

SVETLANA A. ROVENSKAJA¹
NIKOLAJ M. OSTROVSKI²

1 Omsk State University, Omsk,
Russia

2 Omsk Department of Boreskov
Institute of Catalysis, Omsk,
Russia

SCIENTIFIC PAPER

665.633+661.183.48:665.656.6:531.3

AROMATIZATION OF LIGHT NAPHTHA FRACTIONS ON ZEOLITES

1. KINETIC MODEL

On the basis of analyzing kinetic experimental data performed in laboratory integral reactors a lumping kinetic model of the "Zeofforming" process was developed. A reaction scheme of the lumped components was proposed, that was adapted to the technological requirements. The reaction rate constants and activation energies were estimated, that are valid for certain feed compositions. The model is intended for further modeling and optimization of the process.

Lately, in the field of secondary refinery processes (cracking, reforming, isomerization), there has been increasing interest in the hydrogen-free catalytic treatment of light naphtha and gas condensates on high-silica zeolite catalysts [1]. Numerous experiments that were carried out at the SEC "Zeosit" of the Boreskov Institute of Catalysis, confirm the possibility of lead-free gasoline production by the catalytic conversion of low-octane crude naphtha (casing-head gasoline [2], gas condensate [3], oils) using catalysts based on high-silica zeolites. The process, called "Zeofforming", was tested in an experimental-industrial plant for the production of gasoline from casing-head gasoline (capacity of 5000 t/year) and was put into operation in 1992, at the Nizhnevartovsk gas-processing plant. Zeofforming industrial plants (capacity of 40000 t/year) were put into operation in Poland, Kirghizia, Georgia, South Korea, and are intended for the production of Eurosuper-95 gasoline [4]. Now SEC "Zeosit" is working on the design of similar plants in other regions of Russia, mainly in Siberia. Thus, Zeofforming has become one of the important refinery processes. The Zeofforming process may especially be effective in the conversion of secondary light hydrocarbon fractions that include olefins.

Meanwhile, the theoretical basis of this process has practically not been developed. The available kinetic investigations do not exceed the limits of experimental dependencies [1,5,6] that are not brought to kinetic equations and parameters.

The kinetics of individual hydrocarbon conversions on zeolite HZSM-5 in the Zeofforming process were studied in ref. [7]. The activation energies of cyclohexane (127 kJ/mol) and heptane (106 kJ/mol) conversion were determined. It was assumed that [7]:

Author address: S.A. Rovenskaja, Omsk State University, Omsk, Russia

N.M. Ostrovski, Hemijska Industrija HIPOL, 25250 Odžaci, Srbija, ostrovski@hipol.com

Paper received: April 4, 2003

Paper accepted: September 10, 2003

– the scission of C–C bonds is the limiting stage in the conversion of individual hydrocarbons;

– the reaction rates obeyed first order equations.

However, the reaction scheme and kinetic parameters were not presented [7]. Moreover, there are no works in the literature dealing with the modeling and optimization of this process.

For this purpose, at least reaction kinetic model of lumped components is necessary. Such a model has been proposed in this report. The experimental data, which have been published in the literature for several types of feedstocks, were used to construct the model. They were used to estimate the validity of the proposed model for the conversion of various light fractions.

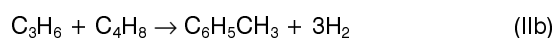
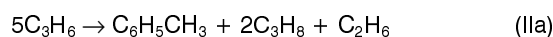
MAIN REACTIONS

Hydrocarbon conversion on zeolite catalysts under the conditions of the Zeofforming process includes a series of consecutive and parallel reactions on acid-base types of active centers. The first stage of paraffin conversion consists of C–C bond scission with the formation of unsaturated fragments followed by hydrogen disproportionation between olefins and light paraffins, as well as the formation of aromatics. For example:

stage 1: C–C bond scission in paraffins

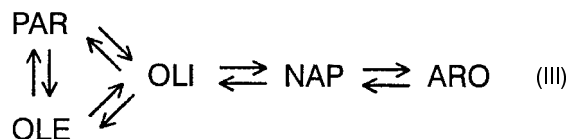


stage 2: olefin disproportionation with the formation of aromatics



Beside the main reactions on the acid sites of the zeolite, additional alkylation and isomerization reactions are possible with the participation of the initial and intermediate compounds. Probably, the general scheme

of conversion is similar to that proposed for the "Cyclar" process [8]:



where: PAR – Paraffins; OLE – Olefins; OLI – Oligomers; NAP – Naphtenes, and ARO – Aromatics.

The feedstocks of the "Cyclar" process consist of C₃–C₄ hydrocarbons, whereas Zeoforming feed fractions contain paraffins, naphthenes and aromatics. Thus, here naphthenes are not only intermediates, but also important components of the feed.

ANALYSIS OF THE EXPERIMENTAL DATA

For substantiation of the reaction scheme and model equations, experimental results were analyzed. The experimental data are presented in the form of dependencies of the product composition on temperature (T), pressure (P) and space velocity (V₀). The experiments, published in references [1,5,6], are presented in Figs. 1–3. In ref. [5] the process was studied in an isothermal reactor with a fixed catalyst bed at T = 300–460°C, P = 0.1–0.4 MPa and V₀ = 0.5–7 h⁻¹.

It is seen from Figs. 1 and 2, that the feed conversion increases with increasing temperature (and decreasing space velocity). These increase the gas product yield and reduce the yield of the liquid fractions. At the same time, in the liquid product, the contents of n-paraffins and naphthenes decreased and the contents of i-paraffins and aromatics increased, leading to a rise in the octane number of the gasoline. The influence of pressure on the yield and composition of the product is individual for each type of feed (Figure 3). Generally, the dependencies of the feed conversion and octane

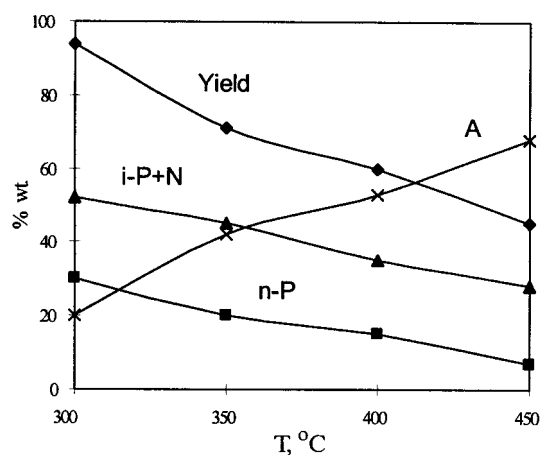


Figure 1. Dependence of the gasoline yield and composition on temperature. Conversion of Orenburg gas condensate [6]. P = 1 MPa, V₀ = 2 h⁻¹.

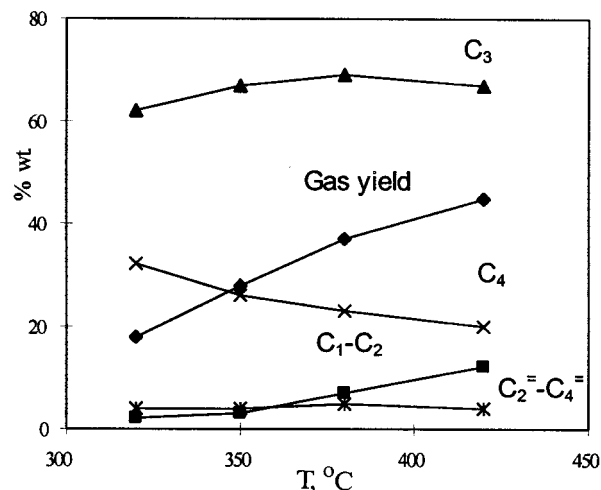


Figure 2. Dependence of the gas yield and composition on temperature. Conversion of gas condensate (45–125°C) [5]. P = 1 MPa, V₀ = 2 h⁻¹.

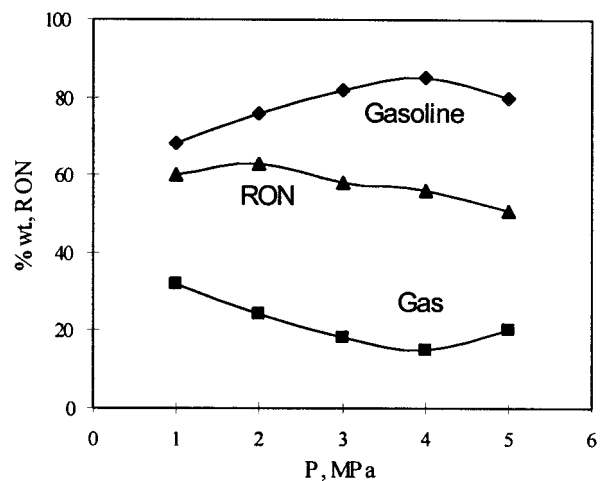


Figure 3. Dependence of the gasoline yield and octane number on pressure [1].

number of the gasoline on pressure are functions that have a maximum.

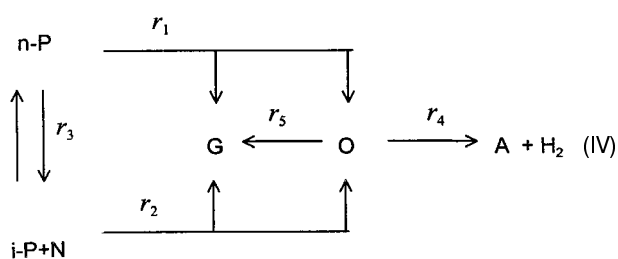
The experiments indicate, that the olefin content in the products is approximately constant under the process conditions and with stepwise temperature increase [5], (Fig. 2). Thus, the reaction rates of olefin formation and consumption are approximately the same. Olefins that are formed during cracking (stage 1) are consumed further in the formation of aromatics (stage 2). Due to the hydrogen-free condition of the Zeoforming process, a considerable amount of olefins and light paraffins are formed. They constitute the gas phase of the products (20–30%). The gas composition, in which propane and butanes dominate, practically does not change. Thus it is possible to consider the gas as one lumped component, without defining its composition. The paraffin isomerization reaction is

reversible and reaches equilibrium under the process conditions.

Since the purpose of the process is to produce high-octane gasoline, the main important components are aromatics, n-paraffins, i-paraffins, naphthenes and gas. Nevertheless, from the point of view of process development, it is rather important to know the concentrations of the olefins and oligomers because of their effect on catalyst deactivation by coking.

KINETIC MODEL

Based on the processing features, available experiments, and assumed reactions on the zeolite acid centers, the following scheme was proposed:



where A, O, G, n-P, i-P+N are the lumped components of aromatics, olefins, gases, n-paraffins, i-paraffins and naphthenes; r_j – the rate of reaction j .

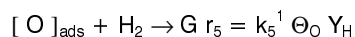
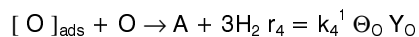
The aggregation of i-paraffins and naphthenes in lumped components is rather convenient for technology and analytical control. Moreover, it has definitely been shown, that the naphthenes/i-paraffins ratio is practically constant under the conditions of the process [9].

The reaction rate equations for scheme (IV) were written assuming the mass action law:

$$\begin{aligned} r_1 &= k_1 Y_{\text{n-P}}, & r_2 &= k_2 Y_{\text{i-P+N}}, \\ r_3 &= k_3 Y_{\text{n-P}} (1 - Y_{\text{i-P+N}} / (K_P Y_{\text{n-P}})) & (1) \\ r_4 &= k_4 Y_{\text{O}}^2, & r_5 &= k_5 Y_{\text{O}} Y_{\text{H}}, \end{aligned}$$

where Y_i is the molar fraction of the i -th component; Y_{H} – the molar fraction of hydrogen; k_j – the reaction rate constant; K_P – the equilibrium constant.

It is natural to suppose that olefins (light ones and especially oligomers) are strongly adsorbed on the active sites of the catalyst. Reactions 4 and 5 can then be presented as:



where Θ_{O} is the fraction of active centers occupied by olefins (dimensionless).

Since Θ_{O} is proportional to the molar fraction of the olefins in the reaction mixture $\Theta_{\text{O}} \sim b_{\text{O}} Y_{\text{O}}$, then $r_4 = k_4^1 b_{\text{O}} Y_{\text{O}}^2$ and $r_5 = k_5^1 b_{\text{O}} Y_{\text{O}} Y_{\text{H}}$, where b_{O} is the adsorption equilibrium constant. Hence, the temperature

dependencies of the apparent reaction rate constants $k_4 = k_4^1 b_{\text{O}}$ and $k_5 = k_5^1 b_{\text{O}}$ become:

$$\begin{aligned} k_4 &= (k_4^1)^{\circ} \exp(-E_4/RT) b_{\text{O}}^{\circ} \exp(Q_{\text{O}}/RT), \\ k_5 &= (k_5^1)^{\circ} \exp(-E_5/RT) b_{\text{O}}^{\circ} \exp(Q_{\text{O}}/RT) \end{aligned}$$

where Q_{O} is the heat of adsorption.

Consequently one may expect that the apparent activation energies will be low, because of $E_4^{\text{a}} = E_4 - Q_{\text{O}}$, $E_5^{\text{a}} = E_5 - Q_{\text{O}}$, and that the reaction rates 4 and 5 will be weakly dependent on temperature. Later on it shall be confirmed by analysis of the experiments.

The mass balance equation in a laboratory reactor is necessary for the determination of the kinetic parameters. In the case of an isothermal integral reactor, it has the form:

$$\sigma \frac{dY_i}{d\tau} + Y_i \frac{d\sigma}{d\tau} = w_i, \quad (2)$$

$$\frac{d\sigma}{d\tau} = \sum_{i=1}^N w_i, \quad w_i = \sum_{j=1}^R v_{ij} r_j \quad (3)$$

where $\sigma = \sum n_i / \sum n_i^{\circ}$ is the coefficient of total number of moles (dimensionless); w_i – the rate of formation of the i -th component ($\text{m}^3 / \text{m}^3 \text{ cat h}$); r_j – reaction rate ($\text{m}^3 / \text{m}^3 \text{ cat h}$); v_{ij} – the stoichiometric coefficient of the i -th component in the j -th reaction; τ – the contact time ($\text{m}^3 \text{ cat h} / \text{m}^3$); Y_i – the molar or volume fraction of the component.

In accordance with scheme (IV), the rates of component formation should be written as:

$$\begin{aligned} w_{\text{n-P}} &= -r_1 - r_3, & w_{\text{i-P+N}} &= -r_2 + r_3, \\ w_{\text{O}} &= r_1 + r_2 - 2r_4 - r_5, & w_{\text{A}} &= r_4, \\ w_{\text{G}} &= r_1 + r_2 + r_5, & w_{\text{H}_2} &= 3r_4 - r_5, \\ \frac{d\sigma}{d\tau} &= r_1 + r_2 + 2r_4 - r_5 \end{aligned} \quad (4)$$

The experimental results presented in Figs. 1–3, were analyzed using the model (1–4). The simplex method of Nelder–Meed [10] was used to calculate the reaction rate constants. The system of differential equations (4) was solved using the Novikov procedure [11].

The values of the reaction rate constants for the experiments in Fig. 4 are presented in Table 1.

Table 1. Values of the reaction rate constants for the conversion of gas condensate (33–155°C).
 $P = 1 \text{ MPa}$, $T = 420^\circ\text{C}$

No.	Reaction	Reaction rate constant k_j , h^{-1} (at $T = 420^\circ\text{C}$)
1	$\text{n-P} \rightarrow \text{O} + \text{G}$	9.2 ± 0.5
2	$\text{i-P+N} \rightarrow \text{O} + \text{G}$	4.0 ± 0.2
3	$\text{n-P} \leftrightarrow \text{i-P+N}$	5.3 ± 0.3
4	$2\text{O} \rightarrow \text{A} + 3\text{H}_2$	257 ± 13
5	$\text{O} + \text{H}_2 \rightarrow \text{G}$	376 ± 19
	Mean error	2.8 %

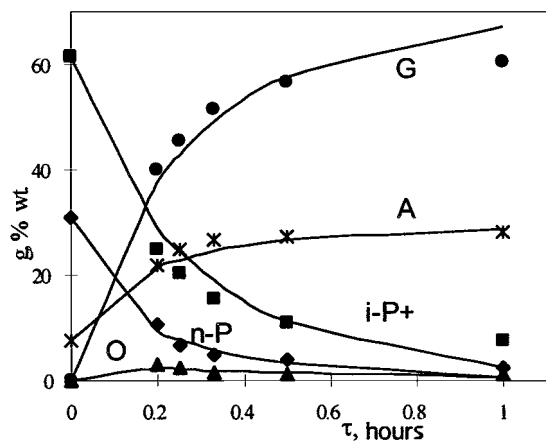


Figure 4. Dependence of the product composition on contact time. Conversion of the light fraction (33–155°C). $P = 1 \text{ MPa}$, $T = 420^\circ\text{C}$. Points – experiment [5]; lines – model prediction.

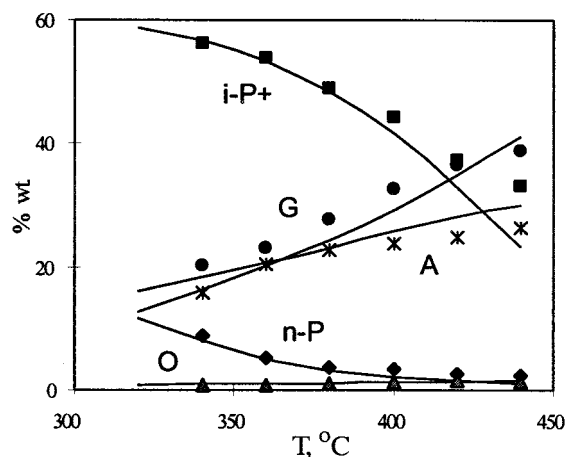


Figure 6. Dependence of the product composition on temperature. Conversion of model feed (*n*-octane / *i*-octane / cyclohexane = 1/1/1). Points – experiment [5]; lines – model prediction.

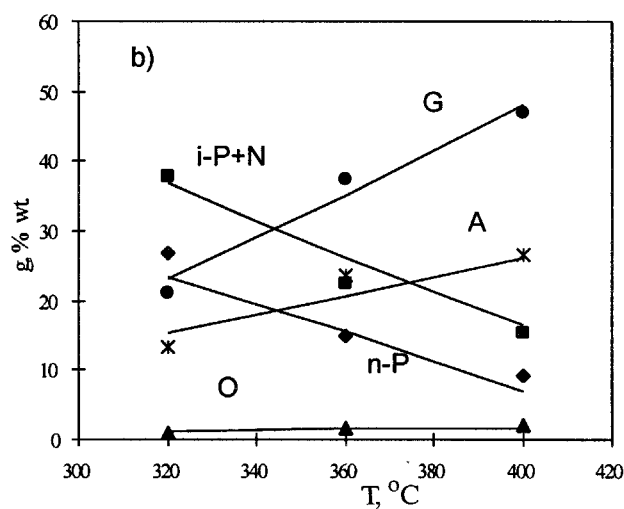
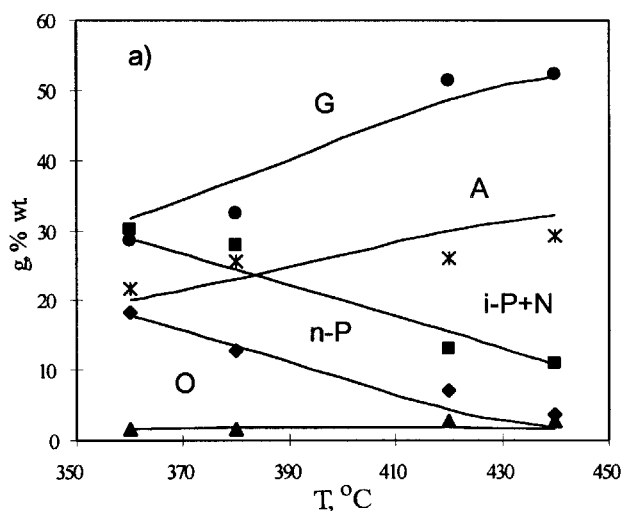


Figure 5. Dependence of the product composition on temperature. (a) – casing-head gasoline of the Nizhnevartovsk gas-processing plant [2]; (b) – gas condensate of the Kherson refinery [3]. Points – experiment; lines – model prediction.

The values of the activation energies are presented in Table 2. The experimental results in Figs. 1, 2, 5 and 6 were used to determine E_a . It may be seen from the table that the highest activation energy was observed for the paraffin cracking reaction. It is characteristic that the rates of reactions 4 and 5 practically do not depend on temperature (Table 2). The reason was discussed previously and has now been confirmed by the calculations. To demonstrate the predictive ability of the model, the experimental data for two types of feed are presented in Fig. 5, together with the simulated curves.

Table 2. Values of the activation energies for the conversion of casing-head gasoline of the Nizhnevartovsk gas-processing plant (a) and the gas condensate of the Kherson refinery (b)

No.	Reaction	Activation energy E_j , kJ/mol	
		Feed (a)	Feed (b)
1	$n\text{-P} \rightarrow \text{O} + \text{G}$	120 ± 6	107 ± 5
2	$i\text{-P+N} \rightarrow \text{O} + \text{G}$	23.2 ± 1.2	35.2 ± 1.8
3	$n\text{-P} \leftrightarrow i\text{-P+N}$	13.0 ± 0.6	14 ± 0.7
4	$2\text{O} \rightarrow \text{A} + 3\text{H}_2$	~ 0	~ 0
5	$\text{O} + \text{H}_2 \rightarrow \text{G}$	0.32 ± 0.02	0.37 ± 0.02
	Mean error	15 %	12 %

It is necessary to note that the feed content demonstrate an ambiguous effect on the reaction kinetics, particularly on the reaction rate constants and activation energies. Thus, the activation energies for different crude fractions (Table 2) are similar, but differ from the values for the model feedstock (Table 3). The differences in the constants of the 4-th and 5-th reactions (see Tables 1 and 3) are especially significant. Consequently, the feed content influences the yield and properties of the Zeofforming gasoline.

Table 3. Values of the kinetic parameters for the conversion of the model feed (*i*-octane/*n*-octane/cyclohexane = 1/1/1), $P = 1 \text{ MPa}$

No.	Reaction	Reaction rate constant k_j, h^{-1} (at $T = 420 \text{ }^\circ\text{C}$)	Activation energy $E_j, \text{kJ/mol}$
1	$n\text{-P} \rightarrow \text{O} + \text{G}$	15.0 ± 0.8	63 ± 3
2	$i\text{-P} + \text{N} \rightarrow \text{O} + \text{G}$	1.40 ± 0.07	106 ± 5
3	$n\text{-P} \leftrightarrow i\text{-P} + \text{N}$	1.30 ± 0.07	97 ± 5
4	$2\text{O} \rightarrow \text{A} + 3\text{H}_2$	330 ± 18	~ 0
5	$\text{O} + \text{H}_2 \rightarrow \text{G}$	60 ± 3	0.97 ± 0.05
	Mean error	3.3 %	7.6 %

Nevertheless, such an influence is typical for catalytic hydrocarbon processes, when not only the feed composition, but also the mean carbon number of the feed vary. Therefore, the main advantage of the proposed model is that the lumped reaction scheme and reaction equations are valid for different feed types. However, the values of the kinetic parameters (as usual) should be evaluated for each type of feedstock and catalyst.

Analysis of the results indicates that scheme (IV) and the proposed model provide good prediction of the product composition dependencies on temperature and contact time. The kinetic parameter values weakly depend on the feed composition for industrial types of crude fractions. Nevertheless, in the case of principal changes of the feed, the kinetic parameters must be corrected. First of all, separate measurement of *i*-paraffins and naphthenes is necessary. Probably, the reaction scheme in this case may be similar to (III).

The practically zero values of the activation energies of olefin conversion into aromatics and gas indicate that their reactivity is related directly to their adsorption, i.e. $E_{4,5} \approx Q_0$. This was confirmed by

investigations of the condensation products (coke precursors) in zeolite catalysts of this process [12]. It was shown that these products fill the zeolite cavity in amorphous condition [12]. Thus, the active sites are permanently covered by intermediate oligomers. The consideration of such a feature of the Zeoforming mechanism enables the completion of this model by a model of catalyst deactivation, which is the subject of a subsequent publication.

REFERENCES

- [1] Agabalyan L.G., Khadzhiyev S.N., Rogovskaya N.Kh. et al. – *Khimiya i Tehnologiya Topliv i Masel*, **5** (1988) 6–7 (in Russian).
- [2] Stepanov V.G., Getinger A.Ya., Snytnikova G.P. et al. – *Neftepererabotka i Neftehimiya*, **12** (1988) 3–6 (in Russian).
- [3] Stepanov V.G., Litvinenko N.G., Ione K.G. – *Neftepererabotka i Neftehimiya*, **10** (1992) 14–22 (in Russian).
- [4] Stepanov V.G., Ione K.G. – In: Proc. 3rd Int. Conf. on Petroleum Chemistry, Tomsk (1997) pp. 123–126.
- [5] Stepanov V.G., Ione K.G., Snytnikova G.P. – In: SSSC, v. 100: Catal. in Refin. and Petrochem., Amsterdam, Elsevier (1995) pp. 477–482.
- [6] Snytnikova G.P., Radchenko M.N., Stepanov V.G., Ione K.G. – *Gazovaya Promishlennost*, **4** (1988) 54–55 (in Russian).
- [7] Stepanov V.G., Kapterev S.W. – In: Eur. Congr. Catal., EUROPACAT–3, Krakow (1997) 779.
- [8] Martindale D.C., Kychar P.J., Olson R.K. – Aromatics from LPG – CYCLAR, UOP Technology Conference. Moscow. 1988.
- [9] Ahmetov A.F., Karatun O.N. – *Neftepererabotka i Neftehimiya*, **1** (2001) 23–26 (in Russian).
- [10] Bandy B. Optimization Methods, Moskva, Radio i svyaz, 1988, 84 p. (in Russian).
- [11] Novikov V.A., Novikov E.A. Two effective algorithms for numerical solution of Cauchy problem for a system of ordinary differential equations, Preprint 5–84, Novosibirsk, 1984 (in Russian).
- [12] Echevskii G.V., Kalinina N.G., Anufrienko V.F., Polubojarov V.A. – *React. Kinet. Catal. Lett.*, **33** (1987) 305–310.

IZVOD

AROMATIZACIJA LAKIH BENZINSKIH FRAKCIJA NA ZEOLITIMA 1. KINETIČKI MODEL

(Naučni rad)

Svetlana A. Rovenskaja¹, Nikolaj M. Ostrovski²

¹Omsk State University, Omsk, Russia

²Omsk Department of Boreskov Institute of Catalysis, Omsk, Russia

Zeoforming proces je razvijen za proizvodnju visokooktanskog benzina iz lakih benzinskih frakcija na zeolitnim katalizatorima bez korišćenja vodonika. Na bazi analize eksperimentalnih podataka koje su urađene u laboratorijskim integralnim reaktorima, postavljen je i razvijen kinetički model procesa.

Predložena je shema osnovnih reakcija među zbirnim komponentama reakcione smeše (*n*-parafini, *i*-parafini, nafteni, olefini, gas), koja je prilagođena tehnološkim zahtevima procesa.

Određeni su kinetički parametri (konstante brzina reakcija, energije aktivacije), koji važe za različite vrste sirovina pogodnih za ovaj proces.

Model je namenjen za primenu u modelovanju i za optimizaciju procesa što će biti problematika budućih istraživanja.

Ključne reči: Proces Zeoforming • Osnovne reakcije • Kinetički model • Kinetički parametri • Key words: Zeoforming process • Main reactions • Kinetic model • Kinetic parameters •

