

## DEVELOPMENT OF COMPUTER MODELLING SYSTEM AS A TOOL FOR LIGHT NAPHTHA ISOMERIZATION IMPROVEMENT

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### Abstract

Prediction and optimization of light naphtha isomerization is a complicated technological issue and includes a variety of factors and many independent parameters. The most effective solution is to use the mathematical modelling method of physical and chemical characteristic of the process. The comprehensive mathematical model was designed as a powerful tool for optimization. It is based on the influence of the feedstock composition for assessment of the current catalyst activity. According to the calculations, the optimal operating parameters are determined by the refined feedstock composition.

**Keywords:** mathematical modelling, isomerization, rectification, efficiency improvement.

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## 1. Introduction

The decrease in aromatic hydrocarbon content of gasoline can be achieved by blending reformat, alkylate and isomerate while meeting high octane rating [1]. Also the isomerization process allows refining the low octane light fractions thereby increasing the overall yield of gasoline. However the maximum conversion of low octane C<sub>5</sub>-C<sub>6</sub> hydrocarbons into high octane dimethylbutanes corresponds to low process temperature which reduces the kinetic factor of reactants conversion. Currently, a great number of works are devoted to the synthesis and experimental study of new catalysts for the isomerization [13-20], besides a lot of attention is paid to the study of the hydrocarbons conversion mechanism during the catalytic isomerization process [2-3]. According to [13, 18], the main problems arise in the study of the mechanism of carbenium ion formation, catalyst acidity role of different promoters and hydrogen in the process. Optimization and prediction of light naphtha isomerization process is a complex technological problem. The most effective solution of this problem is the use of mathematical simulation method of physical and chemical laws of the process.

Application of mathematical modelling method in kinetic and technological analysis of different industrial process provides the ability to estimate kinetic parameters of different types of catalysts by solving the reverse kinetic task and predicting of current and steady activity, selectivity and operating period in industrial conditions [19-20].

## 2. Research subject

The subject of the study is an industrial isomerization of pentane-hexane fraction L-35-11/300, and a naphtha after fractionating block units for primary processing of CVDU - 6, CDU-6, CVDU - 2, CDU-1 oil. Block diagram of the process is shown in fig. 1.

The isomerization process of pentane-hexane fraction of straight-run gasoline at the L-35-11/300 is implemented as a three-reactor scheme "per pass". Hydrotreated feedstock is fed

through the mixing unit with a hydrogen containing gas in the furnace 1, where it is heated to the reaction temperature, it passes successively three isomerization reactors and fed to the separation unit (separators S-7, S-8) for separating the gas containing hydrogen and light hydrocarbon gases. Unstable isomerate is fed to close fractionation block (distillation column C-6, C-7) for separation of dry gas formed during the cracking side reactions. In this process, the implementation of the research octane number of the isomerate obtained is in the range of 82 - 84 points.

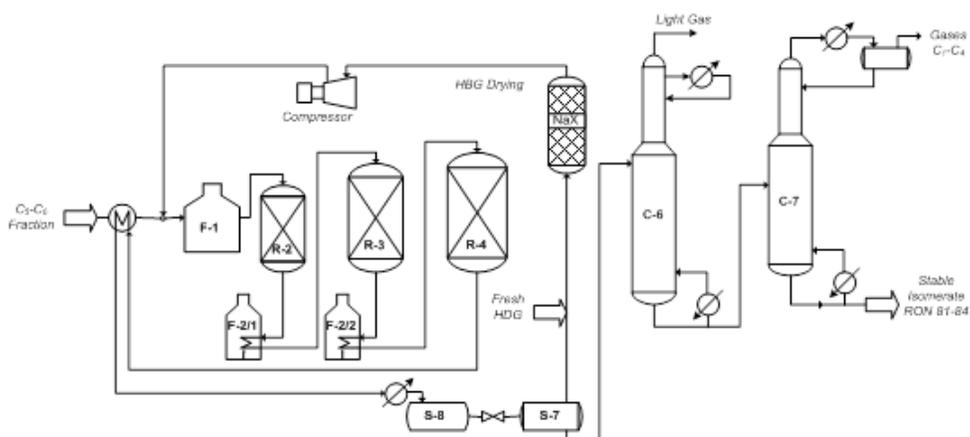


Figure 1. Block diagram of the light naphtha isomerization process

The raw material of the isomerization process is a fraction of the IBP-62° C, coming from the stabilization unit and the after fractionating column block of the straight-run naphtha. A block diagram of the process of material flows preparation of unstable gasoline is shown in fig 2.

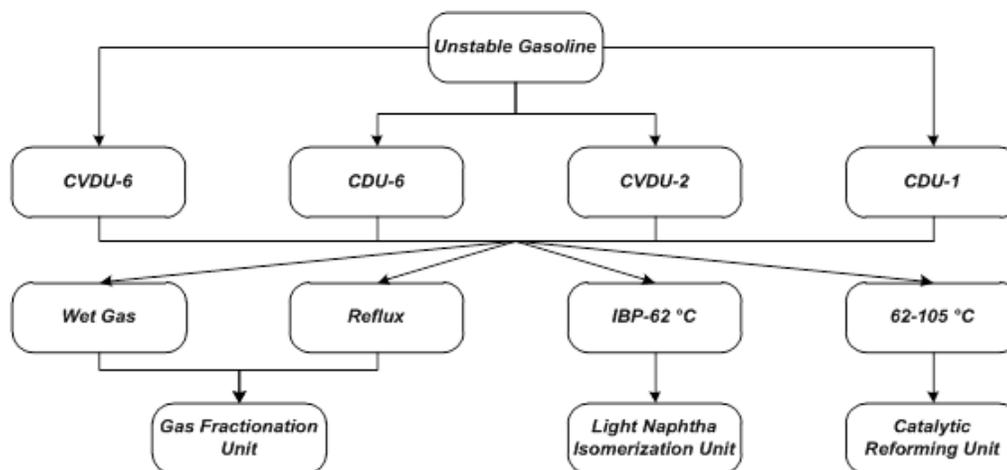


Figure 2. Block scheme of unstable gasoline material streams

The quality of the raw material supplied to the isomerization unit L-35-11/300 is determined by the operating of the block stabilization column block and after fractionating column block of the straight-run naphtha (CVDU-6 CDU-6, CVDU-2, CDU-1). During the stabilization process it is necessary to achieve the maximum separation of the light gases and pentane, filler component of the isomerization process. In dividing IBP-180°C fractions, it is important to maximize the content of hydrocarbons C5-C7 at IBP-105°C fraction. The effectiveness of further IBP-105°C fraction separation is determined by the maximum concentration of hydrocarbons in the C5-C6 in IBP - 62°C fraction. The stabilization and after fractionation unit block-scheme is shown in fig. 3.

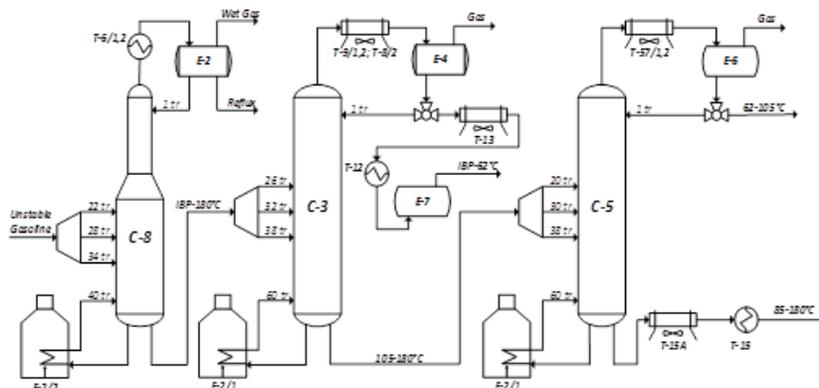


Figure 3. Block-scheme of stabilization and after fractionation unit (CVDU-6)

Unstable gasoline enters the column-stabilizer C-8 for wet gas and reflux separation. IBP-62°C fraction separates in column C-3 and flows as a feedstock to light naphtha isomerization unit L-35-11/300. In column C-5 fractionation of 105-180°C fraction to 62-105°C and 85-180°C occurs.

### 3. Experimental

#### 3.1. Thermodynamics

Linear paraffins have low polarity and strong C-H bonds [3] that is why they have an inert behaviour. Since branched alkanes are thermodynamically more stable than linear alkanes, catalytic conversion into branched isomers are possible.

At any given temperature and pressure the system is in the equilibrium when the Gibbs free energy of any possible reaction is zero.

$$\Delta G = \sum_i \nu_i \bar{G}_i = 0 = \sum_i \nu_i \mu_i = 0$$

In the first step thermodynamic analysis of isomerization reaction was provided. In the tab. 1 the results is shown.

Table 1. Thermodynamic analysis of isomerization process

#	Reactions	$\Delta G$ (kJ/mol)		#	Reactions	$\Delta G$ (kJ/mol)	
		300 K	600 K			300 K	600 K
1	$n-C_5H_{12} \rightarrow i-C_5H_{12}$	-6.46	-4.75	15	$n-C_6H_{14} + H_2 \rightarrow Gas$	-198.00	-294.50
2	$n-C_6H_{14} \rightarrow 2-MP$	-4.75	-2.60	16	$2-MP + H_2 \rightarrow Gas$	-193.30	-291.90
3	$n-C_6H_{14} \rightarrow 3-MP$	-1.85	-0.73	17	$3-MP + H_2 \rightarrow Gas$	-196.20	-295.20
4	$2,3-DMB \rightarrow 2-MP$	-0.97	-5.73	18	$2,3-DMB + H_2 \rightarrow Gas$	-194.20	-297.60
5	$2,3-DMB \rightarrow 2,2-DMB$	-5.53	-3.45	19	$2,2-DMB + H_2 \rightarrow Gas$	-188.70	-294.20
6	$n-C_7H_{16} \rightarrow i-C_7H_{16}$	-3.38	-2.26	20	$n-C_7H_{16} + H_2 \rightarrow Gas$	-165.50	-234.10
7	$MCP \rightarrow CH$	-3.92	-8.75	21	$i-C_7H_{16} + H_2 \rightarrow Gas$	-162.10	-231.80
8	$3-MP \rightarrow 2-MP$	-2.90	-3.34	22	$CH + H_2 \rightarrow Gas$	-71.19	-110.80
9	$c-C_5H_{10} + H_2 \rightarrow n-C_5H_{12}$	-86.30	-192.79	23	$MCP + H_2 \rightarrow 2-MP$	-79.86	-104.70
10	$c-C_5H_{10} + H_2 \rightarrow i-C_5H_{12}$	-92.76	-197.57	24	$MCP + H_2 \rightarrow 3-MP$	-79.96	-104.70
11	$n-C_4H_{10} + H_2 \rightarrow Gas$	-262.70	-414.70	25	$MCP + H_2 \rightarrow 2,2-DMB$	-84.43	-102.40
12	$i-C_4H_{10} + H_2 \rightarrow Gas$	-258.90	-415.60	26	$MCP + H_2 \rightarrow 2,3-DMB$	-78.90	-98.97
13	$n-C_5H_{12} + H_2 \rightarrow Gas$	-230.70	-355.00	27	$B + 3H_2 \rightarrow CH$	-214.90	-254.20
14	$i-C_5H_{12} + H_2 \rightarrow Gas$	-242.20	-350.30	28	$B + 3H_2 \rightarrow MCP$	-211.00	-263.00

According to the thermodynamics all of the reactions taking place in isomerization process are feasible within the wide temperature range. Accounting for all said above, the following hydrocarbons reaction scheme is complete based on experimental data from the industrial isomerization unit (Fig. 4).

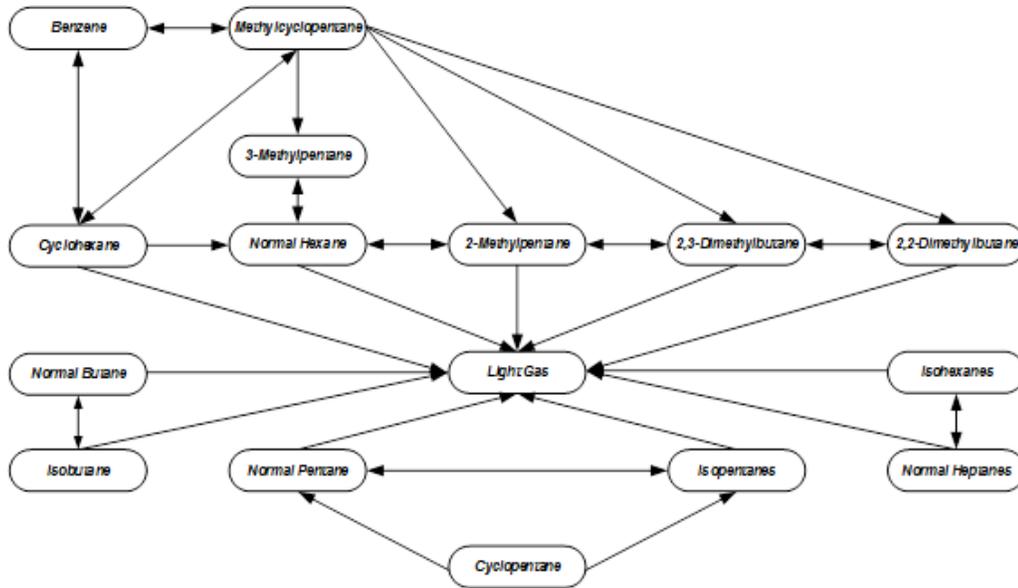


Figure 4. Formalized reaction scheme for isomerization process

### 3.2. Kinetics

According to the chemical reaction rate law elementary reaction rate at the set temperature is proportional to concentration of reacting substances in the degrees showing number of particles entering interaction:

$$r = k \cdot f(C)$$

$$f(C) = C_1^{v_1} \cdot C_2^{v_2} \dots C_n^{v_n}$$

Applying this formalization level for isomerization process the isocomponents change during the reverse reaction can be presented in the equation:

$$\frac{dC_i}{dt} = \sum_j k_j^{app} \cdot C_i \cdot C_{H_2}^{l_j}, \text{ while } t = 0, C_i = C_{i0},$$

In this paper, kinetic parameters for light naphtha isomerization process on bifunctional Pt/SO<sub>4</sub>-ZrO<sub>2</sub> catalyst were determined by solving the reverse kinetic problem. Also rate constants for other types of catalyst were found. The relative rate constants for major reactions are presented in tab. 2.

Table 2. The relative rate constants for major isomerization reactions for different types of catalyst.

Reaction	Pt/SO <sub>4</sub> -ZrO <sub>2</sub>	Pt/zeolite	Pt/Al <sub>2</sub> O <sub>3</sub> -CCl <sub>4</sub>
<i>n</i> -C <sub>5</sub> H <sub>12</sub> → <i>i</i> -C <sub>5</sub> H <sub>12</sub>	1.00	0.48	0.31
<i>i</i> -C <sub>5</sub> H <sub>12</sub> → <i>n</i> -C <sub>5</sub> H <sub>12</sub>	1.00	1.43	0.96
2-Methylpentane → 3-Methylpentane	1.00	1.43	0.96
<i>n</i> -C <sub>6</sub> H <sub>14</sub> → 2-Methylpentane	1.00	0.52	1.72
2-Methylpentane → 2.3 Dimethylbutane	1.00	1.10	0.47
2.2 Dimethylbutane → 2.3 Dimethylbutane	1.00	0.91	1.63

According to the data presented in tab. 2, Pt/SO<sub>4</sub>-ZrO<sub>2</sub> owns the best performance and allows for production of isomerate with higher RON.

### 3.3. Mathematical model

For the description of complicated chemical-technological system in complex, the method of mathematical modelling of physical and chemical principals of reacting and fractionating processes was used [4-12].

Calculation of stabilization and after fractionation unit was performed with Aspen HYSYS software. Initial data for calculation are unstable gasoline fraction composition, distillation columns construction, and operating parameters of distillation process. Block-scheme of complex mathematical model is shown in fig. 5.



For the industrial isomerization of light gasoline cuts in the fixed bed reactor the ideal plug flow models are widely applied [12].

The model of isomerization reactor is presented by system of material and heat balance differential equations:

$$\begin{cases} G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^m a_j \cdot r_j \\ G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^m} \cdot \sum_{j=1}^m Q_j \cdot a_j \cdot r_j \end{cases}$$

if  $Z=0, C=0$ , where  $r=0, C=C_0$ , if  $Z=0, T=T_0$ , where  $r=0, T=T_{in}$ ;

This reactor model takes into account the reduction in catalyst activity in time. The catalyst activity is defined as current rate constant and initial rate constant (on the fresh catalyst) ratio:

$$a_j = \frac{k_{j,current}}{k_{j,initial}}$$

The software of isomerization reactor is developed with Borland Delphi 7.0. The model was validated by experimental data of the industrial isomerization unit L-35-11/300 (tab. 3).

Table 3. The adequacy of the isomerization reactor model

Component	Isomerate, % wt.	
	Calculated	Existing
n-C <sub>4</sub>	0.53	0.54
i-C <sub>4</sub>	0.90	0.86
n-C <sub>5</sub>	12.71	12.67
i-C <sub>5</sub>	35.06	35.05
n-C <sub>6</sub>	5.56	5.22
2-Methylpentane	13.87	13.90
3-Methylpentane	7.56	7.59
2,2-Dimethylbutane	11.10	11.08
2,3-Dimethylbutane	4.21	4.15
n-C <sub>7</sub>	0.00	0.00
Sum i-C <sub>7</sub>	2.97	2.99
Sum C <sub>8</sub>	1.41	1.39
Cyclopentane	0.84	0.82
Methylcyclopentane	0.21	0.20
RON	80.63	80.61

Validation of the performed reactor model have shown the error lies within 1 – 2 %. Thus, this model provides with satisfactory predicting ability to be used for simulation of the real process.

#### 4. Results and discussion

The composition of raw material processed at light naphtha isomerization unit L-35-11/300 widely varies, which certainly affects the quality of the products and also makes it necessary to adjust the technological parameters of the unit.

Investigation of the influence of feedstock on the quality of isomerate performed at a constant process parameters:

- Feedstock rate, m<sup>3</sup>/h . . . . . 90;
- R-2 Inlet Temperature, °C . . . . . 136;
- R-2 Inlet Pressure, kg/cm<sup>2</sup> . . . . . 30.

According to results shown in fig. 6, the isomerate RON can range 1 to 1.5 points depending on the feedstock constitution. The difference in isomerate RON is explained by different key components (normal-pentane, normal hexane) content in the feedstock (tab. 4). Also cyclohexane and methylcyclopentane content influences on isomerate RON because it's negative effect on branched alkanes formation process.

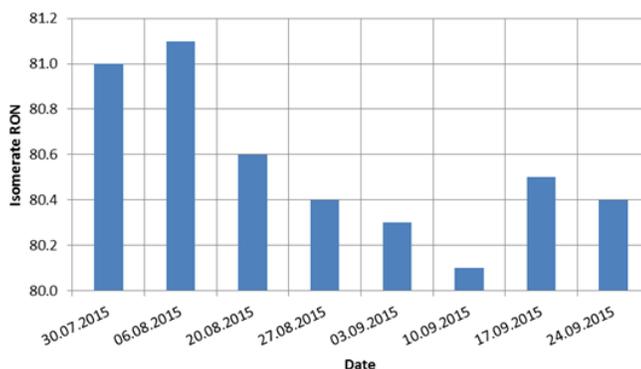


Figure 6. The influence of feedstock composition change on isomerate RON

Table 4.Components content in the isomerization process feedstock

Data	Component content, % mas.			
	Normal Pentane	Normal Hexane	Methylcyclopentane	Cyclohexane
14.05.2015	31.95	15.82	4.85	0.37
21.05.2015	30.43	18.12	6.25	1.01
28.05.2015	29.86	18.98	6.76	1.84
04.06.2015	29.66	19.56	7.40	2.04
11.06.2015	24.79	21.10	7.90	2.03
18.06.2015	29.44	18.67	7.13	2.13
25.06.2015	28.97	19.68	7.58	2.28
02.07.2015	33.79	16.99	5.48	0.39
09.07.2015	30.11	19.01	6.99	1.58
16.07.2015	32.53	16.00	5.54	1.99
23.07.2015	31.76	17.31	6.35	1.85
30.07.2015	33.29	16.70	5.89	1.32
06.08.2015	32.31	17.52	6.25	0.72

In such a way for reaching a maximum isomerate RON in constant operating parameters of isomerization reactors it is necessary to match optimal technological parameters of stabilization and after fractionation units in order to provide maximum content of normal C<sub>5</sub> –

C<sub>6</sub> hydrocarbons and reduction of undesirable components (methylcyclopentane and cyclohexane).

Optimization of stabilization and after fractionation columns operating parameters using complex mathematical model of distillation and catalytic conversion of hydrocarbon feedstock allows to increase isomerate RON in 1.5-2.0 points.

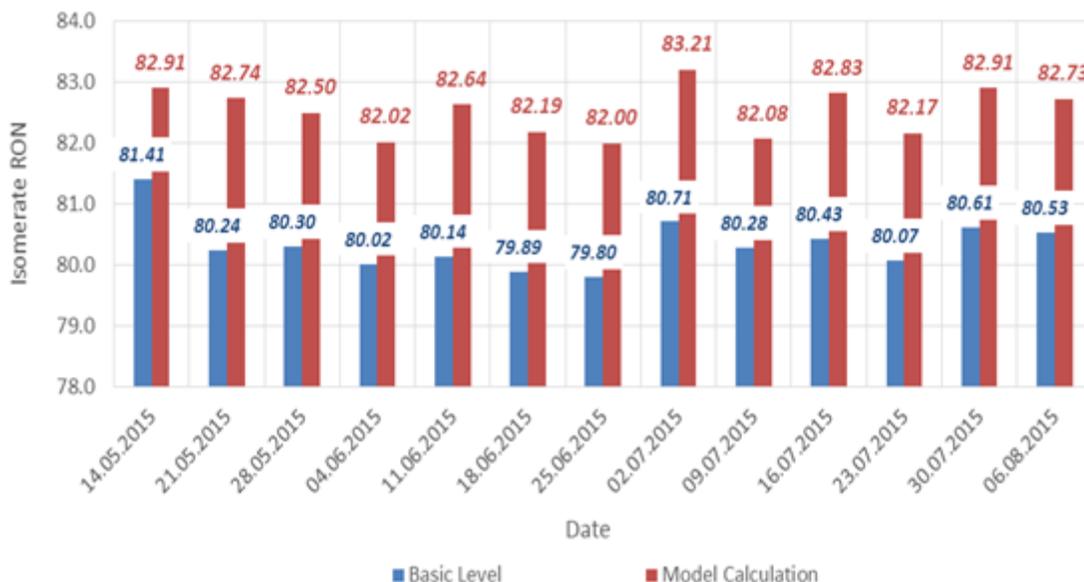


Figure 7. The boost in isomerate RON provided by stabilization and after fractionation columns operation parameters optimization.

## 5. Conclusion

Application of complex mathematical model of distillation and catalytic conversion of hydrocarbon feedstock allows to take into account the influence of operating parameters and feedstock constitution on product quality.

In dependence of feedstock composition isomerate RON can vary in 1.0-1.5 points. That is why it is necessary to correct operating parameters of stabilization and after fractionation units.

Optimization of stabilization and after fractionation blocks of CVDU-6, CDU-6, CVDU-2 and CDU-1 allows to increase isomerate RON in 1.5-2.0 points in dependence on feedstock composition.

### List of symbols

CVDU	Crude Vacuum Distillation Unit;
CDU	Crude Distillation Unit;
IBP	Initial Boiling Point;
$\Delta G$	change in Gibbs energy of reaction, kJ/mole;
MP	Methylpentane;
DMB	Dimethylbutane;
CH	Cyclohexane;
MCP	Methylcyclopentane;
B	Benzene;
$r$	reaction rate;
$k$	rate constant;
$C_i$	initial reactant concentrations;
$v_i$	stoichiometric coefficient;
$j$	1, ..., m - number of chemical reaction;
$C_i$	hydrocarbon concentration;

$k_j^{app}$	apparent rate constant;
$l_j$	reaction order on hydrogen;
$t$	time, s;
$G$	a feedstock flow rate, $m^3/h$ ;
$z$	$G*t$ ( $t$ is a overall time of catalyst work starting from the new catalyst load, h);
$C_i$	a concentration of $i$ th component, $mol/m^3$ ;
$V$	is a volume of the catalyst bed, $m^3$ ;
$a$	a catalyst activity;
$\rho$	density of hydrocarbon mixture, $kg/m^3$ ;
$C_p^m$	a specific heat capacity of hydrocarbon mixture, $J/(kg*K)$ ;
$Q_j$	$j$ th reaction heat, $J/mol$ ,
$T$	temperature, $K$ ;
$r_j$	$j$ th reaction rate, $mol/(m^3 h)$ .
$k_{j,initial}$	the rate constant of $j$ -th reaction on the fresh catalyst;
$k_{j,current}$	the rate constant of $j$ -th reaction on the catalyst at present time;

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