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Modeling of reactor of straight–run gasoline fractions refining on zeolite catalysts

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Abstract

Zeolites are widely used as catalysts and catalyst supports for fuel and lubricants production processes with enhanced performance properties. Design of industrial reactor requires the construction of a mathematical model and selection of optimal operating conditions for reducing the number of scaling stages. The authors have proposed a scheme of hydrocarbons conversion on zeolite catalysts, thermodynamics of reactions has been considered and the inverse kinetic problem has been solved. The model of reactor of straight–run gasoline fractions refining in software HYSYS Aspen Plus™ process simulator has been developed and its adequacy to experimental data has been shown.

Keywords: Zeoforming; zeolte; model of reactor; inverse kinetics problem; straight–run gasoline.

1. Introduction

The efficiency of oil refining is largely based on the use of zeolites as catalysts. The use of zeolites as catalysts in refining and petrochemistry was considered as one of the major accomplishments of the XXth century. Zeolite catalysts were the source of major improvements in gasoline yield and octane as well as in the production of purer fuels and lubricants with enhanced performance properties.

The following advantages make the conversion processes on zeolite catalysts cost–effective and attractive for implementing:

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- Low operating costs and capital investments;
- Simplicity of the technology;
- Low explosive and fire hazards due to the lack of hydrogen;
- Low sensitivity of a catalyst to the quality of raw materials.

Mathematical modeling can reduce development time and industrial processes design to find optimal operating conditions of reactor equipment[1,2]. The formation of conversion scheme and the calculation of thermodynamic and kinetic parameters of reactions are required during the development phase of the model.

The mechanism and kinetics of hydrocarbons reactions on zeolite catalysts has been reported in the numerous papers. For example, the author[3] shows the chemical transformation of saturated acyclic and cyclic hydrocarbons into aromatic compounds by dehydrogenation without reducing the number of carbons of the products with respect to the substrates. Figure 1 presents the elementary transformations that take place in zeoforming process. These transformations include cyclization of acyclic compounds, isomerization of cyclic compounds into cyclohexane and dehydrogenation, and aromatization.
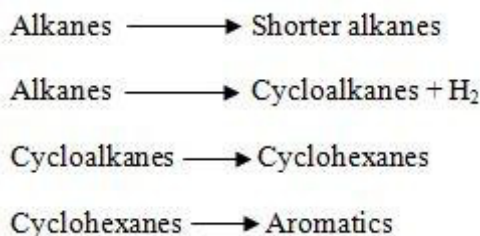
$$Alkanes \longrightarrow Shorter\ alkanes$$

$$Alkanes \longrightarrow Cycloalkanes + H_2$$

$$Cycloalkanes \longrightarrow Cyclohexanes$$

$$Cyclohexanes \longrightarrow Aromatics$$

Fig. 1. Elementary reactions occurring simultaneously in zeforming of naphtha[3]

Several elementary chemical reactions occur during the cracking of alkanes on zeolite catalysts. These classes of reactions include shortening of the chain length of paraffinic hydrocarbons in a raw material, isomerization of the linear into branched alkanes, ring closure and hydrogenation/dehydrogenation of the C – C bond.
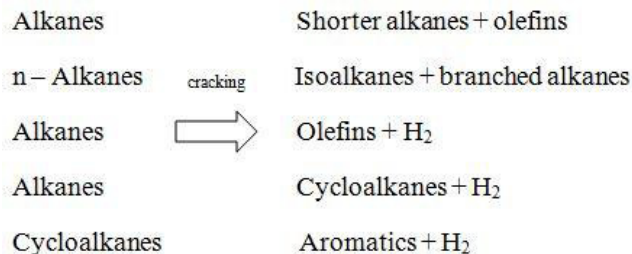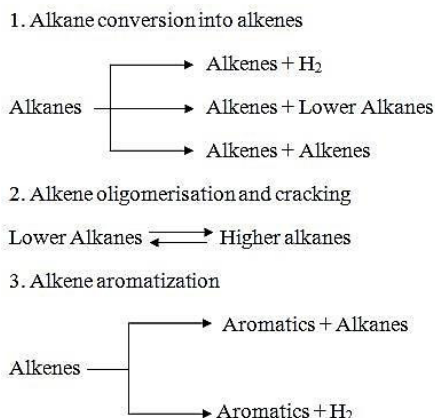
Alkanes		Shorter alkanes + olefins
n – Alkanes	cracking	Isoalkanes + branched alkanes
Alkanes	$\Rightarrow$	Olefins + H$_2$
Alkanes		Cycloalkanes + H$_2$
Cycloalkanes		Aromatics + H$_2$

Fig. 2. Elementary stages occurring simultaneously during cracking[3]

Many researchers[4–6] suggest that the conversion of light alkanes into aromatics on ZSM–5 supported catalyst proceeds through three main stages, which presented in Figure 3:

- alkane transformation into alkenes;
- interconversion of the alkenes;
- alkene aromatization.

1. Alkane conversion into alkenes

$$\text{Alkanes} \begin{cases} \rightarrow \text{Alkenes} + H_2 \\ \rightarrow \text{Alkenes} + \text{Lower Alkanes} \\ \rightarrow \text{Alkenes} + \text{Alkenes} \end{cases}$$

2. Alkene oligomerisation and cracking

Lower Alkanes $\rightleftharpoons$ Higher alkanes

3. Alkene aromatization

$$\text{Alkenes} \begin{cases} \rightarrow \text{Aromatics} + \text{Alkanes} \\ \rightarrow \text{Aromatics} + H_2 \end{cases}$$

Fig. 3. Reaction scheme of alkane aromatisation on ZSM-5 catalysts[6]

The authors[7,8] proposed a scheme for aromatizing paraffinic hydrocarbons, as shown in Figure 4.
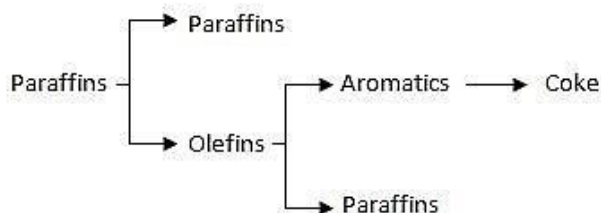
Fig. 4. Aromatization of paraffins on zeolite catalysts[7,8]

The mechanism of the conversion of straight–run gasoline fractions into high–octane gasoline components on zeolite catalysts includes a number of sequential and parallel chemical reactions of the acid–base type involving the intermediate formation of carbonium cations. In general, the conversion of hydrocarbons includes the following basic stages[9]:
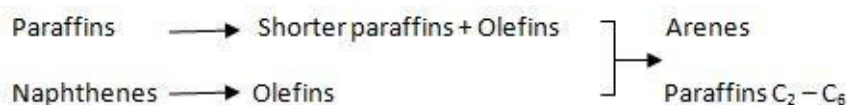
Fig. 5. Conversion of hydrocarbons[9]

At the initial stage, the cleavage of a C – C bond of hydrocarbons and the formation of intermediate olefin fragments occur. At the next stage, olefins transform into paraffinic and aromatic hydrocarbons due to the processes of the migration and redistribution of hydrogen. Generally, the paraffinic hydrocarbons C_5 form an iso structure. Along with the basic processes, some side reactions take place, namely the alkylation of isoparaffinic hydrocarbons and aromatics by intermediate olefins and isomerization of paraffinic hydrocarbons and naphthenes[10,11].

It is evident that the presented schemes are somewhat different from each other. This is determined by using different composition and structure of the catalyst, different composition of raw materials and process conditions.

Kinetic parameters of the reactions are also dependent on the factors mentioned above. The literature[12] shows the results of theoretical and experimental study of the kinetics of hydrocarbons reactions on different zeolite catalysts.

In the work the results of an experimental study of the kinetics of paraffins and naphthenes oxidation on the ZSM–5 zeolite and propane aromatization on H–ZSM–5 zeolite have been presented. The authors note that the aromatization proceeds through the intermediate formation of olefin, moreover the propane conversion and the formation of aromatic compounds occurs on various centers of the zeolite surface. The presented rate constants indicate a relatively low speed of dehydrogenation of propane and high speeds of cracking and aromatization.
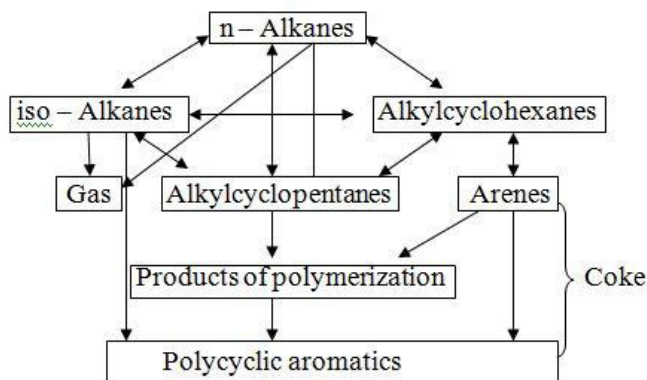

Fig. 6. Conversion of hydrocarbons on zeolite catalysts[10,11]

Reactions of 2–methylpentane on a bifunctional catalyst (platinum on zeolite) were studied in a paper[13]. The authors noted the high isomerization selectivity and low demethylation, cracking and formation of methylcyclopentane in the temperature range of 160–200°C. The observed activation energy for isomerization reactions according to the partial pressures of hydrogen and 2–methylpentane was in the range of 14–25 kcal /mol.

Presence of platinum (2.9 wt%) and a high content of hydrogen in the reaction mixture does not allow extrapolation of kinetic parameters on the reaction of hydrocarbon, which occurring on a zeolite catalyst. Kinetic parameters of methylation of ethylene and propylene on the proton form of zeolites are given in[14], in which the author has studied the reactions occurring during the conversion of methanol–to–hydrocarbons (MTH).

A shortage of the experimental data for hydrocarbons cracking on zeolites, especially for multi–component mixtures, is noted in[15]. The kinetics of the cracking of n–hexane on ZSM–5 zeolites at atmospheric pressure and in the temperature range of 823–923K is investigated in[16]. The diffusion of the reactants/products in the micropores of the catalyst is a limiting stage of the process according to the authors. The activation energies of the cracking reactions are in the range of 123–128 kJ/mol, the effective diffusion coefficient of n–hexane is $130 \cdot 10^{-11}\ \text{m}^2\text{s}^{-1}$.

Kinetic data of other types of hexane reactions on a zeolite catalyst are not shown in the work. Moreover, the process temperature is significantly higher than the temperature at which the refining of gasoline fractions is carried out. The rate constants and activation energies for certain types of reactions are given in[17], the heat of hydrocarbons adsorption on zeolite catalysts are given in[18].

Quantum–chemical calculations of the activation energy of C–C bond cleavage for the C_2–C_4 hydrocarbons on zeolite catalysts in comparison with the experimental data have been presented in[15]. Acceptable accuracy for modeling the kinetics of calculations is shown. However, the growth of the carbon chain of the reacting molecules and the simultaneous occurrence of other types of reactions can significantly complicate the calculations and reduce their accuracy.

In general, there is a lack of experimental and calculated data on the rate constants and activation energies of hydrocarbons reactions on zeolite catalysts. There are practically no data on the thermodynamic characteristics of the calculations and their temperature dependences. Therefore, the initial stage of construction of the reactor model is to analyze thermodynamics of the reactions, formation of the transformation scheme and determination of kinetic parameters.

2. Modeling of reactor of hydrocarbons conversion on zeolite catalysts

2.1. Thermodynamic calculation of reactions and development of scheme of the process

The authors calculated the thermodynamic characteristics for all types of hydrocarbons reactions on zeolite catalysts. The calculation was performed in the temperature range of 593–723 K. Analysis of the results showed a low thermodynamic probability of cyclization reactions of paraffins and isoparaffins (Table 1).

Table 1. The equilibrium constants of cyclization reactions of paraffins and isoparaffins (T = 603 K)

№	Reaction	Equilibrium constants
1	3–methylpentane →Methylcyclopentane+H_2	0.099
2	2–methylpentane →Methylcyclopentane+H_2	0.063
3	Hexane → Cyclohexane + H_2	0.018

The most likely reactions are transformation of isoparaffins and normal paraffins into naphthenes through the formation of olefinic fragments on the basis of thermodynamic calculations.

Table 2. The equilibrium constants of some cyclization reactions of olefins (T = 603 K)

№	Reaction	Equilibrium constants
1	Hexene ↔ Cyclohexane	225.32
2	2 – methylpentene ↔ Methylcyclopentane	198.13
3	3 – methylpentene ↔ Methylcyclopentane	1364.76

We proposed a scheme of hydrocarbons transformation for construction a model of reactor of straight–run gasoline fractions refining on the basis of thermodynamic calculations, experimental and literary data (Figure 7). The scheme includes alkylation of aromatic hydrocarbons with olefins[19–21] in addition to the basic types of reactions for adequate describing experimental results[22].
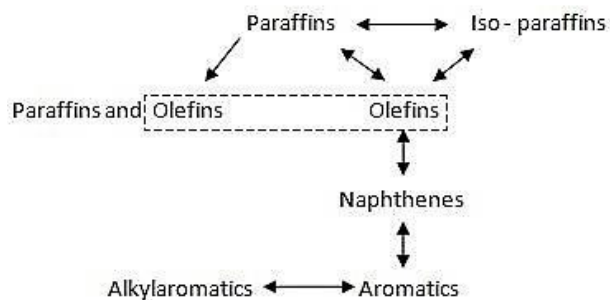

Fig. 7. Elementary reactions of hydrocarbons conversion on zeolite catalysts

2.2. The kinetic of the process and construction the model of the reactor

Model of reactor was developed in program HYSYS Aspen Plus™ process simulator. The scheme of reactor in model is shown in Figure 8. The following characteristics of the reactor adopted in the model such as:
- hydrodynamic regime – a plug flow reactor;
- temperature – 335°C;
- pressure – 1500 kPa;
- mass flow of the inlet mixture – 3500 kg/h.

- catalyst KN–30. The key features are: structural form of zeolite ZSM–5; granule diameter of 3.0–4.3 mm; mass fractions of powdered zeolite: silicon oxide 90.0–97.6%, aluminum oxide 1.4–2.7%, sodium oxide less than 0.1%, iron oxide 0.35–1.25%; mass fraction of the zeolite at least 80%.

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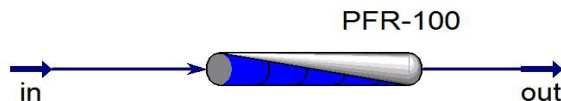in   out

Fig. 8. Scheme of reactor in model

Software HYSYS Aspen Plus™ contains a number of different options for describing chemical reactions. For example, the program presents chemical dissociation reactions, chemical equilibrium reactions, conversion reactions, heterogeneously–catalytic reactions, kinetics and simple reactions. The authors used a type of reaction–the Simple Rate, taking the assumption of pseudo – homogeneous occurring conversions.

Under this type of reaction, the reaction rate is described by the mass action law (1); the temperature dependence of the activation energy is described by the modified Arrhenius equation (2); the temperature dependence of the equilibrium constant is described by equation (3).

$$r = k \cdot (C_a - \frac{C_B}{K'}), \tag{1}$$

where
k – rate constant of reaction;
C_a, C_B – concentration of raw material and the product of reaction;
K' – equilibrium constant.

$$k = A \cdot e^{-\frac{E}{RT}} \cdot T^X , \tag{2}$$

where
A – pre–exponential factor;
E – activation energy, J/mol;
R – universal gas constant, J/(mol · K);
T – absolute temperature, K;
X – free multiplier.

$$\ln(K') = A' + \frac{B'}{T} + C' \cdot \ln(T) + D' \cdot T, \tag{3}$$

where A', B', C', D' – free constants of the equation.

We used data on the constants and activation energies of reactions shown in the literature[13,14,16,17], which were corrected for adequate describing the experimental data for solving the inverse kinetic problem. Some results of these calculations are presented in Table 3.

Table 3. Kinetic parameters of reactions

№	Reaction	K_{direct}, h^{-1}	E_a, kJ/mole
1	Hexane ↔ 2 – methylpentane	6	15
2	2 – methylpentane ↔ 3 – methylpentane	6	20
3	Hexane ↔ Hexene + H$_2$	6	30
4	Hexene ↔ Cyclohexane	15	50
5	Cyclohexane ↔ Benzene + H$_2$	3	40
6	2 – methylpentane ↔ 2 – methylpentene	3	40
7	2 – methylpentene ↔ Methylcyclopentane	15	50
8	Methylcyclopentane ↔ Benzene + H$_2$	3	40
9	Hexane → Propane + Propene	0.58	16
10	Benzene + Ethylene ↔ Ethylbenzene	6	20

where K_{direct}, E_a – rate constants and activation energies of direct reactions.

Based on thermodynamic calculations we obtained the logarithm of the equilibrium constant from temperature in the range of 593–723K, which corresponded to the temperature of the process.

We found that the formula (3) can be simplified without loss of accuracy of the model to a linear equation. Examples for isomerization, aromatization and hydrogenation are shown in Table 4.

Table 4. Dependence of equilibrium constant logarithm on temperature for reactions

№	Reaction	Equation	Confidence factor of approximation, R^2
1	Hexane → 2–methylpentane	$Y = -0.0018 \cdot x + 1.5844$	0.9969
2	2–methylpentane → 2,3–dimethylbutane	$Y = -0.0012 \cdot x - 0.4397$	0.9966
3	Hexane ↔ Hexene + H$_2$	$Y = 0.0363 \cdot x - 31.242$	0.9971
4	Hexene → Cyclohexane	$Y = -0.0237 \cdot x + 19.649$	0.9975
5	Cyclohexane → Benzene + H$_2$	$Y = 0.0612 \cdot x - 33.052$	0.9974
6	2 – methylpentane ↔ 2 – methylpentene + H$_2$	$Y = 0.0354 \cdot x - 29.297$	0.9971
7	2–methylpentene → Methylcyclopentane	$Y = -0.0167 \cdot x + 15.355$	0.9971

3. Results and discussion

The results of reactor model check adequacy to experimental data obtained in the laboratory are shown in Table 5.

Table 5. Composition of transformation products

№	Group of hydrocarbons	Composition, mass frac.	
		Experiment	Model
1	Paraffins	21.50	22.80
2	Isoparaffins	42.77	46.10
3	Aromatics	19.23	15.34
4	Naphthenes	16.11	14.96
5	Olefins	0.40	0.31

For the purpose of designing and scaling comparison of experimental and calculated data shows a satisfactory adequacy of the model. The exception is a concentration of olefin hydrocarbons with a calculation error of 32.3%. This is due to a low concentration of olefins and, accordingly, a relatively large error of its experimental determination.

4. Conclusion

The following conclusions may be made due to the obtained results:
1. The thermodynamic possibility of proposed reactions has been assessed;
2. The scheme of hydrocarbons conversion on zeolites has been developed;
3. The temperature dependence of the logarithm of the equilibrium constant on temperature has been found;
4. The inverse kinetic problem for hydrocarbons conversion on a zeolite catalyst has been solved;
5. The model of reactor in HYSYS Plus™ process simulator has been formed;
6. The adequacy of the model to the experimental data, sufficient for the purposes of designing and scaling, has been shown.

References

1. Hasan Akhtar Zaidi, Kamal Kishore Pant.; Combined experimental and kinetic modeling studies for the conversion of gasoline range hydrocarbons from methanol over modified HZSM – 5 catalyst. Korean J. Chem. Eng. 2010; **27**(5):1404-1411.
2. E.V. Frantsina, E.N. Ivashkina, E.D. Ivanchina, R.V. Romanovskii.; Developing of the mathematical model for controlling the operation
of alkane dehydrogenation catalyst in production of linear alkyl benzene. Chemical Engineering Journal, 2014; **238**:129–139.
3. Primo A., Garcia H.; Chem. Soc. Rev. 2014;**43**:7548-7561.
4. Guisnet, M., Gnep, N. S.; Aromatization of short chain alkanes on zeolite catalysts. Applied Catalysis A: Genaral, 1992; **89**:1-30.
5. Haag, W. O., Dessau, R. M.; Duality of mechanism for acid – catalysed paraffin cracking. In: Proceedings of the Eighth International Congress on Catalysis. 1984; 2: p. 305 – 316.
6. Nguyen, L. H., Vazhnova, T., Kolaczkowski, S. T., Lukyanov, D. B.; Combined experimental and kinetic modelling studies of the pathways of propane and n–butane aromatisation over H – ZSM – 5 catalyst. Chemical Engineering Science, 2006;**61**:881-5894.
7. Stepanov V. G., Snytnikova G. P., Ione K. G.; Chem. and Tech. of Fuels and Oils. 1992; **3**:=27-29 (In Russian).
8. Stepanov V. G., Mastikhin V. M., Ione K. G.; Ser. Khim. 1982; **3**: 619 -625 (In Russian).
9. Boreskov G.K.; Gas Industry. 1985; p. 43 – 50 (In Russian).
10. Snytnikova G.P., Stepanov V.G., Dudarev S.V.; Synthesis and Study of Catalysts. 1988; p. 123 – 129 (In Russian).
11. Kemball C. Chem. Soc. Rev. 1984;**13**:375 – 392.
12. Botavina M. A., Nekrasov N. V., Kiperman S. L.; The Kinetics of Hydrocarbon Conversion on ZSM–5 Zeolites. Kinetics and Catalysis. 2000; 41; **5**:679 – 687.
13. Siffert S., Garin F.; 2 – methylpentane catalytic reactions on Pt (3%wt) – HNaβ – zeolite. Kinetic studies. J. Chim. Phys. 1998;**95**:536 – 580.
14. Aditya Bhan; Selective Catalytic Synthesis of Branched C4–C7 Hydrocarbons by Low Temperature C1 Homologation Reactions over Medium and Large Pore Acidic Zeolites: A Mechanistic Study PhD. 57th Annual Report on Research 2012
15. Xiaobo Zheng; A computational investigation of hydrocarbon cracking: gas phase heterogeneous catalytic reactions on zeolites PhD. 2006; p. 59 – 83 .
16. Konno H., Okamura T., Kawahara T., Nakasaka Y., Tago T., Masuda T., Kinetics of n–Hexane Cracking over ZSM–5 Zeolites Effect of Crystal Size on Effectiveness Factor and Catalyst Lifetime. Chem. Eng. J. 2012; doi: ttp://dx.doi.org/10.1016/j.cej.2012.06.157.
17. Rovenskaya S. A., Ostrovskii N. M.; Theoretical Foundations of Chem. Engineering. 2008;**42**: 643-649 (In Russian).
18. Lalji Dixit, T. S. R. Prasada Rao; J. Chem. Inf. Comput. Sci. 1999;**39**:218-223.
19. Kae Shin Wong; Benzene alkylation with ethane into ethylbenzene over Pt–containing zeolite bifunctional catalysts PhD. 2009; p. 23 – 26 .
20. Ione K. G.; Multifunctional catalysis. 1982; p. 238 (In Russian).
21. Jie ZHU, Xiangju MENG, Fengshou XIAO.; Front. Chem. Sci. Eng. 2013; p. 236 – 237.
22. Vosmerikov A.V., Velichkina L.M.; Chem. Tech. 2005;**10**: 7-15 (In Russian).