Mathematical modeling of light naphtha (C5, C6) isomerization process

Nikita V. Chekantsev, Maria S. Gyngazova *, Emilia D. Ivanchina

National Research Tomsk Polytechnic University, pr. Lenina 30, Tomsk 634050, Russia

HIGHLIGHTS

- The reaction scheme for light alkanes isomerization process is elaborated.
- Kinetic parameters are defined for $Pt/Al_2O_3–CCl_4$, Pt/zeolite and $Pt/SO_4–ZrO_2$ catalysts.
- A new universal mathematical model of light alkanes isomerization process is provided.
- Calculations agree very well with experimental information.
- The examples are given for the schemes with recycle of n-pentane and with deisopentanizer.

ARTICLE INFO

ABSTRACT

In this paper a new universal mathematical model of light alkanes isomerization process valid for different raw materials composition and catalyst is provided. The model is designed to be applied at an industrial isomerization unit. In the formalized reaction scheme components having not more than 7 carbon atoms are considered as individual hydrocarbons, because their reactivity and octane numbers differ a lot. Hydrocarbons C_{7+} are aggregated because usually just a trace amount of these compounds can be found in the feed. The industrial isomerization reactor is considered as an ideal plug flow reactor. The isomerizate composition calculated with the proposed model agrees very well with experimental information. Using the introduced isomerization mathematical model it is possible to compare the different isomerization units work efficiency and choose more suitable variant of process optimization for given raw material. The examples of the calculations are given for the isomerization process scheme with recycle of n-pentane and for the scheme with deisopentanizer.

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1. Introduction

In recent years an increased share of isomerizate has been added to the gasoline pool because of the stringent environmental regulations that call for lower use of aromatics and olefins in gasoline in addition to the strict limits on sulfur content and Reid vapor pressure. Naphtha isomerization is proved to be a simple and cost effective technology to produce clean gasoline components with high octane number [1].

The C5/C6 "light straight-run naphtha" (boiling in the range 27–70 °C) has a very low octane number of about 70 due to a limited amount of "naturally occurring" branched isomers. By isomerizing this cut it is possible to transform it into a valuable 84–92 RON blending component [2]. Isomerization converts linear paraffins into their respective isoparaffins of substantially higher octane number (Appendix B). For instance although n-hexane has only 25 RON, mono-branched hexane such as 2-methylpentane or 3-methylpentane has from 74 to 76 RON. Furthermore di-branched hexanes (such as 2,2-dimethylbutane and 2,3-dimethylbutane) have RON in the range of 94–105. Higher octane numbers mean lower knocking intensity that is related to better engine performance.

Pentane–hexane isomerization takes place in fixed bed reactors in the presence of hydrogen added to minimize carbon deposits on the catalyst. In order to remove potential catalyst contaminants the feed and make-up gas undergo pretreatment steps such as adequate hydrotreating and molecular sieves dryers. The flowsheet of the simplest industrial isomerization process is given in Fig. 1.

Catalysts that are used in the industrial isomerization process nowadays are chlorinated aluminum oxide ($Pt/Al_2O_3–CCl_4$), zeolite catalysts (Pt/zeolite) and sulfated zirconia ($Pt/SO_4–ZrO_2$). Typical operating conditions for the mentioned above isomerization catalysts are given in Table 1.

Isomerization of straight chain alkanes to their branched isomers is a slightly exothermic reaction (a few kcal/mol). Thus the yield of the product is thermodynamically favored by low reaction temperature. On the other hand at higher temperature the equilibrium yield will be more easily reached due to a higher reaction rate. Thus at higher temperature the yield of isoalkanes is limited

* Corresponding author. Tel.: +7 9069551067.
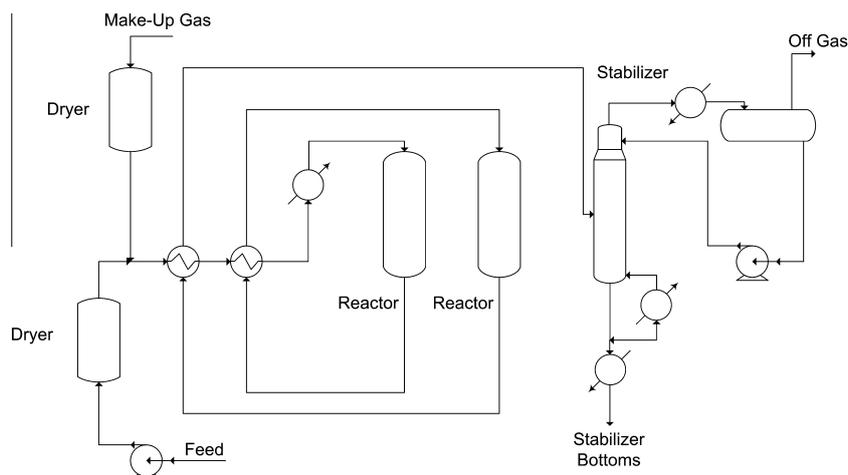 *E-mail address:* maria.gyngazova@gmail.com (M.S. Gyngazova).

Fig. 1. Flowsheet of industrial isomerization process.

Table 1
Operating conditions and feed limitations for the industrial isomerization catalysts.

	Pt/Al$_2$O$_3$-CCl$_4$	Pt/zeolite	Pt/SO$_4$–ZrO$_2$
Temperature (°C)	120–160	220–300	130–180
Pressure (MPa)	3	3	3
Feed limitations	Sensitive to water Low sulfur resistance Require continuous addition of chloride => Can cause corrosion problems	Resistant to water and sulfur in feed	Resistant to water and sulfur in feed Sensitive to C$_{7+}$
RON	82–84	76–78	83–85

by the thermodynamic equilibrium and at lower temperature it is limited by low reaction rate (kinetic limitation). The results of estimation of isoparaffins content in the catalysate for different types of isomerization catalysts are given in [2,3]. Conversion of n-paraffins on chlorinated-alumina catalysts and sulfated metal oxides is higher than on zeolite catalysts because of high equilibrium content of isocomponents in product mixture. Therefore the isomerizate yield is directly related to the catalyst type, operating conditions used and the concentration of linear paraffins.

The mechanism of alkane isomerization has been discussed for years and seems to be established. The details of the mechanism are however still unresolved. According to [4,5] the main problems to be solved include the way of formation of carbenium ions, acidity requirements of the catalysts and the role of different promoters and hydrogen during isomerization.

Most of the recent papers concerning light alkanes isomerization process are devoted to the synthesis and experimental investigation of the new catalysts [6–14], mechanism of catalytic isomerization [4], also a lot of attention is paid to the phenomenon of hydrogen spillover over different types of catalysts [15,16].

Some of the papers propose the new variants or some modifications of the industrial isomerization process technology. For instance, the authors [17] applied experimentally zeolite membrane reactor concept for the hydroisomerization of n-hexane. In [18] a coupled technology (adsorption after rectification) to produce high-purity normal and isomeric pentane from reforming topped oil is introduced. The paper [19] proposes new isomerization process with Pt/SO$_4^{2-}$/ZrO$_2$ catalyst for petrochemical raffinate. The articles [2,3] give the review of existing technologies of isomerization processes (scheme of a once-through isomerization process, deisopentanizer scheme, deisohexanizer scheme, scheme with recycle of n-pentane, scheme with recycle of n-pentane and

n-hexane, molecular sieve separation: Ipsorb and Hexorb processes.

The literature overview has revealed that in few papers the attention is paid to the mathematical modeling of the industrial process of isomerization of light alkanes. The authors of [20] report simulation results based on microkinetics approach. Alkoxy species were assumed to be the reactive intermediates, carbenium ions were considered to be part of the transition state. The authors state that the resulting model describes experimental measurements very well, but it seems to be very complicated and difficult to solve. It is not really possible to apply such a model into practice at the industrial plant. In [1] the industrial reactor is considered as an ideal plug-flow reactor and the kinetic parameters of the main isomerization reactions are found. The coauthors of [21] studied the effects of hydrogen partial pressure on isomerization catalyst activity and n-paraffins conversions. Kinetic equations for n-C$_5$ and n-C$_6$ in light straight run gasoline were also proposed. In [22] the network of n-hexane isomerization over Pt/Al$_2$O$_3$ and Pd/HM catalysts was given in a simplified form. Rate constants were calculated mathematically. Huibin Liu with coworkers [23] investigated reaction performance and disappearance kinetics of n-pentane isomerization catalyzed by chloroaluminate ionic liquid. In [24] n-hexane skeletal isomerization over sulfated zirconia catalysts with different Lewis acidity was studied. The calculations of the rate constants, characterizing catalyst activity and selectivity was performed on the base of mathematical model of plug flow reactor. The key role of Lewis acidity for the activity and selectivity of Pt/SO$_4^{2-}$/Al$_2$O$_3$/ZrO$_2$ catalysts was experimentally revealed.

As seen, most of the models mentioned above [1,20–24] are elaborated for the specific feed and catalyst. The goal of this paper is to provide new universal mathematical model of light alkanes isomerization process that could be used for different raw
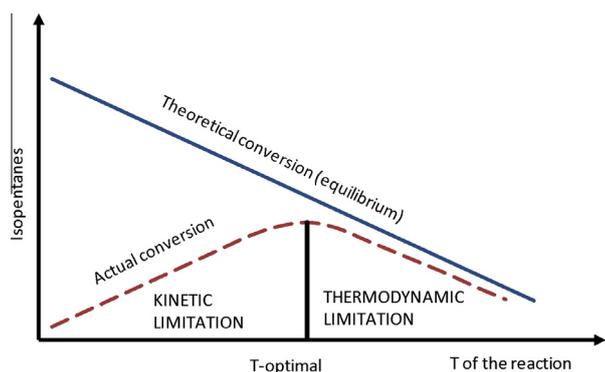
Fig. 2. Dependence of n-paraffins conversion on reaction temperature [3].

materials composition and catalysts. The model is designed to be applied at an industrial isomerization unit.

2. Thermodynamics

The isomerization of light paraffins is a slightly exothermic reaction. Thus the yield of isoalkanes is thermodynamically favored by a low reaction temperature. On the other hand, according to the Arrhenius' law an increase in temperature always corresponds to an increase in reaction rates, higher temperature improves the catalyst activity. A compromise between the catalyst activity and thermodynamic equilibrium or selectivity must be found (Fig. 2). The composition of the products can be close to chemical equilibrium in case of very high residence time and low flow rates. In practice at the industrial unit this cannot be realized. But there are some optimal temperatures for each type of catalyst when the conversion is close the thermodynamically possible (Table 2).

Pt/Al$_2$O$_3$–CCl$_4$ catalyst is highly effective at low temperatures and supplies the highest product yield and product octane numbers. This catalyst demonstrates good selectivity but it is sensitive to water and sulfur in the feedstock. Pt/SO$_4$–ZrO$_2$ catalyst is active at low and higher temperatures. It is resistant to poisonous impurities and able for regeneration. Pt/zeolite catalyst is the least active in the desired reactions. Higher operating temperatures decrease selectivity and cause coking, that is the reason for high hydrogen/feed ratio when using Pt/zeolite catalyst.

3. Kinetics of C5/C6 isomerization process

The feedstock for the industrial isomerization process is light straight-run naphtha (boiling in the range 27–70 °C) that is mainly composed of n-paraffins: n-pentane and n-hexane. In order to obtain the formalized reaction scheme of the industrial isomerization process it is necessary to analyze the composition of the feed and the product (presented in Table 3, received at the industrial unit).

Industrial isomerization of light naphtha is generally carried out over bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acid sites for skeletal isomerization via carbenium ions:

$${}^{n}C_5H_{12} \rightleftharpoons {}^{n}C_5H_{10} + H_2 \text{ (on Pt)}$$

$${}^{n}C_5H_{10} + H^+ \rightleftharpoons {}^{n}C_5H_{11}^+ \text{ (on acid sites)}$$

$${}^{n}C_5H_{11}^+ \rightarrow {}^{iso}C_5H_{11}^+ \text{ (on acid sites)}$$

$${}^{iso}C_5H_{11}^+ \rightleftharpoons {}^{iso}C_5H_{10} \text{ (on acid sites)}$$

$${}^{iso}C_5H_{10} + H_2 \rightleftharpoons {}^{iso}C_5H_{12} \text{ (on Pt)}$$

Therefore the following steps in the reaction mechanism can be mentioned [1]:

Table 2
The comparative estimation of isopentanes content in sum of pentanes (in %) for different types of catalysts [from Ref. [3]].

Temperature (°C)	Thermodynamically possible equilibrium yield	Pt/Al$_2$O$_3$-CCl$_4$	Pt/SO$_4$-ZrO$_2$	Pt/zeolite
100	81	65	40	–
150	78	73	55	–
200	74	70	73	40
300	65	–	62	62

Table 3
Experimentally defined compositions of feed and product in the isomerization process (received at the industrial unit).
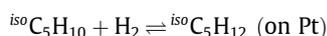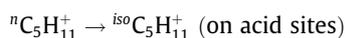
Components	Feed, wt.%	Product, wt.%	Components	Feed (wt.%)	Product (wt.%)
Propane	0	0.08	3,3-Dimethylpentane	0	0.01
i-Butane	0.03	0.94	Cyclohexane	1.13	1.63
n-Butane	2.77	4.20	2-Methylhexane	0.01	0.03
2,2-dimethylpropane	0.04	0.07	2,3-Dimethylpentane	0	0.01
i-Pentane	18.04	35.97	1,1-Dimethylcyclopentane	0	0.02
Olefins C$_5$	0.01	0	3-Methylhexane	0	0.03
n-Pentane	30.54	14.60	1c,3-Dimethylcyclopentane	0	0.03
2,2-Dimethylbutane	0.26	9.47	1t,3-Dimethylcyclopentane	0	0.03
Cyclopentane	3.66	3.76	1t,2-Dimethylcyclopentane	0	0.04
2,3-Dimethylbutane	1.44	3.65	n-Heptane	0	0.01
2-Methylpentane	12.01	11.35	Methylcyclohexane	0	0.27
3-Methylpentane	6.97	6.61	2,2-Dimethylhexane	0	0.02
Olefins C$_6$	0.01	0	Ethylcyclopentane	0	0.01
n-Hexane	15.43	4.55	1c,2t,4-Trimethylcyclopentane	0	0.01
2,2-Dimethylpentane	0.03	0.02	1t,2c,3-Trimethylcyclopentane	0	0.01
Methylcyclopentane	6.28	2.28	Olefins C$_8$	0	0.01
2,4- Dimethylpentane	0.09	0.01	n-octane	0	0.03
Benzene	1.25	0	Naphthenes C$_8$	0	0.15

1. Dehydrogenation: a n-alkane is adsorbed on Pt-center and an olefin is formed.
2. Isomerization: the formed molecule goes to an acid center where it gains a proton, the hydrocarbon chain is branched and the resulting isoolefin releases the proton.
3. Hydrogenation: isoolefin goes back to the metallic center where it is fast hydrogenated.

The rate-determining step of the isomerization is the rearrangement of carbenium ions. Carbenium ions are easily deprotonated and form alkenes, which polymerize to give coke precursors [4]. Due to the Pt-centers catalyzing dehydrogenation-hydrogenation reactions and the presence of hydrogen into the system almost no coke accumulation takes place.

A number of papers discuss isomerization mechanism in more or less detailed way. Obtaining the data from the industrial isomerization unit it is impossible to determine the reactions rates for intermediate substances. That is why our reaction scheme contains the overall isomerization reactions without intermediate steps. The goal of this paper is to elaborate a reliable kinetic model that could be valid for different feed composition and for different catalyst types. The model is designed to be applied at an industrial isomerization unit.

In this paper components having not more than 7 carbon atoms are considered as individual hydrocarbons in the formalized scheme, because their reactivity and octane numbers differ a lot (octane number is a very important characteristic of a fuel). Hydrocarbons C_{7+} are aggregated because usually just a trace amount of these compounds can be found in the feed.

Therefore, the following reaction scheme for isomerization process is proposed in Fig. 3 on the basis of experimental data, received at the industrial unit.

According to the thermodynamics all of the reactions shown in the reaction scheme (Fig. 3) are feasible within the wide temperature range (Table 4).

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:

$$r = k \cdot f(C) \tag{1}$$

$$f(C) = C_1^{v_1} \cdot C_2^{v_2} \cdots C_n^{v_n} \tag{2}$$

where r is reaction rate; k is rate constant; C_i is initial components concentration; v_i is stoichiometric coefficient in gross-equation of chemical reaction.
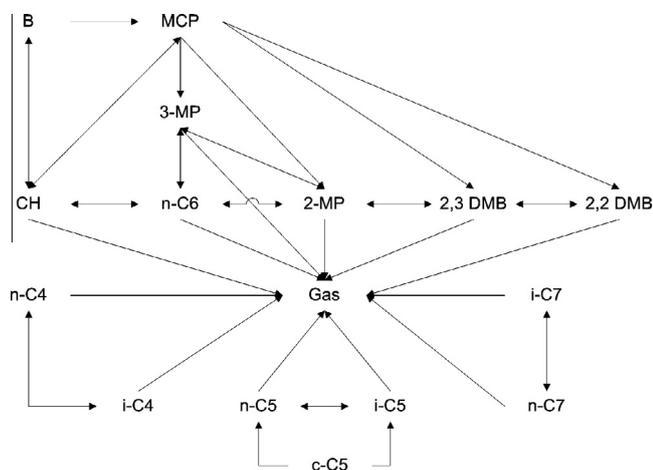
Table 4
Gibbs energies for the reactions taking place at the industrial isomerization process and estimated values of the rate constants at $T = 130^{\circ}C$ and $p = 3.0$ MPa for Pt/SO$_4$–ZrO$_2$ catalyst.

#	Reactions	ΔG (kJ/mol)		Rate constants (s^{-1})
		300 K	600 K	
1	n-C$_5$H$_{12}$ → i-C$_5$H$_{12}$	−6.46	−4.75	0.0717
2	i-C$_5$H$_{12}$ → n-C$_5$H$_{12}$	6.46	4.75	0.0249
3	n-C$_6$H$_{14}$ → 2-MP	−4.75	−2.6	0.2790
4	2-MP → n-C$_6$H$_{14}$	4.75	2.6	0.2100
5	n-C$_6$H$_{14}$ → 3-MP	−1.85	−0.73	0.4840
6	3-MP → n-C$_6$H$_{14}$	1.85	0.73	0.590
7	2,3-DMB → 2-MP	−0.97	−5.73	0.0386
8	2-MP → 2,3-DMB	0.97	5.73	0.0288
9	2,3-DMB → 2,2-DMB	−5.53	−3.45	0.0581
10	2,2-DMB → 2,3-DMB	5.53	3.45	0.1270
11	n-C$_7$H$_{16}$ → i-C$_7$H$_{16}$	−3.38	−2.26	0.7180
12	i-C$_7$H$_{16}$ → n-C$_7$H$_{16}$	3.38	2.26	0.2154
13	MCP → CH	−3.92	−8.75	0.0021
14	CH → MCP	3.92	8.75	0.0004
15	3-MP → 2-MP	−2.9	−3.34	0.5260
16	2-MP → 3-MP	2.9	3.34	0.3230
17	c-C$_5$H$_{10}$ + H$_2$ → n-C$_5$H$_{12}$	−86.30	−192.79	0.0001
18	c-C$_5$H$_{10}$ + H$_2$ → i-C$_5$H$_{12}$	−92.76	−197.54	0.0001
19	n-C$_4$H$_{10}$ + H$_2$ → Gas	−262.7	−414.7	0.0001
20	i-C$_4$H$_{10}$ + H$_2$ → Gas	−258.9	−415.6	0.0001
21	n-C$_5$H$_{12}$ + H$_2$ → Gas	−230.7	−355	0.0001
22	i-C$_5$H$_{12}$ + H$_2$ → Gas	−224.2	−350.3	0.0001
23	n-C$_6$H$_{14}$ + H$_2$ → Gas	−198	−294.5	0.0002
24	2-MP + H$_2$ → Gas	−193.3	−291.9	0.0002
25	3-MP + H$_2$ → Gas	−196.2	−295.2	0.0002
26	2,3-DMB + H$_2$ → Gas	−194.2	−297.6	0.0004
27	2,2-DMB + H$_2$ → Gas	−188.7	−294.1	0.0004
28	n-C$_7$H$_{16}$ + H$_2$ → Gas	−165.5	−234.1	0.0210
29	i-C$_7$H$_{16}$ + H$_2$ → Gas	−162.1	−231.8	0.0421
30	CH + H$_2$ → n-C$_6$H$_{14}$	−71.19	−110.8	0.0010
31	MCP + H$_2$ → 2-MP	−79.86	−104.7	0.0010
32	MCP + H$_2$ → 3-MP	−76.96	−101.4	0.0010
33	MCP + H$_2$ → 2,2-DMB	−84.43	−102.4	0.0020
34	MCP + H$_2$ → 2,3-DMB	−78.9	−98.97	0.0020
35	B + 3 H$_2$ → CH	−214.9	−254.2	0.0210
36	B + 3 H$_2$ → MCP	−211	−263	0.0210

Having such level of mechanism specification the change of concentration of i-component in reversible j-reaction of the first order can be written as a system of the material balance equations:

$$\frac{dC_i}{dt} = \sum_j k_j^{app} \cdot C_i \cdot C_{H_2}^{l_j} \tag{3}$$

at $t = 0$, $C_i = C_{i0}$,

where $j = 1, \ldots, m$ is a number of chemical reaction; C_i and k_j^{app} are respectively hydrocarbons concentration and apparent rate constants; l_j is a reaction order on hydrogen; t is time. For the aromatics hydrogenation reactions $l_j = 3$, for the hydrocracking and hydrodealkylation reactions $l_j = 1$, for the isomerization reactions $l_j = 0$. The apparent rate constants take into consideration the reaction rates inhibition depending on the feed composition, pressure and adsorption properties of the components.

As an example the kinetic equations for key components n-pentane and isopentane are given below:

$$\frac{dC_{n-C5}}{dt} = -k_1^{app} \cdot C_{n-C5} + k_2^{app} \cdot C_{i-C5} + k_{15}^{app} \cdot C_{c-C_5} \cdot C_{H_2} - k_{19}^{app} \cdot C_{n-C5} \cdot C_{H_2}$$

$$\frac{dC_{iso-C5}}{dt} = k_1^{app} \cdot C_{n-C5} - k_2^{app} \cdot C_{i-C5} + k_{16}^{app} \cdot C_{c-C_5} \cdot C_{H_2} - k_{20}^{app} \cdot C_{i-C5} \cdot C_{H_2}$$

Fig. 3. Formalized reaction scheme for isomerization process [25,26] (B-benzene; MCP-Methylcyclopentane; MP-methylpentane; CH-cyclohexane; DMB-dimethylbutane; n-normal; i-isomer; c-cyclo).

Table 5
Relative isomerization rate constants normalized by the rate constants of Pt/SO$_4$–ZrO$_2$ catalyst (all the constants were calculated for operating conditions for each type of catalyst).

Catalyst Main reactions	Pt/SO$_4$–ZrO$_2$	Pt/zeolite	Pt/Al$_2$O$_3$–CCl$_4$
n-C$_5$H$_{12}$ → i-C$_5$H$_{12}$	1	0.48	0.31
i-C$_5$H$_{12}$ → n-C$_5$H$_{12}$	1	1.43	0.96
2-MP → 3-MP	1	0.52	1.72
n-C$_6$H$_{14}$ → 2-MP	1	1.10	0.47
2-MP → 2,3-DMB	1	0.91	1.63
2,2-DMB → 2,3-DMB	1	1.27	0.85

All the reactions are shown in Fig. 3 and Table 4.

Practically kinetic parameters can be obtained experimentally measuring the reagents concentration change with time. From the kinetic curves it is possible to estimate the rate constants. The Arrhenius plot let us determine pre-exponential factors and activation energies. However the same parameters estimation can be done mathematically. The procedure of parameters estimation is carried out by minimization of the sum of the squares of the deviations between the plant and the calculated values of the key variables such as the composition of effluent from the last reactor and the outlet temperatures of the reactors.

At this paper kinetic parameters were defined mathematically. Having the reactants concentrations as the input data, the reactions rates as the responses and an initial guess of unknown parameters (taken from the literature) the least square parameters estimate was found. The optimization method based on the determination of the fixed points of the rate constants admitted region was applied. According to the Scarf's theorem [27] a completely-labeled simplex (all vertices have different labels) is to be found. The fixed point is situated inside the simplex. The same technique for the rate constants estimation was used in our previous papers [28–30]. Using this approach the rate constants for the reactions at the industrial unit were defined (apparent rate constants). To verify the parameters found the data from the industrial isomerization unit (situated in Russia) were computed starting from 2007 and up to now. The conditions in the simulations were the same as they were at the industrial unit. The simulation data therefore can be directly compared to the experimental data. The calculated composition, octane number and yield of isomerizate (simulation results) were in a very good agreement with each set of experimental data taken at the industrial unit for the whole period under consideration (6 years). The relative error for each case did not exceed 5%. This error is acceptable because the feed composition is measured experimentally by means of chromatography. And that experimental method has its own error. The similar study [1] reports higher errors (medium error 6.1% and maximum error 21.2%). The results of the rate constants estimation for Pt/SO$_4$–ZrO$_2$ catalyst are given in Table 4.

The rate constants for other catalyst types were also determined. The relative isomerization rate constants normalized by the rate constants of Pt/SO$_4$–ZrO$_2$ catalyst are presented in Table 5 for the main reactions. For reactions that are not present in Table 5 the differences between the reaction rates are rather modest.

According to the results shown in Table 5 the best characteristics has Pt/SO$_4$–ZrO$_2$ catalyst. For instance for the main reaction of isomerization of i-pentane the rate constant for Pt/SO$_4$–ZrO$_2$ catalyst is twice larger than for Pt/zeolite and three times larger compared to Pt/Al$_2$O$_3$–CCl$_4$ catalyst. Pt/SO$_4$–ZrO$_2$ allows obtaining isomerizate with higher RON. The data from the industrial isomerization unit show that the application of Pt/SO$_4$–ZrO$_2$ leads to the increase in RON by 10–14 at temperature range of 125–165 °C (compared to the application of other catalysts for the same raw material). The results presented in this paper allow recommending the application of Pt/SO$_4$–ZrO$_2$ for the industrial isomerization process.

4. Reactor model

The application of an ideal plug flow model is possible to describe the industrial isomerization process in a fixed-bed reactor. According to the calculation of Reynolds (Re = 7.2, laminar flow) and Peclet numbers (Pe = 339.2) we can assume that diffusion plays insignificant role in the process of mass transfer which occurs by means of convection. For the industrial isomerization process the reaction limited regime is observed (Thiele modulus $\Phi_j < 1$, internal effectiveness factor $\eta_j = 0.98$-1).

For the mathematical description of hydrodynamic and heat model of isomerization reactor some assumptions are accepted:

- Consider the industrial reactor as an ideal plug flow reactor.
- Mass and heat transport occurs by means of convection.
- Adiabatic operation.
- The formalized mechanism of hydrocarbons transformation (Fig. 3).

The model of isomerization reactor, presented by a system of equations of material balance for components and the equation of heat balance is the following:

$$G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^{m} a_j \cdot r_j$$

$$G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^m} \sum_{j=1}^{m} Q_j \cdot a_j \cdot r_j \tag{4}$$

The conditions are: at $z = 0$ $C_i = C_{i,0}$; $T = T_{en}$; $V = 0$ $C_i = C_{i,0}$; $T = T_{en}$. where z is a volume of raw material processed from the moment when the fresh catalyst was loaded, m^3; G is a raw material flow rate, m^3/h; $z = G \cdot t$ (t is a time of catalyst work from the new catalyst load, h); C_i is a concentration of ith component, mol/m^3; V is a volume of the catalyst layer, m^3; a is a catalyst activity; ρ is density of mixture, kg/m^3; C_p^m is a heat capacity of mixture, J/(kg·K); Q_j is jth reaction heat, J/mol, T is temperature, K; r_j is jth reaction rate, mol/(m^3 h). The parameter z is used in the Eq. (4) instead of t because G is not a fixed value and changes in the wide range. The term of equation $\partial C_i / \partial z$ shows the change of ith component concentration against the catalyst deactivation because of aging.

In the model the catalyst deactivation with time is considered. The catalyst activity can be defined as the ratio of current rate constants to the initial rate constants that were observed when the fresh catalyst was used:

$$a_j = \frac{k_{j,current}}{k_{j,initial}} \tag{5}$$

where $k_{j,initial}$ is the rate constant of jth reaction on the fresh catalyst, $k_{j,current}$ is the rate constant of jth reaction on the catalyst at present time.

The catalyst activity can be lost due to poisoning by harmful impurities containing sulfur and nitrogen, and by water and due to coking. The decrease in the dispersion of Pt also makes the catalyst less active. At present time the empirical dependence of catalyst activity on time was used in our work (obtained due to processing the data from the industrial unit for a 6-year period). We are working at defining the exact input of each phenomenon to the process of catalyst deactivation. These are the scope of our future works.

Another important problem is the calculation of isomerizate octane number according to the catalysate composition obtained as a result of modeling. Octane number (ON) is one of the most important properties of gasoline and is a measure of its antiknock property. All the octane numbers calculations at the present paper were done with the help of the model described in our previous paper [28].

5. Results and discussion

The example of calculation of isomerization process is given in Table 6 and Fig. 4. The experimental data were obtained from the industrial isomerization units of Russian refineries. Specifications of operating conditions for isomerization processes using different catalysts are presented in Table 7.

Comparing the values presented in Table 6, we can see, that isomerizate composition calculated on model coincides with experimental data from the industrial unit with the set accuracy (in our case the calculation error should not exceed an error of chromatographic analysis). Calculated values agree very well with the experimental data from different industrial units using different types of catalyst.

The simulation results delivered by our model are compared to values from the industrial isomerization plant (Fig. 4). The obtained simulation results of isomerizate octane number is in very good agreement with the actual data from the industrial unit.

While using isomerization mathematical model it is also possible to compare the different isomerization units work efficiency and choose more suitable variant of process optimization for given raw material [31]. The examples will be given below for the isomerization process scheme with recycle of n-pentane (Fig. 5) and for the scheme with deisopentanizer (Fig. 6).

Normal pentane is one of the main components of isomerization feed, its content can be as high as 35 wt.%. However the conversion on n-pentane in the simplest once-through isomerization process is not too large and usually does not exceed 60–65%. In such a case isomerizate can contain up to 15 wt.% of unreacted n-pentane. In the present paper the process with the recycle of n-pentane (Fig. 5) is simulated taking into account the feed composition and operating conditions (data are taken from the

industrial once-through isomerization unit of Russian refinery). The results are shown in Table 8.

It was shown (Table 8) that the application of the scheme with the recycle of n-pentane will allow increasing the isomerizate RON by 2.9–3.6 depending on the operating conditions and feed composition. Scheme with the recycle of n-pentane requires providing with depentanizer of isomerizate after the reaction section. The application of this scheme causes the light naphtha feed conversion increase that leads to the more efficient raw material utilization.

Further analysis shows that the high iso-pentane content in the isomerization feed (as high as 16 wt.% for the raw material from a number of oil fields) causes the decrease of feed conversion. In that case the isomerization process scheme with deisopentanizer is reasonable. The process with deisopentanizer (Fig. 6) is simulated taking into account the feed composition and operating conditions

Table 7
Specifications of operating conditions for the technologies with different catalyst types (for Table 6).

Parameter	Numerical value	Unit
Type of the catalyst	Pt/Al$_2$O$_3$-CCl$_4$	
Light naphtha feed stock	20.6	m^3/h
Pressure	3.4	MPa
Reactors inlet temperature	149	°C
Type of the catalyst	Pt/zeolite	
Light naphtha feed stock	25	m^3/h
Pressure	2.7	MPa
Reactors inlet temperature	245	°C
Type of the catalyst	Pt/SO$_4$-ZrO$_2$	
Light naphtha feed stock	90	m^3/h
Pressure	3	MPa
Reactors inlet temperature	130	°C

Table 6
Results of calculation of isomerization process with the mathematical model for the technologies with different catalyst types[a].

	RON	n-C$_4$H$_{10}$	i-C$_4$H$_{10}$	n-C$_5$H$_{12}$	i-C$_5$H$_{12}$	n-C$_6$H$_{14}$	2-MP	3-MP	2,2-DMB	2,3-DMB	n-C$_7$H$_{16}$	i-C$_7$H$_{14}$	c-C$_7$H$_{14}$	CP	MCP	CH	B
Pt/Al$_2$O$_3$-CCl$_4$																	
Feed (wt.%)	72.2	1.1	0.18	36.18	20.33	7.15	15.52	6.73	0.7	1.82	0.03	0	0	7.81	2.36	0.09	0
Simulation. wt.%	83.6	0.22	0.21	25.51	31.46	0.04	9.33	0.44	15.84	7.06	0.01	0.01	0	8.99	0.66	0.21	0.01
Experiment (wt.%)	83.6	0.06	0	25.64	31.42	0.03	9	0.61	16.31	7.28	0	0	0	8.78	0.02	0.85	0
Pt/zeolite																	
Feed (wt.%)	64.0	0.22	0.02	24.5	15.26	17.68	14.34	10.01	0.27	2.22	4.44	0	0	2.99	5.86	2.19	0
Simulation (wt.%)	72.5	1.45	0.67	19.12	21.73	10.87	14.95	9.78	4.79	4.77	2.7	0.05	0	2.68	4.91	1.52	0.01
Experiment. wt.%	71.8	1.22	0.63	19.63	21.94	11.33	14.85	10.08	4.35	4.1	2.73	0	0	2.82	5.03	1.29	0
Pt/SO$_4$–ZrO$_2$																	
Feed (wt.%)	65.4	0.00	0.00	34.03	10.64	18.09	13.83	7.45	0.00	1.06	0.00	0.00	0.00	4.26	7.45	2.13	1.06
Simulation (wt.%)	81.1	0.19	1.19	13.57	36.38	5.17	13.54	8.49	11.48	4.48	0.00	0.00	0.00	1.99	2.25	1.16	0.11
Experiment(wt.%)	81.0	0.00	1.06	13.83	36.17	5.32	13.83	8.51	11.70	4.26	0.00	0.00	0.00	2.13	2.13	1.06	0.00

[a] Raw material composition was characterized by chromatographic analysis.
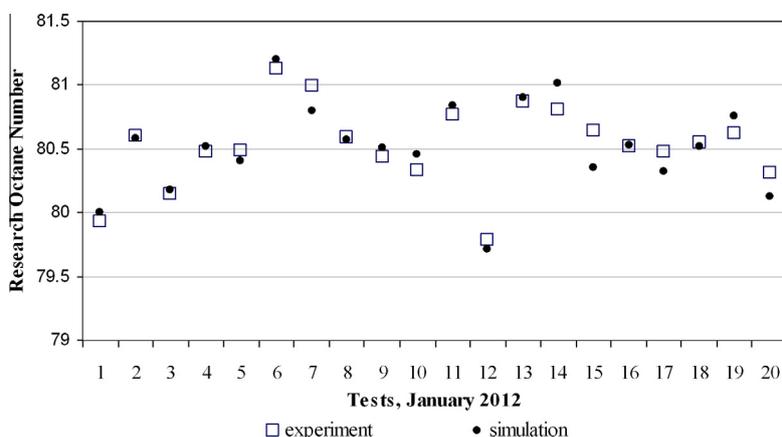
Fig. 4. Model verification. Comparison between actual data and simulation results of isomerizate RON for different feedstock.
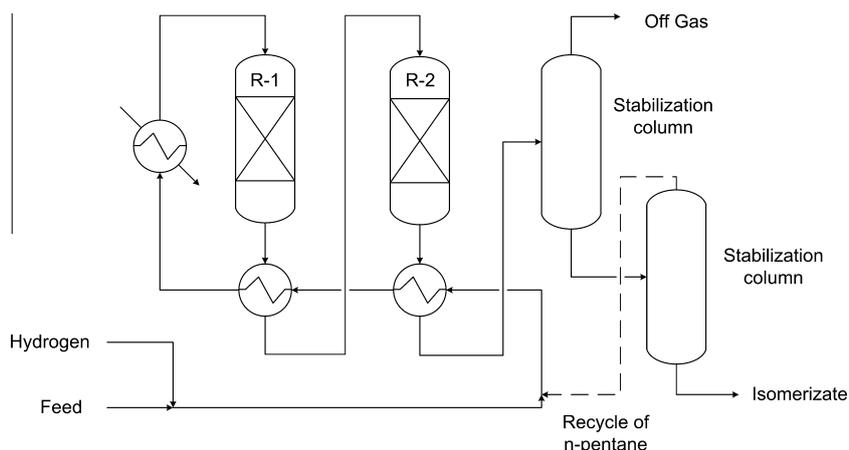
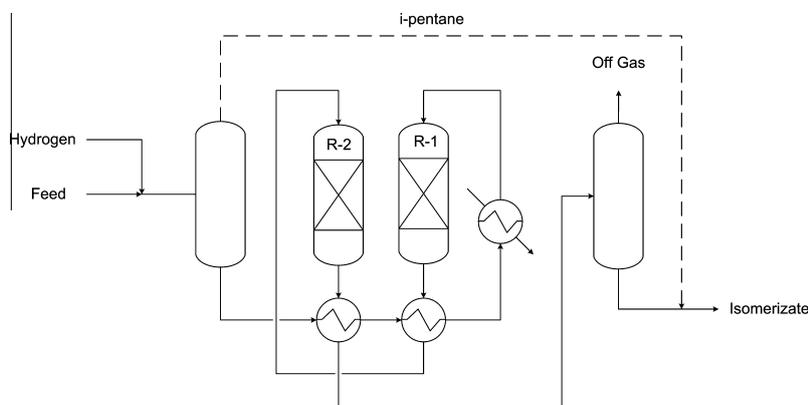**Fig. 5.** Isomerization process scheme with recycle of n-pentane (R-1, R-2 are isomerization reactors).

Fig. 6. Isomerization process scheme with deisopentanizer (R-1, R-2 are isomerization reactors).

Table 8
Simulation results for isomerization process scheme with the recycle of n-pentane.

Tests	Concentration of unreacted n-pentane, wt.%	RON		
		Without recycle (real data)	With recycle (simulation)	Δ
1	13.3	81.3	84.9	3.6
2	14.6	81.8	85.3	3.5
3	14.4	81.5	84.9	3.4
4	13.9	81.2	84.6	3.4
5	14.5	81.2	84.8	3.5
6	13.8	81.5	85.1	3.6
7	14.3	81.3	84.6	3.4
8	15.0	81.0	84.5	3.5
9	14.1	81.2	84.6	3.4

Table 9
Simulation results for isomerization process scheme with deisopentanizer.

Tests	RON			
	Feed	Product (without deisopentanizer)	Product (with deisopentanizer)	Δ
1	68.3	83.2	86.1	2.9
2	68.2	80.9	83.8	2.9
3	68.3	81.1	84.3	3.1
4	68.0	79.4	81.5	2.1
5	64.2	77.0	78.4	1.3
6	66.0	79.0	80.4	1.4
7	66.1	78.8	80.6	1.8
8	65.9	79.6	81.5	1.9
9	67.5	83.0	85.2	2.2

(data are taken from the industrial once-through isomerization unit of Russian refinery). The results are shown in Table 9.

Therefore the application of the scheme with deisopentanizer allows increasing the isomerizate RON by 1–3 depending on the operating conditions and feed composition. We observe this phenomenon due to the equilibrium shift of the reaction n-$C_5 \leftrightarrow$ i-C_5 in favour of i-C_5 formation.

The scheme mentioned above is not the only one variant of isomerization process but it can become an effective solution in the case of the feed with high isoalkanes content. Thus using the introduced isomerization mathematical model it is possible to compare the different isomerization units work efficiency and choose more suitable variant of process optimization for given raw material.

6. Conclusion

The formalized reaction scheme for light naphtha isomerization is elaborated based on the thermodynamics analysis. Both main and side reactions are considered. In the reaction scheme components having not more than 7 carbon atoms are considered as individual hydrocarbons, because their reactivity and octane numbers differ a lot. Hydrocarbons C_{7+} are aggregated because usually just a trace amount of these compounds can be found in the feed. Such level of specification allows applying the proposed model for the feed of different composition.

Kinetic parameters are defined mathematically for Pt/Al_2O_3–CCl_4, Pt/zeolite and Pt/SO_4–ZrO_2 catalysts. Therefore for the given feed composition it is possible to simulate the application of different catalysts and to select the better one for the industrial unit.

The calculation of Reynolds and Peclet numbers shows that diffusion plays insignificant role in the process of mass transfer which occurs by means of convection. The ideal plug flow model is

applied to describe the industrial isomerization process in a fixed-bed reactor. According to the calculation of Thiele modulus and internal effectiveness factor the reaction limited regime is observed for the industrial isomerization process.

The isomerizate composition calculated with the proposed model agrees very well with experimental information.

Using the introduced isomerization mathematical model it is possible to compare the different isomerization units work efficiency and choose more suitable variant of process optimization for given raw material. The examples of the calculations are given for the isomerization process scheme with recycle of n-pentane and for the scheme with deisopentanizer.

Thus in this paper a new universal mathematical model of light alkanes isomerization process valid for different raw materials composition and catalyst is provided. The model is designed to be applied at an industrial isomerization unit.

Appendix A. Nomenclature

Parameter	Description
a	catalyst activity ($-$)
C_i	concentration of component i (mol/m^3)
$C_{i,0}$	inlet concentration of component i, (mol/m^3)
C_p^m	heat capacity of hydrocarbons mixture (J/(kg K))
G	raw material flow rate (m^3/h)
ΔG	Gibbs free energy (kJ/mol)
i	numerator ($-$)
j	numerator ($-$)
k	rate constant (h^{-1})
k^{app}	apparent rate constant (h^{-1})
l_j	reaction order on hydrogen ($-$)
ON	gasoline octane number ($-$)
Pe	Peclet number, $- Pe = \dfrac{\text{Rate of transport by convection}}{\text{Rate of transport by diffusion or dispertion}}$
Q_j	jth reaction heat (J/mol)
r	reaction rate (mol/(m^3 h))
Re	Reynolds number ($-$)
t	time (h)
T	temperature (K)
T_{en}	inlet temperature (K)
V	volume of the catalyst layer (m^3)
v_i	stoichiometric coefficient in gross-equation of chemical reaction (-)
z	volume of raw material processed from the moment when the fresh catalyst was loaded (m^3) $z = G\,t$ (t is a time of catalyst work from the new catalyst load (h))
Greek letters	
η_j	internal effectiveness factor ($-$) $\eta = \dfrac{\text{actual rate of reaction}}{\text{reaction rate if entire interior surface exposed to concentration at the external pellet surface}}$
ρ^m	density of hydrocarbons mixture (kg/m^3)
τ	residence time (h)
Φ_j	Thiele modulus, ($-$) $\Phi_n^2 = \dfrac{''a'' \text{ surface reaction rate}}{''a'' \text{diffusion rate}}$ For a first-order reaction $\Phi_1 = R \cdot \sqrt{\dfrac{k_1 \cdot \rho_c \cdot S_a}{D_e}};$ $[k_1 \cdot \rho_c \cdot S_a] = (\frac{m}{s} \cdot \frac{g}{m^3} \cdot \frac{m^2}{g}) = \frac{1}{s}; \frac{k_1 \cdot \rho_c \cdot S_a}{D_e} = (\frac{1/s}{m^2/s}) = \frac{1}{m^2};$ $\Phi_1 = R \cdot \sqrt{\dfrac{k_1 \cdot \rho_c \cdot S_a}{D_e}} = m \cdot (\frac{1}{m^2})^{1/2} = \frac{1}{1} \text{(Dimensionless)}$
Abbreviation	
B	benzene
c-	cyclo
CH	cyclohexane
DMB	dimethylbutane
FBP	final boiling point (°C)
i-	isomer
IBP	initial boiling point (°C)
MCP	methylcyclopentane
MON	motor octane number
MP	methylpentane
n-	normal
RON	research octane number
TBP	true boiling point (°C)

Appendix B. Octane numbers of some paraffins [from Ref. [2,6,32]].

Compound	RON*	MON**
n-Butane	95.0	89.6
Isobutane	100.2	97.6
n-Pentane	62.0	62.0
2-Methylbutane	92.0	90.0
2,2-Dimethylpropane	85.0	80.0
n-Hexane	25.0	26.0
2,2-Dimethylbutane	94.0	95.5
2,3-Dimethylbutane	105.0	104.3
2-Methylpentane	74.4	74.9
3-Methylpentane	75.5	76.0
n-Heptane	0	0
2,2-Dimethylpentane	93.0	96.0
2,2,3-Trimethylbutane	112.1	101.3
2,2-Dimethylpentane	92.8	95.6
2,4-Dimethylpentane	83.1	83.8
3,3-Dimethylpentane	80.8	86.6
2,3-Dimethylpentane	91.1	88.5
2-Methylhexane	42.4	46.4
3-Methylhexane	52.0	55.8
3-Ethylpentane	65.0	69.3

*The research octane number (RON) simulates fuel performance under low severity engine [32].

**The motor octane number (MON) simulates more severe operation that might be incurred at high speed or high load [32]

References

[1] C.I. Koncsag, I.A. Tutun, C. Safta, Study of C5/C6 isomerization on Pt/H-zeolite catalyst in industrial conditions, Ovidius Univ. Annal. Chem. 22 (2) (2011) 102–106.

[2] S. Graeme, J. Ross, Advanced solutions for paraffins isomerization Annual meeting of National petrochemical and refiners association, March 21–23, 2004.

[3] E.A. Yasakova, A.V. Sitdikova, A.F. Achmetov, Tendency of isomerization process development in Russia and foreign countries Oil and gas business, 2010

[4] Y. Ono, A survey of the mechanism in catalytic isomerization of alkanes, Catal. Today 81 (2003) 3–16.

[5] T. Løften, E.A. Blekkan, Isomerisation of n-hexane over sulphated zirconia modified by noble metals, Appl. Catal. A: Gen. 299 (2006) 250–257. January 1S7.

[6] L.O. Aleman-Vazquez, J.L. Cano-Dominguez, E. Torres-Garcia, J.R. Villagomez-Ibarra, Industrial application of catalytic systems for n-heptane isomerization, Molecules 16 (2011) 5916–5927.

[7] Shi Zhen-min, Wu Xiao-hui, Liu Zhi-chang, Meng Xiang-hai, Influence of initiators on isomerization of normal hexane catalyzed by ionic liquids, J. Fuel Chem. Technol. 36 (3) (2008) 306–310.

[8] H. Al-Kandari, F. Al-Kharafi, A. Katrib, Isomerization reactions of n-hexane on partially reduced MoO₃/TiO₂, Catal Commun. 9 (2008) 847–852.

[9] A. Farid, A. Boucenna, Isomerization of light naphtha (C5, C6) by catalysts containing molybdenum and tungsten prepared by sol–gel method, Eur. J. Sci. Res 44 (3) (2010) 430–436.

[10] M. Khurshid, S.S. Al-Khattaf, n-heptane isomerization over Pt/WO3-ZrO2: a kinetic study, Appl Catal. A: Gen. 308 (2009) 56–64.

[11] A.K. Sinha, S. Sivasanker, Hydroisomerization of n-hexane over Pt-SAPO-11 and Pt-SAPO-31 molecular sieves, Catal. Today 49 (1999) 293–302.

[12] J. Macht, R.T. Carr, E. Iglesia, Consequences of acid strength for isomerization and elimination catalysis on solid acids, J. Am. Chem. Soc. 131 (2009) 6554–6565.

[13] A. Chica, A. Corma, P.J. Miguel, Isomerization of C5-C7 n-alkanes on unidirectional large pore zeolites: activity selectivity and adsorption features, Catal. Today 65 (2001) 101–110.

[14] A. Corma, J.M. Serra, A. Chica, Discovery of new paraffin isomerization catalysts based on SO42-/ZrO2 and WOx/ ZrO2 applying combinatorial techniques, Catal. Today 81 (2003) 495–506.

[15] A. Zhang, I. Nakamura, K. Aimoto, K. Fujimoto, Isomerization of n-pentane and other light hydrocarbons on jybrid catalyst. Effect of hydrogen spillover, Ind. Eng. Chem. Res. 34 (1995) 1074–1080.

[16] S. Triwahyono, A.A. Jalil, R.R. Mukti, M. Musthofa, N.A.M. Razali, M.A.A. Aziz, Hydrogen spillover behavior of Zn/HZSM-5 showing catalytically active protonic acid sites in the isomerization of n-pentane, Appl. Catal. A: Gen. 407 (2011) 91–99.

[17] M.L. Maloncy, L. Gora, J.C. Jansen, Th. Maschmeyer, Conceptual processes for zeolite membrane based hydroisimerization of light alkanes Ars, Separatoria Acta 2 (2003) 18–28.

[18] B. Shen, J. Cao, J. Liu, X. Wang, A coupled technology to produce high-purity normal and isomeric pentane with reforming topped oil, Fuel 90 (2011) 364–368.

[19] K. Watanabe, N. Chiyoda, T. Kawakami, Development of new isomerization process for petrochemical by-products 18th Saudi Arabia-Japan Joint Symposium Dhahran, Saudi Arabia, November 16–17, 2008

[20] A. van de Runstraat, J. van Grondelle, R.A. van Santen, Microkinetics modeling of the hydroisomerization of n-hexane, Ind. Eng. Chem. Res. 36 (1997) 3116–3125.

[21] J.S. Ahari, K.Khorsand, A.A. Hosseini, A. Farshi, Experimental study of C5/C6 isomerization in light straight run gasoline (LSRG) over platinum mordenite zeolite, Petroleum Coal 48 (3) (2006) 42–50.

[22] C.L. Li, Z.-L. Zhu, Network of n-hexane isomerization over Pt/Al₂O₃ and Pd/HM catalysts.

[23] H. Liu, X. Meng, R. Zhang, Z. Liu, J. Meng, C. Xu, Reaction performance and disappearance kinetics of n-pentane isomerization catalyzed by chloroaluminate ionic liquid, Catal. Commun. 12 (2010) 180–183.

[24] G.G. Volkova, S.I. Reshetnikov, L.N. Shkuratova, A.A. Budneva, E.A. Paukshtis, n-hexane skeletal isomerization over sulfated zirconia catalysts with different Lewis acidity, Chem. Eng. J. 134 (2007) 106–110.

[25] A.V. Kravtsov, E.D. Ivanchina Intellektual'nie sistemy v himicheskoy tehnologii i inzhenernom obrazovanii: neftehimicheskie processy na Pt-katalizatorah (Intellectual systems in chemical engineering and engineering education: petrochemical processes on Pt-catalysts) Novosibirsk: NAUKA. Siberian Publishing Firm RAS, 1996–200 (in Russian).

[26] N.V. Chekantsev, E.D. Ivanchina Mathematical modeling of pentane-hexane fraction isomerization process on si-2 catalyst. Abstracts XVIII International Conference on Chemical Reactors CHEMREACTOR-18 – Malta, September 29 – October 3, 2008.

[27] H. Scarf, The approximation of fixed points of a continuous mapping, SIAM J. Appl. Math. 15 (5) (1967) 1328–1343.

[28] M.S. Gyngazova, A.V. Kravtsov, E.D. Ivanchina, M.V. Korolenko, N.V. Chekantsev, Reactor modeling and simulation of moving-bed catalytic reforming process, Chem. Eng. J 176–177 (2011) 134–143.

[29] E.S. Sharova, D.S. Poluboyartsev, N.V. Chekantsev, A.V. Kravtsov, E.D. Ivanchina, Monitoring of the commercial operation of reforming catalysts using a computer simulation system catalysis in industry, -т. 1, No. 2-c, 2009, pp. 128–133.

[30] M.S. Gyngazova, A.V. Kravtsov, E.D. Ivanchina, M.V. Korolenko, D.D. Uvarkina, Kinetic model of the catalytic reforming of gasolines in moving-bed reactors catalysis in industry, vol. 2, No. 4, 2010, pp. 374–380.

[31] E. Litvak, A. Kravtsov, E. Ivanchina, N. Chekantsev Influence of chemical-engineering system structure on efficiency of pentane-hexane fraction isomerization process CHEMREACTOR-19: XIX. In: International Conference on Chemical Reactors, Vienna, Austria, 5–9 September, 2010.

[32] A.D. Estrada-Villagrana, C. De La Paz-Zavala, Application of chemical equilibrium for hydrocarbon isomerization analysis, Fuel 86 (2007) 1325–1330.