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## Efficiency improvement of the light gasoline fractions isomerization by mathematical modeling

Chuzlov V.A.<sup>a</sup>\*, Ivanchina E.D.<sup>a</sup>, Chekantsev N.V.<sup>a</sup>, Molotov K.V.<sup>b</sup><sup>a</sup> National Research Tomsk Polytechnic University, 30, Lenina Pr., Tomsk 634050, Russian Federation<sup>b</sup> «Kinef», Shosse Jentuziastov, 1, Kirishi, Leningradskaja obl., 187110, Russian Federation

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### Abstract

Optimization and forecasting of light gasoline fractions isomerization is a complex technological issue, as it includes a variety of factors and independent parameters. The most effective solution is to use the mathematical modeling method of physical and chemical laws of the process. In this paper, we propose a method of intensification of the combined fractionation and isomerization processes of pentane-hexane fraction with the aim to improve the service durability of the catalyst SI-2 on the L-35-11 / 300 production unit. The developed complex mathematical model takes into account the influence of the feedstock composition, allows for assessment of the catalyst current activity and it is also a powerful optimization tool. According to the survey results the optimizing the feedstock composition will increase the octane number of the isomerate at 1.6-2.2 points.

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*Keywords:* isometrization; catalyst; reactor; rectification; mathematical modeling.

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### 1. Introduction

Efficiency improvement of industrial processes of light gasoline fractions isomerization is an important technological issue including many factors and independent parameters. This article provides an optimization method of the combined processes of naphtha separation and catalytic conversion of hydrocarbons using of complex mathematical model of the process.

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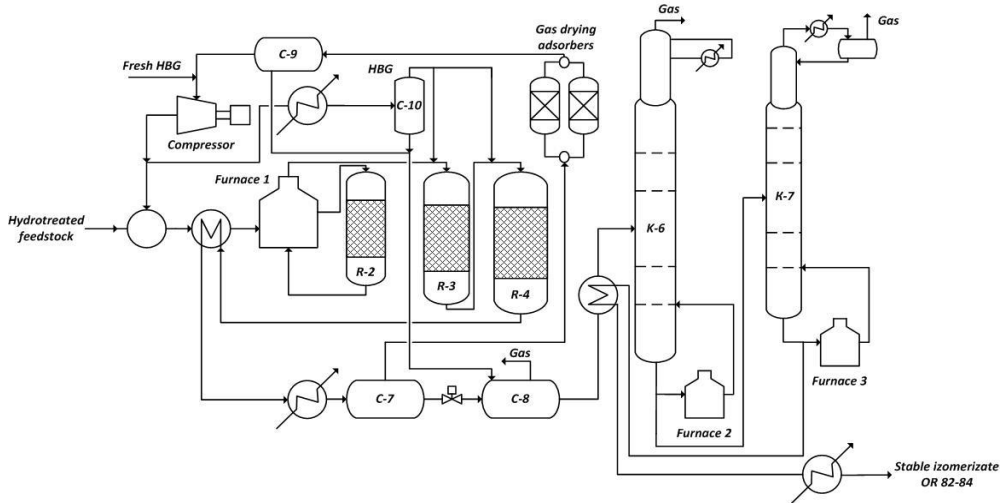
\* Corresponding author. Tel.: +7-962-782-6615.

E-mail address: [sonicsky24@gmail.com](mailto:sonicsky24@gmail.com)

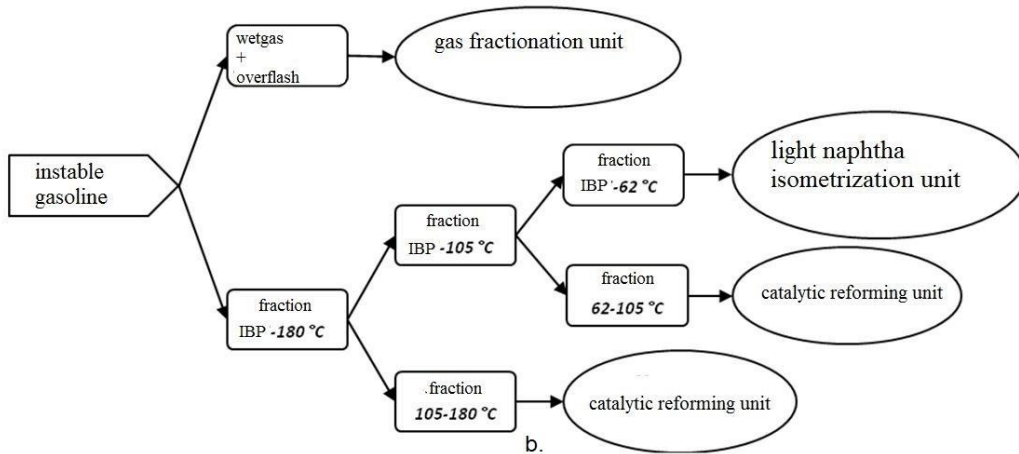
The aim of the paper is to optimize the feedstock composition of the production unit of the pentane-hexane fraction L-35-11 / 300 isomerization for resource efficiency due to the work intensification of the afterfractionating column block of the straight-run naphtha.

**2. Study subject**

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



a.



b.

Fig. 1. (a) block diagram of the isomerization process of pentane-hexane fraction; (b). The block diagram of unstable gasoline preparation material flows.

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.

The raw material of the isomerization process is a fraction of the IBP-62° C, coming from the stabilization unit and the afterfractionating column block of the straight-run naphtha. A block diagram of the process of material flows preparation of unstable gasoline is shown in Fig 1 B.

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 afterfractionating column block of the straight-run naphtha (CDU-6 CD-6, CDU-2, CD-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.

### 3. Methods

In accordance with the established methodology [2-4], the construction of a mathematical model is a sequential execution of stages of the thermodynamic and kinetic analysis, constructing the reactor model and the entire chemical-technological system (CTS) model. CTS modeling allows a quantitative or formal description in a form of equations system, presenting the operation of each technological scheme unit. The mathematical model consists of two groups of equations:

1. CTS mathematical description, i.e. processes in the apparatus in the form of functional dependence:

$$\vec{y}_k = F_k(\vec{x}_k, \vec{z}_k, \vec{u}_k) \quad (1)$$

where  $\vec{y}_k$  is the output parameters vector,  $\vec{x}_k$  is the input parameters vector,  $\vec{z}_k$  is the structural parameters vector,  $\vec{u}_k$  is the vector control parameters,  $F_k$  is an algebraic/differential functional [3,4].

2. Description of the technological connections:

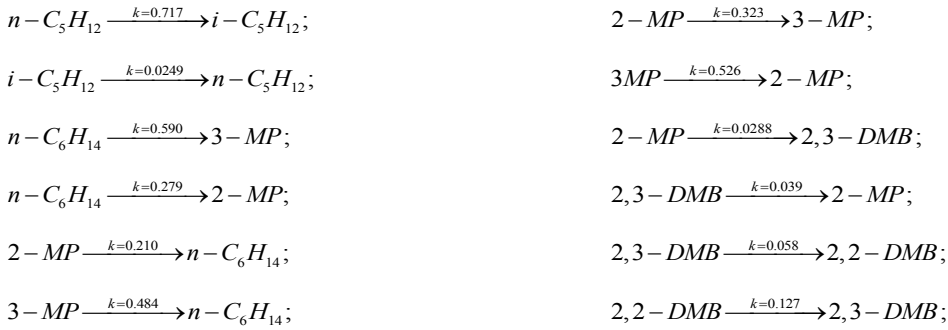
$$\vec{x}_k = L_{l-k}(\vec{Y}_l) \quad (2)$$

where  $L_{l-k}$  takes the value if there is a communication between the apparatus l and k, namely, the output parameters of the apparatus k are input parameters of the apparatus l;  $L_{l-k} = 0$  if the connection between these apparatus is missing.

Complex modeling system allows to set a relationship between stabilization process of rectification, afterfractionating and reaction processes in the isomerization reactor.

Much attention is given to the synthesis and experimental study of new isomerization catalysts [5-13]. An important aspect is the study of the catalytic isomerization mechanism [14]. According to [14, 15], the main problems arise in the study of the carbenium ions formation mechanism, catalyst acidity, different promoters roles in the process, and the hydrogen.

In this paper we use proved formalization of the substances conversions scheme, based on the reactivity of hydrocarbons [16]. We take the hydrocarbons conversions scheme, made on their reactivity for the isomerization process of light naphtha. Isomerization \* primary reactions are shown below:



\* reaction rate constants are calculated at 130 ° C [5].

Complete mathematical description of the catalytic process conversion of hydrocarbons is based on component material and heat balances and in general terms have the following form:

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

when  $Z=0, C=0, r=0, C=C_0, Z=0, T=T_0, r=0, T=T$  input water

where  $G$  is raw material capacity in  $m^3/s$ ;  $C_i$  is concentration of the  $i$ -component,  $mol/m^3$ ;  $Z$  is the amount of recycled raw materials,  $m^3$ ;  $i=1, \dots, N$ ;  $j=1, \dots, M$ ;  $N$  is the number of substances involved in the reaction;  $M$  is the number of reactions;  $r_j$  is the rate of the  $j$ -reaction  $mol/m^3 \cdot s$ ;  $V$  is the volume of the isomerization reactor,  $m^3$ ;  $T$  is the reactor temperature, ° C;  $\rho$  is the density,  $mol/m^3$ ;  $Q_j$  is the thermal effect of the  $j$ -reaction  $J/mol$ ;  $C_p$  is the specific heat of the gas mixture,  $J/(mol \cdot eg)$ ,  $a$  is the activity of the catalyst.

In calculating the multicomponent distillation the quantity of reflux, the number of theoretical stages, the position of the feed supply stage are selected as independent parameters. Equilibrium compositions are determined from the following relations:

$$y_i^* = \alpha_i x_i / \sum_{i=1}^b \alpha_i x_i; \quad x_i^* = y_i / \alpha_i / \sum_{i=1}^b y_i / \alpha_i \quad (3)$$

where  $y_i^*$  is the equilibrium content of the  $i$ -component in the pair,  $x_i^*$  is the equilibrium content of  $i$ -component in the liquid,  $\alpha_i$  is the relative volatility of the  $i$ -component.

The equations describing the process of a multicomponent separation are shown in the following form:

$$Fx_{F,i} = Px_{P,i} + Wx_{W,i} \quad Gy_{n-1,i} = Lx_{n,i} + Px_{P,i} \quad (n > f) \quad Lx_{n,i} = Gy_{n-1,i} + Wx_{W,i} \quad (n \geq f)$$

where  $F, P, W$  are consumption of feed, distillate, stillage bottoms, respectively,  $kmol/h$ ,  $x_{F,i}, x_{P,i}, x_{W,i}$  are the share of  $i$ -component in the feed, distillate, stillage bottoms,  $G$  is steam flow rate,  $L$  is liquid,  $n$  is number of separation stages,  $f$  is feeder plates.

Software implementation of the model is made in the IDE Delphi 7 [16-17]. Initial data for calculation are the composition of the feedstock and process parameters. The adequacy of the model was verified by comparing the experimental data with the industrial isomerization unit L-35-11/300 with the calculated values (Table 1).

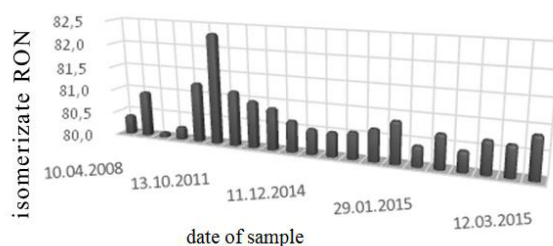
Table 1. Evaluation of the model adequacy.

Flow, % mass.	n-C <sub>4</sub>	i-C <sub>4</sub>	n-C <sub>5</sub>	i-C <sub>5</sub>	n-C <sub>6</sub>	2-MP	3-MP	2,2- DMB	2,3- DMB	Cyclo- C <sub>5</sub>	Mecyclo- C <sub>5</sub>	Cyclo- C <sub>6</sub>	Benzene	RON
Feedstock	0,02	0,00	34,65	13,64	15,32	15,14	8,62	0,4	2,14	3,61	4,53	0,4	1,47	<b>67,00</b>
Is. (expe rimental).	0,13	0,10	15,16	36,05	5,73	14,43	7,22	11,65	4,34	2,51	1,86	0,56	0,25	<b>80,67</b>
Is. (calcu lated)	0,16	0,15	14,71	36,44	5,38	13,3	7,82	11,42	4,28	2,05	1,43	0,97	0,00	<b>80,64</b>

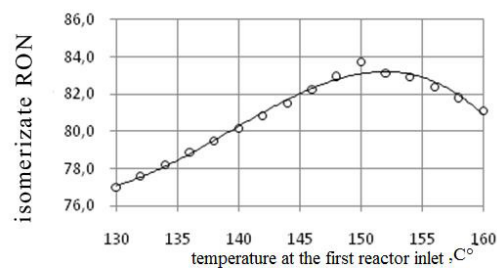
According to the data presented in Table 1, the model shows low deviations of calculated values from operational and can be used to describe the actual process.

#### 4. Results and discussion

The feedstock composition at the L-35-11/300 varies widely depending on the composition and properties of the supplied oil, and also on the naphtha afterfractionating operation unit. Fig. 2 shows the research finding of the feedstock composition effect on the isomerate quality.



a.



b.

Fig. 2. Study of the RON effect on isomerate: (a) feedstock composition; (b) temperature at the reactor inlet.

The study of the feedstock composition effect is carried out with constant process parameters: reactor unit loading is 70 m<sup>3</sup>/h, temperature of the first reactor inlet is 135 °C, pressure is 32 atm. According to the results presented in Fig. 2 A, RON isomerate may vary within 2-2.2 points depending on the feedstock composition, and therefore, it is necessary to select optimal operation of stabilizing unit columns and naphtha afterfractionating operation unit in order to provide the maximum content in the raw materials of the key components of the isomerization process (n-pentane, n-hexane) and to reduce the content of filler component (isopentane, cyclohexane). The study of the temperature effect on the inlet to the isomerization reactor (Fig. 2) showed that the rise in temperature above 145-150 °C leads to a significant increase in the proportion of the hydrocracking side reactions and reduces the yield of isomerate on 3-3.5%. In Fig. 3 A, B show the results of the stabilization unit columns and the afterfractionating operation optimization.

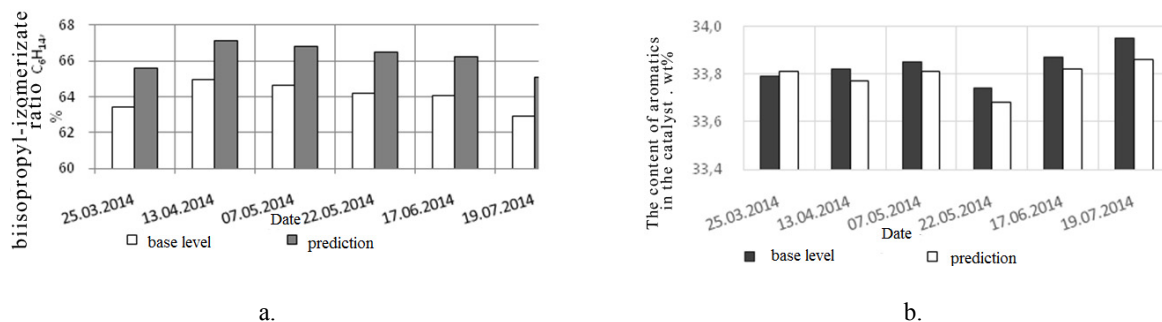


Fig. 3. (a) Bimethylbutane concentration increase in the in the isomerate composition; (b) The content of aromatic hydrocarbons in the reformat.

As a result of feedstock optimization the dimethylbutane ratio (Fig. 3a) in isomerate increased by 2-3%, which positively affects the octane number isomerate. Content optimization of the IBP 62 °C fraction has little effect on the quality of the product produced during the reforming process: reduction of aromatic content does not exceed 1% (Fig. 3b).

The increase in the octane number as a result of optimization of the naphtha afterfractionating column unit for the primary oil processing is presented in Table 2.

Table 2. RON isomerate increase in feedstock composition optimization.

RON isomerate	25.03.2014	13.04.2014	07.05.2014	22.05.2014	17.06.2014	19.07.2014
Current engineering factors	81,64	81,90	81,90	81,90	81,90	80,36
Optimal engineering factors	83,82	83,50	83,50	83,50	84,00	81,79
Increase	2,18	1,60	1,60	1,60	2,10	1,43

Thus, the operation optimization of the stabilizing unit columns and naphtha afterfractionating operation unit improved the RON isomerate at 1.6-2.2 points.

## 5. Conclusion

On the basis of the above mentioned approach to the mathematical description of hydrocarbons catalytic conversion, we have a complex model of the isomerization of pentane-hexane fraction and naphtha afterfractionating unit. In accordance with the study, the feedstock composition can vary widely, leading to RON isomerate fluctuation within 2-2.2 points. Optimization of the stabilization columns unit and afterfractionating unit reduces the filler component content in the isomerization raw materials and increase the commercial RON isomerate at 1.6-2.2 points, depending on the feedstock composition.

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