89	3.88	11.95	0.81
7	5.0	34.94	49.3	3.51	11.49	0.76
8	5.5	36.18	49.05	3.4	10.65	0.72
9	6.0	34.82	48.2	3.37	12.92	0.69
10	6.5	36.46	48.58	3.21	11.07	0.68

**Table 6. Yield of five lumped compounds at 550 °C (wt%)**

No.	WHSV	C4 <sup>-</sup>	C4 <sup>0</sup>	Propylene	Liquid and coke	Low molecule hydrocarbon
1	2.0	28.74	51.58	4.52	12.89	2.27
2	2.5	28.97	52.91	4.36	11.82	1.94
3	3.0	31.59	51.13	3.87	11.77	1.64
4	3.5	33.39	50.54	3.67	10.98	1.42
5	4.0	34.42	50.32	3.59	10.33	1.34
6	4.5	34.93	49.79	3.57	10.55	1.16
7	5.0	36.03	49.71	3.20	9.99	1.07
8	5.5	37.88	49.02	2.8	9.29	1.01
9	6.0	37.34	48.80	2.98	9.89	0.99
10	6.5	37.89	48.91	2.74	9.55	0.91

**Table 7. Reaction velocity constant of five lumped models in the different temperature ((g/cm<sup>3</sup>)<sup>-1</sup> h<sup>-1</sup>)**

Reaction	Reaction temperature, °C		
	450	500	550
k1	196.79	855.72	1,423.67
k2	645.00	723.74	834.39
k3	58.39	245.63	436.02
k4	243.42	380.41	555.80
k5	209.32	230.61	586.96
k6	104.09	161.60	371.77

After  $\Delta k$  is solved,  $k^*=k+\Delta k$  as the initial value will be computed until the number convergence.

## 5. Experimental Result

By using Huabei liquefied petroleum gas as a feedstock and LBO-A as catalysts and a confined fluidized bed as a reactor, the aromatization reaction of liquefied petroleum gas has been studied at 450 °C, 500 °C, 550 °C, respectively. The experimental results are listed in Tables 4, 5 and 6.

## 6. Resolved Lumped Kinetics Parameter

The lumped kinetics parameters based on the above data are obtained by using the Matlab appliance procedure. The reaction velocity constant in the temperature and active energy and frequency factor are shown in Table 7 and Table 8, respectively.

**Table 8. Active energy and frequency factor of five lumped models**

Reaction	Active energy, KJ/mol	Frequency factor, (g/cm <sup>3</sup> ) <sup>-1</sup> h <sup>-1</sup>
k1	19.83	$5.43 \times 10^3$
k2	13.05	$5.88 \times 10^3$
k3	51.21	$3.01 \times 10^5$
k4	0.42	$2.61 \times 10^3$
k5	51.13	$1.05 \times 10^5$
k6	63.25	$4.00 \times 10^5$

**Table 9. The relative error values (TREV) of calculated value and experimental value of five lumped models at 500 °C**

No.	C4 <sup>-</sup>	C4 <sup>0</sup>	Propylene	Liquid and coke	Low molecule hydrocarbon
1	-5.73	-0.32	14.59	6.24	-7.96
2	-6.93	-1.87	9.32	17.06	-22.53
3	0.22	-0.44	-5.75	3.44	-8.41
4	4.09	0.07	-6.07	-7.10	-0.19
5	2.22	-0.19	-7.22	-2.40	2.35
6	-4.00	0.48	2.83	6.40	12.27
7	-5.44	1.19	9.02	5.78	17.07
8	-6.43	1.32	8.77	8.71	20.79
9	-0.15	2.73	6.43	-15.57	23.34
10	-2.79	1.72	7.80	-3.19	23.57

The relative error values (TREV)=(experimental value-calculated value)/experimental value.

**Table 10. The relative error values (TREV) and experimental value of propylene at the different temperature**

	450 °C		500 °C		600 °C	
	Propylene	TREV	Propylene	TREV	Propylene	TREV
1	4.26	2.71	4.64	14.59	4.56	0.77
2	4.16	0.83	4.53	9.32	4.25	-2.53
3	4.04	-0.64	4.41	-5.75	3.99	2.93
4	3.91	-2.84	4.27	-6.07	3.75	2.18
5	3.77	1.56	4.13	-7.22	3.54	-1.34
6	3.63	-10.51	3.99	2.83	3.35	-6.41
7	3.49	3.21	3.86	9.02	3.19	-0.45
8	3.36	3.00	3.73	8.77	3.03	7.66
9	3.24	-3.23	3.60	6.43	2.89	-3.03
10	3.12	6.96	3.48	7.80	2.78	1.44

Table 9 shows that the relative error values of product yield (C4<sup>-</sup>, C4<sup>0</sup>, propylene, liquid and coke) are below 17%. This indicates that the five lumped kinetics models can describe the product distribution of the liquefied petroleum gas aromatization reaction. But the relative error values of low molecule hydrocarbon are partly above 20%.

Table 10 shows that the relative error values of propylene, which is the aromatization reaction's aim production, at the different temperature (450 °C, 500 °C and 550 °C), are below 10%. That indicates that the five lumped kinetics models can describe the product

distribution of the aimed production and prove the model to have a higher accuracy.

## CONCLUSIONS

In this paper, the author has found that the five lumped kinetics model leads to and is closely in accordance with predicting the practical experimental values. The yield of liquefied petroleum aromatization reactions can be accurately estimated. The four lump models point out that deeply comprehending the reaction mechanism of the aromatization of liquefied petroleum gas not only has a very important significance, but also provides a theoretical foundation for the chemical plant. It is important for the aromatization of liquefied petroleum gas to design and operate correctly and optimize the reaction processing and increase the plant's benefits. This mathematical method is effective, economic, simple and convenient and thus it is suitable for refineries in China.

## NOMENCLATURE

$c_j$  : concentration of component j [kmol/m<sup>3</sup>]  
 $u$  : liquefied petroleum gas linear velocity of a fluidized bed [m/s]  
 $\Omega$  : lateral section of a fluidized bed [m<sup>2</sup>]  
 $r_j$  : reaction velocity of Component j [kmol/(s·m<sup>3</sup>)]  
 $\rho$  : liquefied petroleum gas density of a fluidized bed [kg/m<sup>3</sup>]  
 $p$  : reaction pressure [Mpa]  
 $\overline{MW}$  : mean molecular weight [kg]  
 $R$  : atmosphere constant  
 $T$  : reaction temperature [K]  
 $\rho_{cat}$  : catalyst's density [kg/m<sup>3</sup>]  
 $\psi_{c/o}$  : mass ratio catalyst to oil  
 $\alpha$  : catalyst's deactivation constant

$C_{c4}$  : catalyst's coke yield [s]  
 $L$  : reactor's high [m]  
 $v_{ij}$  : chemistry measuring coefficient of lump I becoming to lump J  
 $k_{ij}$  : velocity constant of lump I becoming to lump J  
 $M_i$  : relative molecule quality;  $R_{wo}$  is mass ratio water to oil

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