Improvement of resource efficiency of the catalytic isomerization process by mathematical modeling

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Abstract. The article examines main schemes of reaction networks of the catalytic isomerization of the pentane-hexane fraction. The selection of the kinetic model for the most complete description of the basic chemical processes based on the mechanism of the reactions proceeding is substantiated. The mathematical model is constructed on the basis of kinetic model. The foundations for the subsequent modeling of the entire chemical-technological process system are laid.

1. Introduction

In connection with the change-over of the domestic oil refining industry to the production of motor gasoline compliant with the Euro-5 and Euro-6 standards, the current task is to reduce the content of aromatic hydrocarbons and, in particular, benzene in motor fuel while preserving the octane value. It is known that the main amount of aromatics in motor gasolines is formed in the process of catalytic reforming. Catalytic isomerization of light paraffins, in its turn, makes it possible to obtain a high-octane component of motor gasoline with a minimum content of aromatics. The purpose of the process of catalytic isomerization of the pentane-hexane fraction is the production of high-octane components of automobile gasolines. This process has a high efficiency, because such low-octane oil components as fractions 62-70 ^{0}C, as well as catalytic reforming raffinates are used as raw materials. The process is carried out in a hydrogen environment in the presence of bifunctional catalysts [1, 2].

It should be noted that in the postwar years, during the design and construction of most installations, including reactors and devices, inadequate attention has been given to an intensive study of the mechanism of processes. The intensive development of such modern information technologies as parallel computing technology, artificial neural networks (ANN), 3D modeling, simulation modeling, etc., allow us to develop detailed kinetic models of complex processes. Then, based on these models, it is possible to increase significantly the yield of the target product, while minimizing energy and material resources [3].

There are often problems associated with the description of kinetics when studying refining processes. First of all it can be associated with a large component composition of raw materials, as well as the flow of a huge number of chemical reactions taking place on the acid and metal centers of bifunctional catalysts [4, 5]. In this connection, to simplify the description of the kinetics, the stage of formation of the intermediates that are not present in the composition of the target products is usually not considered.

2. Experimental

The object of the study is the reactor section of the catalytic isomerization unit of the pentane-hexane fraction, consisting of three series reactors. Hydrotreated gasoline fraction with a boiling range of 62-70 ° C, containing mainly pentane and hexane was used as a raw material.

The raw material load was 47.6 m3 / h. Consumption of hydrogen bearing gas (HBG) – 3400 nm^3/h. The composition of the fresh HBG is shown in Table. 1. The pressure in the reaction zone was 3.2 MPa. The temperatures at the inlet of the first, second and third reactors were 147, 160 and 145 ° C, respectively. The temperatures at the outlet of the first, second and third reactors were 160, 170 и 146 ^{0}C, respectively. The bifunctional catalyst of the domestic production SI-2 was used as the catalyst of the process. As noted, the reactor unit of the research object consists of three reactors in which the catalyst was distributed at 9,000 kg.

Table 1. The composition of fresh HBG.

Component	Mass fraction of components, % (GOST 14920)
Nitrogen	1.44
Hydrogen	83.61
Isobutane	0.4
Isopentane	0.99
Oxygen	0.58
Methane	8.18
n-butane	0.16
n-pentane	0.14
Propane	1.06
C_5H_{10} (sum)	0.43
Ethane	3.01

Characteristics of raw materials and product (stable isomerizate) are given in Table. 2 (operation data of the industrial unit for the catalytic isomerization of the pentane-hexane fraction).

Table 2. Characteristics of raw materials and product.

Analyzed indicator	Method	Value	
		Raw material	Stable isomerate
Density at 20 ° C, kg / m3	GOST R 51069	653.6	643.2
Octane number (research method)	GOST 8226	67	81
Fractional composition, ^{0}C	GOST 2177		
boiling point		42	36
90% boils away		62	59
97% boils away		64	63
end of boiling		65	64
Yield, %		98	98

The composition of raw material and product of the catalytic isomerization process of the pentane-hexane fraction is given in Table 3 shows (industrial unit data).

It is obvious that for developing a detailed kinetic model it is enough to model only a cascade of reactors. The composition of the gas product mixture after the reactor unit is calculated from the product data after the stabilization unit, that is available. Here it should be noted that with such a calculation, the indicators of productive flows have a large effect on the final result.

In such cases, the instruments error can reach 5% for flows in the gaseous state and 3% for the flows in the liquid state. Therefore, the use of such data without preliminary verification (balance on carbon and hydrogen) is absolutely unacceptable.

Table 3. The composition of raw material and product.

Component	Raw material, % weight	Isomerizate, % weight
2,2- DMB	0.36	21.13
2,3- DMB	2.15	6.57
2-MP	19.32	19.58
3-MP	14.73	11.23
Benzene	1.25	-
Isopentane	10.75	23.56
Methylcyclopentane	2.7	0.12
N-hexane	18.19	7.27
N-pentane	30.81	7.80
Isobutane	-	1.04
N-butane	-	0.87
Propane	-	0.61
Ethane	-	0.13
Methane	-	0.09

where 2-MP – 2-methylpentane, 3-MP – 3-methylpentane, 2.2-DMB – 2.2-dymethylbutane, 2.3-DMB – 2.3-methylbutane.

3. Scheme of reaction networks of the catalytic isomerization of the pentane-hexane fraction

The first stage of the mathematical description of the object is the scheming of hydrocarbon reactions during the process. It should be noted that the accuracy of calculations and the adequacy of the mathematical model to the actual process directly depend on the degree of detail of chemical transformations. Therefore, the transformation scheme should sufficiently reflect the physico-chemical nature of the process [6, 7].

In this article there was an attempt to make more detailed analysis of the scheme of reaction networks proceeding from the mechanism.

It is known that reactions in the process of isomerization in the presence of bifunctional catalysts proceed along the carbon-ion mechanism [8-10]. The thermodynamics of the process is the basis. The result of thermodynamic analysis is a list of reactions that probably proceed under given conditions [11, 12]. The probability of reactions under the process conditions of the catalytic isomerization of the pentane-hexane fraction (temperature-150 ° C (423 K) and pressure-3.2 MPa) was estimated from the value of Gibbs energy ΔG (Table 4).

From the Table 4 we can see that isomerization, dehydrocyclization, naphthene conversion, dehydrogenating reactions are reversible. Whereas hydrocracking reactions are irreversible [13].

According to the equations of reactions taking place in the process of catalytic isomerization of the pentane-hexane fraction, we write the kinetic equations as follows (Table 5).

Table 4. The reaction equations for the catalytic isomerization of the pentane-hexane fraction and the values of the thermodynamic characteristics.

	Reaction	ΔH, kJ/mol	ΔG, kJ/mol
1.	$n\text{-}C_5H_{12} \leftrightarrow i\text{-}C_5H_{12}$	-8.22	-5.76
2.	$n\text{-}C_6H_{14} \leftrightarrow$ 2-MP	-6.98	-3.77
3.	$n\text{-}C_6H_{14} \leftrightarrow$ 3-MP	-4.44	-7.60
4.	$n\text{-}C_6H_{14} \leftrightarrow$ 2.2-DMB	-18.53	-5.60
5.	$n\text{-}C_6H_{14} \leftrightarrow$ 2.3-DMB	-10.93	-0.99
6.	2-MP ↔ 3- MP	-2.54	-3.02
7.	2.2-DMB ↔ 2.3-DMB	-7.61	-4.61
8.	BZ $+H_2 \leftrightarrow$ CH	-213.94	-52.65
9.	BZ $+H_2 \leftrightarrow$ MCP	-197.03	-53.83
10.	CH ↔ MCP	-112.34	49.10
11.	$n\text{-}C_6H_{14} \leftrightarrow$ CH$+H_2$	8.57	7.82
12.	2-MP ↔ MCP + H_2	-66.96	-29.59

13.	$3\text{-}MP \leftrightarrow MCP + H_2$	-64.42	-26.58
14.	$2.2\text{-}DMB \leftrightarrow MCP + H_2$	-78.51	-31.43
15.	$2.3\text{-}DMB \leftrightarrow MCP + H_2$	-70.91	-26.82
16.	$MCP + H_2 \rightarrow 3\text{-}MP$	-64.42	-26.58
17.	$n\text{-}C_5H_{12}+ H_2 \rightarrow C_3H_8+C_2H_6$	-44.49	-49.96
18.	$n\text{-}C_5H_{12}+ H_2 \rightarrow n\text{-}C_4H_{10}+CH_4$	-56.57	-61.66
19.	$n\text{-}C_6H_{14}+ H_2 \rightarrow 2C_3H_8$	-37.94	-48.88
20.	$n\text{-}C_6H_{14}+ H_2 \rightarrow n\text{-}C_4H_{10}+C_2H_6$	-45.91	-51.80
21.	$n\text{-}C_6H_{14}+ H_2 \rightarrow n\text{-}C_5H_{12}+CH_4$	-56.14	-47.34
22.	$n\text{-}C_6H_{14}+ H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	-64.35	-66.71
23.	$2\text{-}MP + H_2 \rightarrow i\text{-}C_4H_{10}+C_2H_6$	-47.38	-49.82
24.	$3\text{-}MP + H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	-59.91	-65.95
25.	$2.3\text{-}DMB +H_2 \rightarrow i\text{-}C_4H_{10}+C_2H_6$	-43.44	-52.63
26.	$2.3\text{-}DMB +H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	-53.43	-65.71
27.	$i\text{-}C_5H_{12}+ H_2 \rightarrow i\text{-}C_4H_{10}+ CH_4$	-56.82	-57.71
28.	$2.2\text{-}DMB +H_2 \rightarrow i\text{-}C_4H_{10}+C_2H_6$	-35.83	-48.05
29.	$2.2\text{-}DMB +H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	-45.82	-61.11

where 2-MP – 2-methylpentane, 3-MP – 3-methylpentane, 2.2-DMB – 2.2-dymethylbutane, 2.3-DMB – 2.3-methylbutane, CH – cyclohexane, MCP – methylcyclopentane, BZ – benzene.

Table 5. Kinetic equations of the process of catalytic isomerization of pentane-hexane fraction.

	Reaction	Kinetic equations
1.	$n\text{-}C_5H_{12} \leftrightarrow i\text{-}C_5H_{12}$	$W_1=k_1*x_1-k_2*x_2$
2.	$n\text{-}C_6H_{14} \leftrightarrow 2\text{-}MP$	$W_2=k_3*x_3-k_4*x_4$
3.	$n\text{-}C_6H_{14} \leftrightarrow 3\text{-}MP$	$W_3=k_5*x_3-k_6*x_5$
4.	$n\text{-}C_6H_{14} \leftrightarrow 2,2\text{-}DMB$	$W_4=k_7*x_3-k_8*x_6$
5.	$n\text{-}C_6H_{14} \leftrightarrow 2,3\text{-}DMB$	$W_5=k_9*x_3-k_{10}*x_7$
6.	$2\text{-}MP \leftrightarrow 3\text{-}MP$	$W_6=k_{11}*x_4-k_{12}*x_5$
7.	$2.2\text{-}DMB \leftrightarrow 2.3\text{-}DMB$	$W_7=k_{13}*x_6-k_{14}*x_7$
8.	$BZ +H_2 \leftrightarrow CH$	$W_8=k_{15}*x_8*x_9^3-k_{16}*x_{10}$
9.	$BZ +H_2 \leftrightarrow MCP$	$W_9=k_{17}*x_8*x_9^3-k_{18}*x_{11}$
10.	$CH \leftrightarrow MCP$	$W_{10}=k_{19}*x_{10}-k_{20}*x_{11}$
11.	$n\text{-}C_6H_{14} \leftrightarrow CH+H_2$	$W_{11}=k_{21}*x_3-k_{22}*x_{10}*x_9$
12.	$2\text{-}MP \leftrightarrow MCP + H_2$	$W_{12}=k_{23}*x_4-k_{23}*x_{11}*x_9$
13.	$3\text{-}MP \leftrightarrow MCP + H_2$	$W_{13}=k_{25}*x_5-k_{26}*x_{11}*x_9$
14.	$2.2\text{-}DMB \leftrightarrow MCP + H_2$	$W_{14}=k_{27}*x_6-k_{28}*x_{11}*x_9$
15.	$2.3\text{-}DMB \leftrightarrow MCP + H_2$	$W_{15}=k_{29}*x_7-k_{30}*x_{11}*x_9$
16.	$MCP + H_2 \rightarrow 3\text{-}MP$	$W_{16}=k_{31}*x_{11}*x_9$
17.	$n\text{-}C_5H_{12}+ H_2 \rightarrow C_3H_8+C_2H_6$	$W_{17}=k_{32}*x_1*x_9$
18.	$n\text{-}C_5H_{12}+ H_2 \rightarrow n\text{-}C_4H_{10}+CH_4$	$W_{18}=k_{33}*x_1*x_9$
19.	$n\text{-}C_6H_{14}+ H_2 \rightarrow 2C_3H_8$	$W_{19}=k_{34}*x_3*x_9$
20.	$n\text{-}C_6H_{14}+ H_2 \rightarrow n\text{-}C_4H_{10}+C_2H_6$	$W_{20}=k_{35}*x_3*x_9$
21.	$n\text{-}C_6H_{14}+ H_2 \rightarrow n\text{-}C_5H_{12}+CH_4$	$W_{21}=k_{36}*x_3*x_9$
22.	$n\text{-}C_6H_{14}+ H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	$W_{22}=k_{37}*x_3*x_9$
23.	$2\text{-}MP + H_2 \rightarrow i\text{-}C_4H_{10}+C_2H_6$	$W_{23}=k_{38}*x_4*x_9$
24.	$3\text{-}MP + H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	$W_{24}=k_{39}*x_5*x_9$
25.	$2.3\text{-}DMB +H_2 \rightarrow i\text{-}C_4H_{10}+C_2H_6$	$W_{25}=k_{40}*x_7*x_9$
26.	$2.3\text{-}DMB +H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	$W_{26}=k_{41}*x_7*x_9$
27.	$i\text{-}C_5H_{12}+ H_2 \rightarrow i\text{-}C_4H_{10}+ CH_4$	$W_{27}=k_{42}*x_2*x_9$
28.	$2.2\text{-}DMB +H_2 \rightarrow i\text{-}C_4H_{10}+C_2H_6$	$W_{28}=k_{43}*x_6*x_9$
29.	$2.2\text{-}DMB +H_2 \rightarrow i\text{-}C_5H_{12}+CH_4$	$W_{29}=k_{44}*x_6*x_9$

where x_i – concentration of components in mole fractions, x_1 – n-pentane, x_2 – isopentane, x_3 – n-hexane, x_4 – 2-MP, x_5 – 3-MP, x_6 – 2,2-DMB, x_7 – 2,3-DMB, x_8 – benzene, x_9 – hydrogen, x_{10} – cyclohexane, x_{11} – methylcyclopentane, x_{12} – propane, x_{13} – ethane, x_{14} – н-butane, x_{15} – methane, x_{16}

– isobutane, k_j – kinetic constant of the j-th reaction, $L\cdot mol^{-1}\cdot h^{-1}$ (j=8, 9, 11-29), h^{-1} (j=1-7, 10), W_j – rate of the j-th reaction, mol/(l·h).

The reaction rates entering into the kinetic model (Table 5) were written according to the law of mass action [14]. The mathematical model of the process is a system of nonlinear differential equations [15, 16]:

$$\begin{cases}
\dfrac{dx_1}{dt} = -W_1 - W_{17} - W_{18} + W_{21} \\
\dfrac{dx_2}{dt} = W_1 + W_{22} + W_{23} + W_{24} + W_{26} - W_{27} + W_{29} \\
\dfrac{dx_3}{dt} = -W_2 - W_3 - W_4 - W_5 - W_{11} - W_{19} - W_{20} - W_{21} - W_{22} \\
\dfrac{dx_4}{dt} = W_2 - W_6 - W_{12} - W_{23} \\
\dfrac{dx_5}{dt} = W_3 + W_6 - W_{13} + W_{16} - W_{24} \\
\dfrac{dx_6}{dt} = W_4 - W_7 - W_{14} - W_{28} - W_{29} \\
\dfrac{dx_7}{dt} = W_5 + W_7 - W_{15} - W_{25} - W_{26} \\
\dfrac{dx_8}{dt} = -W_8 - W_9 \\
\dfrac{dx_9}{dt} = -3W_8 - 3W_9 + W_{11} + W_{12} + W_{13} + W_{14} + W_{15} - W_{16} - W_{17} - W_{18} - W_{19} - W_{20} - \\
- W_{21} - W_{22} - W_{23} - W_{24} - W_{25} - W_{26} - W_{27} - W_{28} - W_{29} \\
\dfrac{dx_{10}}{dt} = W_8 - W_{10} + W_{11} \\
\dfrac{dx_{11}}{dt} = W_9 + W_{10} + W_{12} + W_{13} + W_{14} + W_{15} - W_{16} \\
\dfrac{dx_{12}}{dt} = W_{17} + 2W_{19} \\
\dfrac{dx_{13}}{dt} = W_{17} + W_{25} + W_{27} + W_{28} \\
\dfrac{dx_{14}}{dt} = W_{18} \\
\dfrac{dx_{15}}{dt} = W_{18} + W_{21} + W_{22} + W_{23} + W_{24} + W_{26} + W_{29} \\
\dfrac{dx_{16}}{dt} = W_{25} + W_{27} + W_{28}
\end{cases}$$

With initial conditions t=0, $x_i(0)=x_{i,0}$, where i – corresponding hydrocarbon.

Thus, the dimension of the system of a mathematical model equations is coincides with the number of substances whose concentration is determined in calculations.

To apply the obtained model, it is first necessary to make a comparative assessment of the kinetic parameters.

When solving the inverse kinetic task, it is planned to use the method of parabolic descent. It is also planned to use a modified Kutta-Merson method of the fifth order of accuracy to solve the system of ordinary nonlinear differential equations [17].

The solution algorithm of a system of differential equations $\frac{dx}{dt}=f(x)$ requires a fivefold calculation of the right-hand sides f(x) [18]:

$$F_1=f(x_k)\cdot h,$$
$$F_2=f(x_k+F_1/3)\cdot h,$$
$$F_3=f(x_k+(F_1+F_2)/6)\cdot h,$$
$$F_4=f(x_k+(F_1+3\cdot F_2)/8)\cdot h,$$
$$x_{k+1}=x_k+(F_1-3\cdot F_2+4\cdot F_4)/2,$$
$$F_5=f(x_{k+1})\cdot h,$$
$$x^*_{k+1}=x_k+(F_1+4\cdot F_4+F_5),$$

where h – step of integration over a spatial or temporal coordinate, x_k – values of variables at the beginning of the integration interval. At the end of the integration interval, two solutions are obtained: x_{k+1} – by the Runge-Kutta method with accuracy $O(h^4)$ and x^*_{k+1} – by the Kutta-Merson method with accuracy $O(h^5)$.

4. Findings

- With the help of calculations, it has been shown that all reactions occurring in the transformation scheme is probable from the point of view of thermodynamics under the conditions of the process.
- The detailed mathematical model is proposed, consisting in consideration of all components of the raw material fraction with the boiling range of 62-70 ° C (pentane-hexane fraction).

5. Conclusion

Development on the basis of the reaction mechanism of an adequate kinetic model is an important stage in the creating of a mathematical model. Due to the fact that by solving inverse kinetic tasks, the parameters that will serve as the basis for the mathematical model are determined, and also taking into account physicochemical aspects of the process, the mathematical model will allow to carry out predicted calculations, to select the optimal technological conditions for increasing the resource efficiency of the catalytic isomerization process of pentane-hexane faction.

6. References

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