Numerical simulation of the catalytic process of isomerization of pentane-hexane cut

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Abstract. The basic schemes for the transformation of the pentane-hexane fraction catalytic isomerization, which are probable from the point of view of thermodynamics, have been considered. Based on the literary analysis of possible transformation schemes, the mechanism of the process and on the basis of experimental data, a mathematical model of the reactor block of the process was constructed and the kinetic parameters were determined. The foundations were laid for the subsequent solution of the tasks of the multi-purpose optimization of the catalytic isomerization process of the pentane-hexane fraction.

1. Introduction
Currently, the production of environmentally friendly high-octane gasoline is a complex problem for a number of domestic refineries. Since, besides the ubiquitous catalytic reforming process, this requires energy-intensive processes such as catalytic cracking, alkylation and isomerization of light paraffins, as well as more severe hydrotreating processes. In addition, strict restrictions are imposed on the content of aromatic hydrocarbons and, in particular, benzene in motor gasoline, while maintaining the octane number. By structurally altering the carbon skeleton, the catalytic isomerization of light paraffins makes it possible to obtain a high-octane component of automobile gasoline with a minimum content of aromatic hydrocarbons. The efficiency of this process is explained by the use of low-octane oil components as a raw material, as a fraction of 62–70 ° C, and also of catalytic reforming refined materials. The process is carried out in an environment of hydrogen in the presence of bifunctional catalysts [1, 2].

In the middle of the 20th century, when energy and material resources were not so limited, in the design and construction stages of most industrial plants, including reactors, insufficient attention was paid to the in-depth study of the mechanism of most processes. Intensive development of information technologies, such as analysis theory and big data storage, parallel computing technology, artificial neuron networks, etc., have led to creation of the universal software systems that allow developing a preliminary detailed kinetic model (PDKM) of complex industrial processes. PDKM is a starting point for constructing a kinetic model of a higher adequate level (KMHAL) [3].
In our case, the development of KMHAL allows solving optimization problems, for example a significant increasing in isocomponents yield, reducing in gas formation (hydrocracking reactions) while rationally using energy and material resources.

The wide component composition of the raw materials, as well as the occurrence of a large number of parallel-sequential chemical reactions at acid and metal centers of bifunctional catalysts, often make it difficult to describe the kinetics [4,5]. Therefore, to simplify the description of kinetics, the intermediate formation stages of components that are not presented in the target products are not usually considered. It is unacceptable when necessary to determine the dynamic effective conditions for industrial processes operation.

2. Experimental part
The object of the study is the reactor unit of the catalytic isomerization unit of the pentane-hexane fraction, consisting of a cascade of three reactors. As the feedstock was used the hydrotreated gasoline cut with boiling points within 62-70 °C and flow rate of 65449 kg/h. The flowrate of hydrogen-rich gas (HRG) was 16104 kg/h.

The composition of HRG and hydrocarbon gas (HC gas) from unit is shown in table 1. Pressure in reaction zone was 3.2 MPa. Inlet temperature of the 1st, 2nd and 3rd reactors was 147, 160 and 147 °C, respectively. Outlet temperature of each reactor was 160, 172 and 150 °C, respectively. A bifunctional catalyst of domestic production SI-2 (Izomalk-2 technology) was used as a catalyst of the process. The catalyst mass was 9000 kg in each reactor.

| Component | Mass fraction, % (GOST 14920) |
|-----------|--------------------------------|
| HRG       |                               |
| H2        | 34.11                          |
| iso-C4    | 4.28                           |
| iso-C5    | 14.11                          |
| C1        | 21.48                          |
| n-C4      | 1.40                           |
| n-C5      | 2.69                           |
| C3        | 7.59                           |
| C2        | 14.35                          |
| HC gas    |                               |
| H2        | 1.68                           |
| iso-C4    | 22.25                          |
| iso-C5    | 8.64                           |
| C1        | 6.57                           |
| n-C4      | 4.24                           |
| n-C5      | 0.20                           |
| C3        | 34.68                          |
| C2        | 21.75                          |

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

| Analyzed indicator | Methodology | Feed | Stable isomerizate |
|--------------------|-------------|------|--------------------|
| Density at 20 °C, kg/m³ | GOST P 51069 | 653.6 | 643.2 |
| RON                | GOST 8226   | 67   | 81                 |
| Fractional composition, °C | GOST 2177 | 42   | 36                 |
| IBP                |             | 62   | 59                 |
| 90% boiling at     |             | 64   | 63                 |
| 97% boiling at     |             | 65   | 64                 |
| FBP                |             | 98   | 98                 |

Obviously, to develop a detailed kinetic model, modeling a cascade of reactors alone is sufficient. The composition of the gas-product mixture after the reactor block is calculated from the data on the products after the stabilization block that is available. It should be noted here that with such a calculation, the indicators of productive flows have a great influence on the final result. In such cases,
the accuracy of the instruments can reach 5% for flows in the gaseous state and 3% for flows in the liquid state. Therefore, the use of such data without prior verification (carbon and hydrogen balance) is completely unacceptable.

In this regard, the amount of carbon and hydrogen to the reactor block was calculated, after which the exact values were selected to maintain the balance in full accordance with the accepted errors.

Thus, at the inlet of 1st reactor the composition and consumption of the feed and HRG were determined (by accounting the recycle flow). By analogy, data on the composition and flow rate of the gas-product mixture, recycled HRG and HC gas at the outlet of the 3rd reactor were calculated. Table 3 presents the material balance of the catalytic isomerization process of the pentane-hexane fraction on the basis of industrial installation data and the adjusted material balance based on the results of verification calculations.

### Table 3. Material balance.

| Flow                   | Mass flow rate on initial data, kg/h | Adjusted mass flow rate by balance of C and H, kg/h | Difference, % |
|------------------------|--------------------------------------|----------------------------------------------------|--------------|
| Reactor block upstream |                                      |                                                    |              |
| Feed                   | 65578.38                             | 65449.45                                           | 0.2          |
| HRG                    | 16169.24                             | 16103.96                                           | 0.4          |
| Total                  | 81747.62                             | 81553.40                                           |              |
| Reactor block downstream|                                      |                                                    |              |
| Isomerization products | 63384.00                             | 63942.19                                           | 0.8          |
| HRG (reactor downstream)| 15275.70                             | 15485.18                                           | 1.4          |
| HC gas                 | 2054.71                              | 2126.04                                            | 3.4          |
| Total                  | 80714.41                             | 81553.40                                           |              |

### 3. Mathematical description of pentane-hexane process isomerization

The first stage of the mathematical description of the object is the building of the scheme 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 detailing of chemical transformations. Therefore, the transformation scheme should sufficiently reflect the physico-chemical nature of the process [6,7].

In all known models [7–9] of the catalytic isomerization process of the pentane–hexane fraction, all the hydrocracking gases are combined into one product component, as a result of which it is impossible to predict the exact composition of hydrocarbon gases and HRG.

In this paper, an attempt was made to more detailed analysis of the transformation scheme based on the mechanism, including the reactions of hydrocracking products formation.

Due to the fact that industrial installations have great performance, it is impossible to carry out the process in isothermal conditions. Therefore, for a more detailed description of the process kinetics, it is necessary to take into account the non-isothermal nature of the process.

In the isomerization process reactions in the presence of bifunctional catalysts proceed via the carboxylic-ion mechanism [10-12]. The basis is the thermodynamics of the process. The result of thermodynamic analysis is a list of reactions that probably proceed under given conditions [13-15]. The probability of reactions under the process conditions of catalytic isomerization of pentane-hexane cut (temperature - 150 °C (423 K) and pressure - 3.2 MPa) was estimated by the Gibbs energy ΔG.

Reaction rates in the kinetic model were written according to the law of mass action [16]. The mathematical model of the process is a system of nonlinear differential equations [17,18]:

\[
\frac{dx}{d\tau} = u(r) \sum_{j=1}^{I} v_j w_j, \quad i = 1, \ldots, I,
\]

\[
w_j = k_j^0 \cdot \exp \left( -\frac{E_j^a}{RT} \right) \cdot \prod_{i=1}^{I} (x_i)^{\nu_{ij}} - k_j^0 \cdot \exp \left( -\frac{E_j^a}{RT} \right) \cdot \prod_{i=1}^{I} (x_i)^{\nu_{ij}}
\]

(1)
with initial conditions: \( \tau = 0, x_i(0) = x_i^0 \); where \( v_{ij} \) - the stoichiometric coefficients of the schemes of chemical transformations; \( J \) – number of stages, \( x_i \) - the substances concentration participating in the reaction in a molar fraction; \( I \) – number of components; \( \nu \) – the speed of the \( j \)-th phase, 1/h; \( E_j^+ \), \( E_j^- \) – activation energy of direct and reverse reactions, j/mol; \( R \) – gas constant, equal to 8.31 j/(mol·K); \( T \) – temperature, K; \( \alpha_{ij}, \beta_{ij} \) – negative matrix elements (<\( \nu \)), \( kj_0, k_j^{-} \) – preexponential multipliers kmol/(h·kg cat.); \( \tau \) - contact time, kg·h/mol. 

The mathematical model (1) is a Cauchy problem [17,18], which includes the feed flow rate with in the reactor. In addition, as noted above, it is necessary to take into account the non-isothermal nature of the process [19], so the temperature change equation (2) should be added to the model (1).

\[
\frac{dT}{d\tau} = - \sum_{i=1}^{I} \sum_{j=1}^{J} \frac{dx_i}{d\tau} H_j(T) \left( \sum_{i=1}^{I} x_i C_{pi}(T) \right),
\]

with initial conditions: at \( \tau = 0, T(0) = T^0 \); where \( T \) – temperature, K, \( H_j(T) \) - enthalpy, J/mol, \( C_{pi}(T) \) - heat capacity, J/(mol·K).

After approbation of several explicit and implicit methods for numerical solution of systems of differential equations (1) and (2), a suitable method turned out to be Rosenbrock's one-iteration method of the 3rd order of accuracy [20]. This method was successfully used to solve the chemical kinetics problems in [17,18]. The inverse problem was solved by a genetic algorithm. Preexponential multipliers \( k_{0,j}, k_{j}^{-} \) and activation energy of direct and reverse reactions \( E_j^+, E_j^- \) were chosen as optimized parameters. The number of optimization parameters \( n = 102 \).

The genetic algorithm minimizes the fitness function. The value of this function is the criterion deviation of industrial and calculated data in compare with the direct problem solving of chemical kinetics. The mean relative deviation of the calculated and industrial concentrations was used as this criterion:

\[
F = \frac{1}{M} \sum_{i=1}^{I} \left( \frac{|y_{ij}^{exp} - y_{ij}^{calc}|}{y_{ij}^{exp}} \right) \rightarrow \text{min},
\]

where \( I \) – the number of observed substances (\( I=17 \)), \( y_{ij}^{exp} \) – industrial data of concentrations of components at the output, mass fractions, \( y_{ij}^{calc} \) – calculated in the course of solving the direct problem of concentration of components, mass fractions.

A software module in Matlab for constructing a kinetic model of the catalytic isomerization of the pentane-hexane cut was developed.

**Table 4.** Optimal values of the process kinetic parameters.

| \( i \) | Reaction | \( \ln k_{ij}^{0} \), kmol/(h·kg cat.) | \( E_j \), j/mol |
|---|---|---|---|
| 1 | \( n-C_5H_{12} \rightarrow \text{iso } C_5H_{12} \) | 35.23 | 150100 |
| 2 | \( \text{iso-C}_5H_{12} \rightarrow n-C_5H_{12} \) | 35.93 | 158308 |
| 3 | \( n-C_6H_{14} \rightarrow 2\text{-MP} \) | 17.46 | 143420 |
| 4 | \( 2\text{-MP} \rightarrow n-C_6H_{14} \) | 18.37 | 150408 |
| 5 | \( n-C_6H_{14} \rightarrow 3\text{-MP} \) | 41.62 | 150980 |
| 6 | \( 3\text{-MP} \rightarrow n-C_6H_{14} \) | 42.67 | 155420 |
| 7 | \( 2\text{-MP} \rightarrow 3\text{-MP} \) | 37.27 | 152960 |
| 8 | \( 3\text{-MP} \rightarrow 2\text{-MP} \) | 37.27 | 149945 |
| 9 | \( 2\text{-MP} \rightarrow 2,2\text{-DMB} \) | 26.37 | 128230 |
| 10 | \( 2,2\text{-DMB} \rightarrow 2\text{-MP} \) | 29.14 | 139766 |
Changes in the concentrations of the reaction components are shown in figure 1. 

On figure 1 the profiles of calculated concentration of components in all three reactors are presented (the change in the concentration profile is divided into three parts corresponding to three reactors by vertical lines) taking into account the heating the upstream mixture of each reactor and the temperature profiles in the reactors. Industrial data for the reaction were obtained only for the first reactor upstream and the last reactor (3rd) downstream (on figure 1 marked with marker). The calculated values for the presented model for most components have an error of no more than 5% in compare with the industrial data.

where 2-MP – 2-methylpentane, 3-MP – 3-methylpentane, 2,2-DMB – 2,2-dimethylbutane, 2,3-DMB – 2,3-dimethylbutane, CH – cyclohexane, MCP – methylcyclopentane, CP – cyclopentane, BZ – benzene.
Figure 1. Changes in concentrations of reaction components: $n$-pentane and $n$-hexane caused with the sequential conversion of these components into the corresponding isomers (figure 1(b)). It should be noted here that $n$-hexane is first converted to 2-methylpentane and 3-methylpentane, which in turn form 2,2-dimethylbutane and 2,3-dimethylbutane.

Figure 1(c) shows the complete consumption of benzene due to hydrogenation reactions with the formation of cyclopentane and methylcyclopentane. It’s also confirmed by the gradual consumption of hydrogen.

Figure 1(d) seen the highest growth of hydrocracking products corresponds to the zone of higher temperatures. And such a low change in the concentration of methane indicates that hydrocracking reactions with methane formation occur with the least probability.

Figure 2. Temperature profile in the reactor. Vertical lines indicate the areas of the reactor block.

On figure 1(d) seen the highest growth of hydrocracking products corresponds to the zone of higher temperatures. And such a low change in the concentration of methane indicates that hydrocracking reactions with methane formation occur with the least probability.
Figure 2 shows that the reactions of isomerization occur with a small exothermic effect. This in turn affects the formation of hydrocracking by-products (figure 1d). It can be seen that after heat removal before the third reactor, the reaction rates of the by-products formation decrease.

4. Conclusion

The development of an adequate kinetic model based on the reaction mechanism is an important step in the construction of a mathematical model. The solving the inverse kinetic problems allows defining the parameters that will serve as the basis for the mathematical model and allows taking into account the physical and chemical aspects of the process. Ultimately, the mathematical model will allow making predicted calculations, choosing the optimal technological conditions with purpose to improve the resource efficiency of the process of pentane-hexane cut catalytic isomerization.

The mathematical model of the three-cascaded reactor block, adequately describing the chemical transformations within the reactors has been built and 102 kinetic parameters have been obtained (table 4). Thanks to a fairly accurate description of temperature changes (when compared with the data of an industrial plant), it can be argued that the model reliably describes not only the final composition of the downstream product of the last reactor, but also the nature of the compositions curves along the reactor section. Therefore, this model can be used to retrofit the reactor blocks of existing plants and allows defining the optimal amount of catalyst and reactors sizing within cascades. Thus, in the article the foundations for the subsequent modeling of the entire chemical-technological system of the catalytic isomerization process have been laid.

5. References

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