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Development of Complex Mathematical Model of Light Naphtha Isomerization and Rectification Processes

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Abstract

The technique of developing a mathematical model of catalytic isomerization of light naphtha is stated. Using experimental data from an industrial isomerization unit shows adequacy of the mathematical model to the real process. The paper presents a method for optimizing the operation of the plant together with catalytic isomerization unit and separation columns. Selection of optimal modes of separation columns allows achieving the desired flow separation between units, as well as extension of the life of the catalyst SI-2.

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1. Introduction

Mathematical modelling of industrial catalytic refining processes is an important direction for technology improvement, as well as for the preparation of highly qualified specialists.

The problem of aggregation in the kinetic description of multicomponent catalytic reactions is solved in the scientific literature (R.B. Smith, N.M. Ostrovsky, A.V. Kravtsov, etc.)¹⁻⁵. These studies have greatly contributed to the improvement of the method of mathematical modelling of catalytic reforming of straight-run gasoline, as one of the most common and high-tech industrial process.

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A mathematical model is based on a combination of computation and industrial experiment, and the usage of mathematical models in production leads to the formulation of new scientific and applied problems. Despite the fact that the most notable of these models (system PIMS, ASPEN REFSYS) are widely used in industries, they are not able to predict the production situation (change in composition of the feedstock and the catalyst activity). These models cannot be used for monitoring and improvement of the catalytic unsteady processes efficiency. If the phenomenon of catalyst deactivation is considered as transient non-equilibrium process, the system of equations of material and heat balances of quasistationary process in the reactor must be supplemented by the kinetic model of deactivation. The reaction rate constants are influenced by catalyst activity. As seen, most of the models mentioned above^{6, 7-11} are elaborated for the specific feed and catalyst. The goal of this paper is to provide new universal mathematical model of light alkanes isomerization and rectification processes that could be used for different raw materials composition and catalysts.

2. Technological scheme and reactions

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.

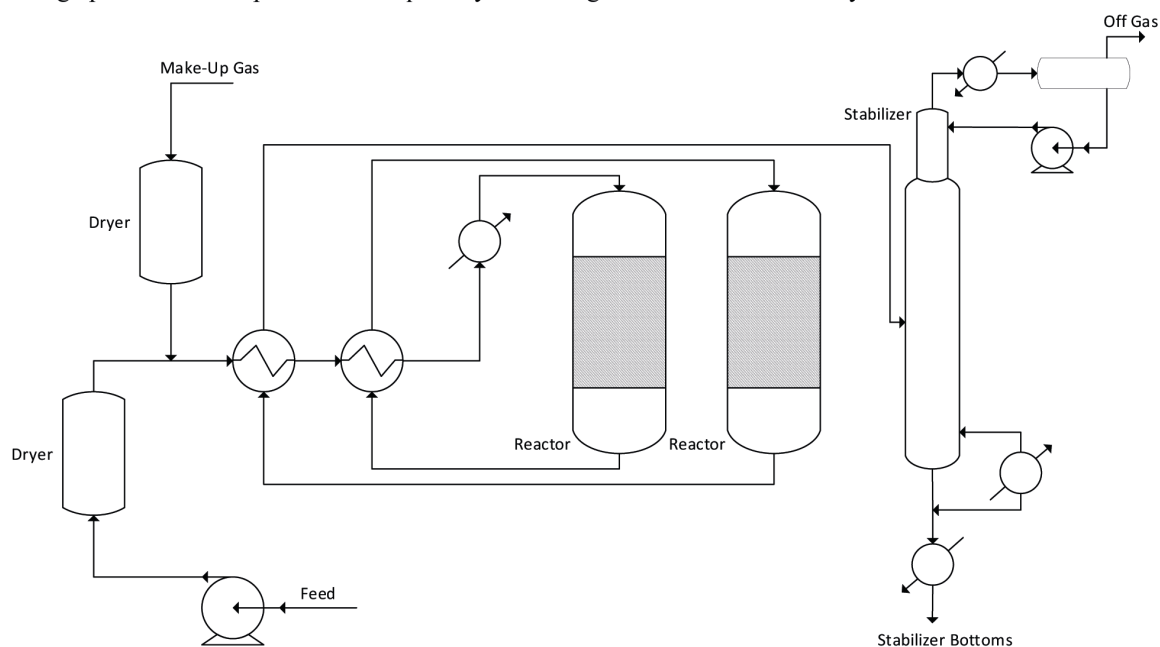
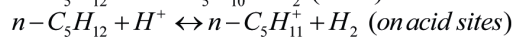
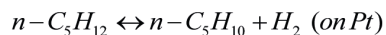
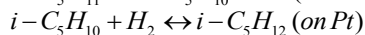
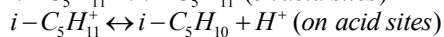
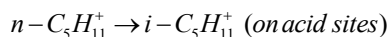


Fig. 1. Flowsheet of industrial isomerization process

At an industrial isomerization unit (Fig. 1), a catalyst based on sulphated zirconia (Pt/SO₄-ZrO₂) SI-2 is used. Bifunctional catalyst comprises metal hydrogenation-dehydrogenation centers and acid sites for skeletal isomerization via carbenium ions:





Thus, the reaction mechanism consists of the following steps¹¹:

- A. Dehydrogenation: a n-alkane is adsorbed on Pt-center, and an olefin is formed.
- B. 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.
- C. Hydrogenation: the 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 precursors¹². Due to the Pt-centers catalyzing dehydrogenation-hydrogenation reactions and the presence of hydrogen into the system, almost no coke accumulation takes place.

3. Determination of the reaction rate constants

Kinetic parameters of the isomerization reactions were defined by solution of the inverse kinetic problem using experimental data from industrial plant L-35-22/300. The rate constants in arbitrary units are presented in Table 1. Rate constant of target reaction of n-pentane isomerization is taken as a unit.

Table 1. The relative rate constants of the main reactions of isomerization process

Reaction	Pt/SO ₄ -ZrO ₂
$n-C_5H_{12} \rightarrow i-C_5H_{12}$	1.00
$i-C_5H_{12} \rightarrow n-C_5H_{12}$	0.35
$2-MP \rightarrow 3-MP$	4.50
$n-C_6H_{14} \rightarrow 2-MP$	3.89
$2-MP \rightarrow 2,3-DMB$	0.40
$2,2-DMB \rightarrow 2,3-DMB$	1.77

Table 2. Technological conditions of the isomerization process

Parameter	Value
Temperature in the reactor 1, °C	133
Temperature in the reactor 2, °C	146
Pressure, MPa	2.6
Feed rate, m ³ /h	90
Make-up gas rate, m ³ /h	24957

4. Reactor model

Material and heat balance of isomerization reactor with a fixed-bed catalyst in a general form:

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

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

if $Z=0$, $C=0$, where $r=0$, $C=C_0$, if $Z=0$, $T=T_0$, where $r=0$, $T=T_{in}$

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 i th 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_{mp} is a heat capacity of mixture, $J/(kg \cdot K)$; Q_j is j th reaction heat, J/mol , T is temperature, K ; r_j is j th reaction rate, $mol/(m^3 \cdot h)$.

Table 3. Convergence of calculation results estimate and experimental data from an industrial isomerization unit L-35-11/300

Parameter	Feed, % wt.	Isomerizate (calc.), % wt.	Isomerizate (exp.), % wt.
RON	66.33	81.51	81.56
n-C ₄ H ₁₀	0.01	0.12	0.54
i-C ₄ H ₁₀	0.00	0.16	0.53
n-C ₅ H ₁₂	38.59	14.76	13.84
i-C ₅ H ₁₂	12.22	35.97	40.37
n-C ₆ H ₁₄	14.82	5.02	5.13
2-MP	13.09	12.64	12.85
3-MP	7.53	6.35	7.58
2,2-DMB	0.33	11.55	12.69
2,3-DMB	1.74	4.15	4.20
n-C ₇ H ₁₆	0.00	0.00	0.01
Cyc-C ₆	3.78	3.69	1.06
M-Cyc-C ₅	4.90	2.12	0.59
i-C ₇ H ₁₄	0.60	0.40	0.07
Benzene	1.11	0.98	0.00

Adequacy of the mathematical model is verified by comparing the calculated and experimental data on the industrial plant.

5. Fractional column optimization

In this research work the feedstock composition of L-35-11/300 unit ("OOO Kinef") was optimized. Modes of secondary distillation column of unit installations AT-6, AVT-6, AVT-2, AT-1 were selected in order to optimize the composition of fractions NK-62 °C. Rectification block was simulated with software package HYSYS. The two systems were compared with the help of a text file containing information about the composition and properties of isomerization feedstock. The data file was generated automatically by HYSYS. Then this file is read by a computer system "IZOMER" which calculates the isomerization reactor unit (fig. 2).

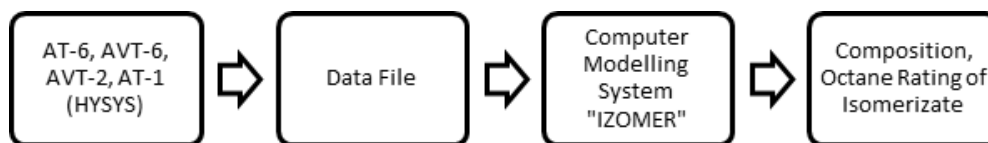


Fig. 2. Block diagram of isomerization process model

The estimated flowsheet of the secondary distillation block of AT-6 unit is shown in Fig. 3.

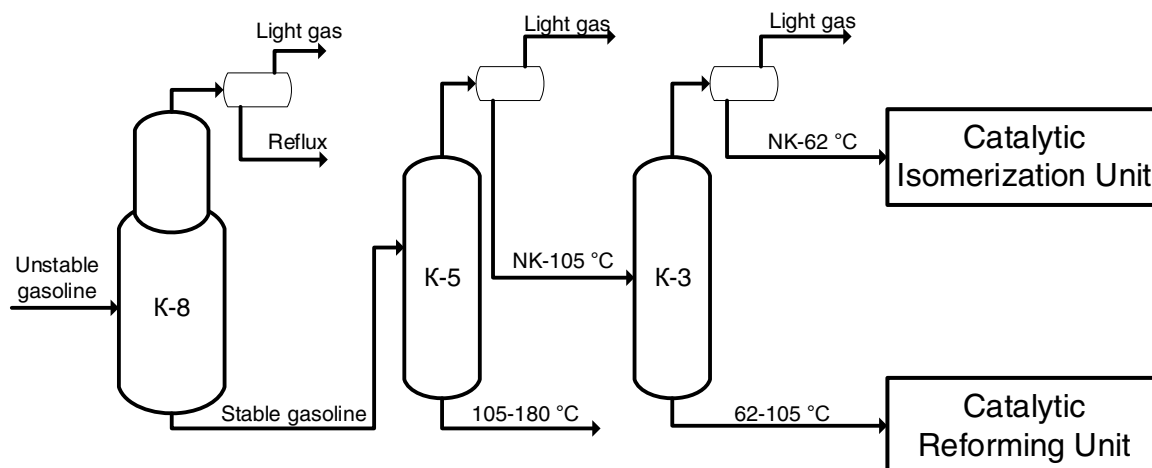


Fig. 3. The estimated flowsheet of the secondary distillation block of AT-6 unit

The initial composition of feedstock is listed in table 4.

Table 4. The initial composition of feedstock.

Component	Feed of K-3 (AT-6)	Component	Feed of K-3 (AT-6)
Ethane		223-Mbutane	5.33
Propane		Benzene	2.41
i-Butane		33-Mpentane	0.98
n-Butane	0.10	Cyclohexane	0.30
22-Mpropane	0.00	2-Mhexane	2.77
i-Pentane	7.70	23-Mpentane	1.08
n-Pentane	18.29	11-Mcyclopentane	0.90
22-Mbutane	0.01	3-Mhexane	0.21
4-M-Cyc-C5	0.17	1-ci3-MCC5	1.88
Cyclopentane	0.01	1-tr3-MCC5	1.97
23-Mbutane	2.46	3-Epentane	0.04
2-Mpentane	1.36	1-tr2MCC5	0.36
3-Mpentane	10.84	n-Heptane	
n-Hexane	7.09	1-ci-2-MCC5	0.03
22-Mpentane	20.67	M-Cyclohexane	
Mcyclopentane	0.11	22-Mhexane	
24-Mpentane	10.28	Ecyclopentane	
Ethane	0.71	25-Mhexane	
Total:			100

Due to the optimization of NK-62 °C fraction, the concentration of target components of the isomerization process increases which positively affects the octane rating of isomerizate. Increase in the octane number was calculated using a computer modeling system “IZOMER” which is a software mathematical model of the reactor block of isomerization process on the catalyst SI-2. The result of optimization is shown in Fig. 4.

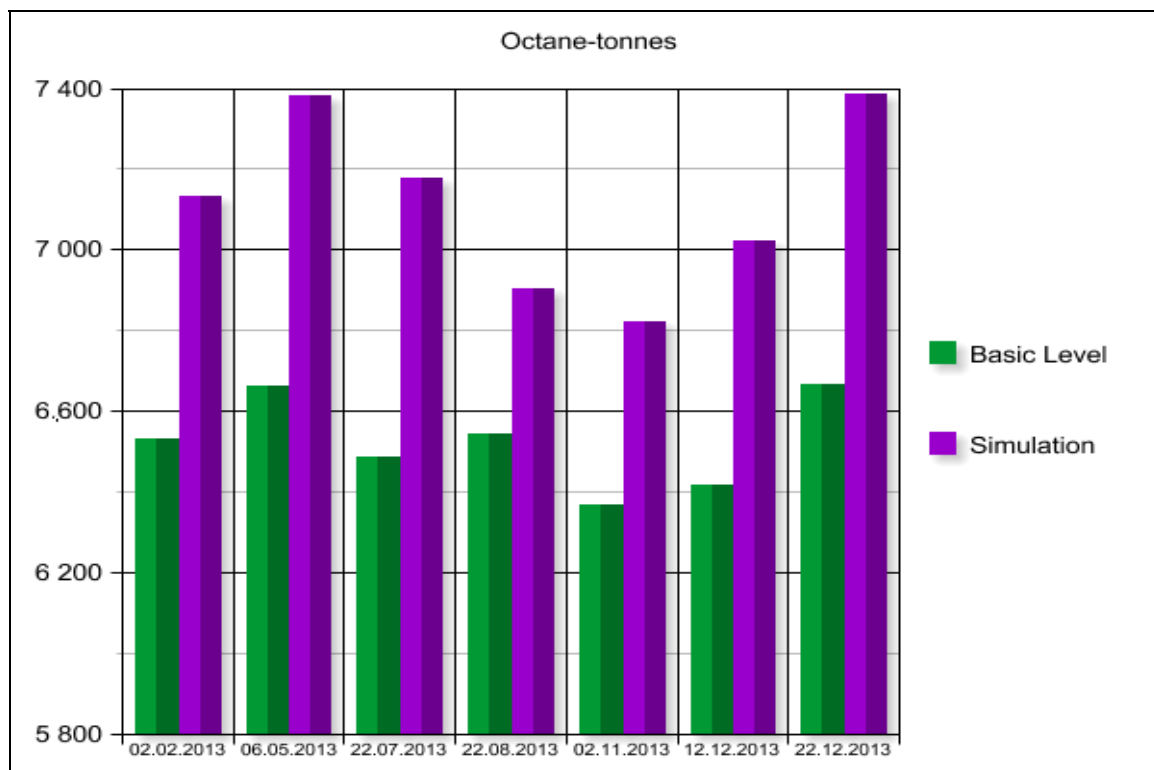


Fig. 4. Increase in octane-tones due to optimization

Thus, by optimization of distillation columns, average increase in octane-tones is 9% with a decrease in flow fr. NK-62 °C in an average of 1.7%. Average increase is 1.6 RON point.

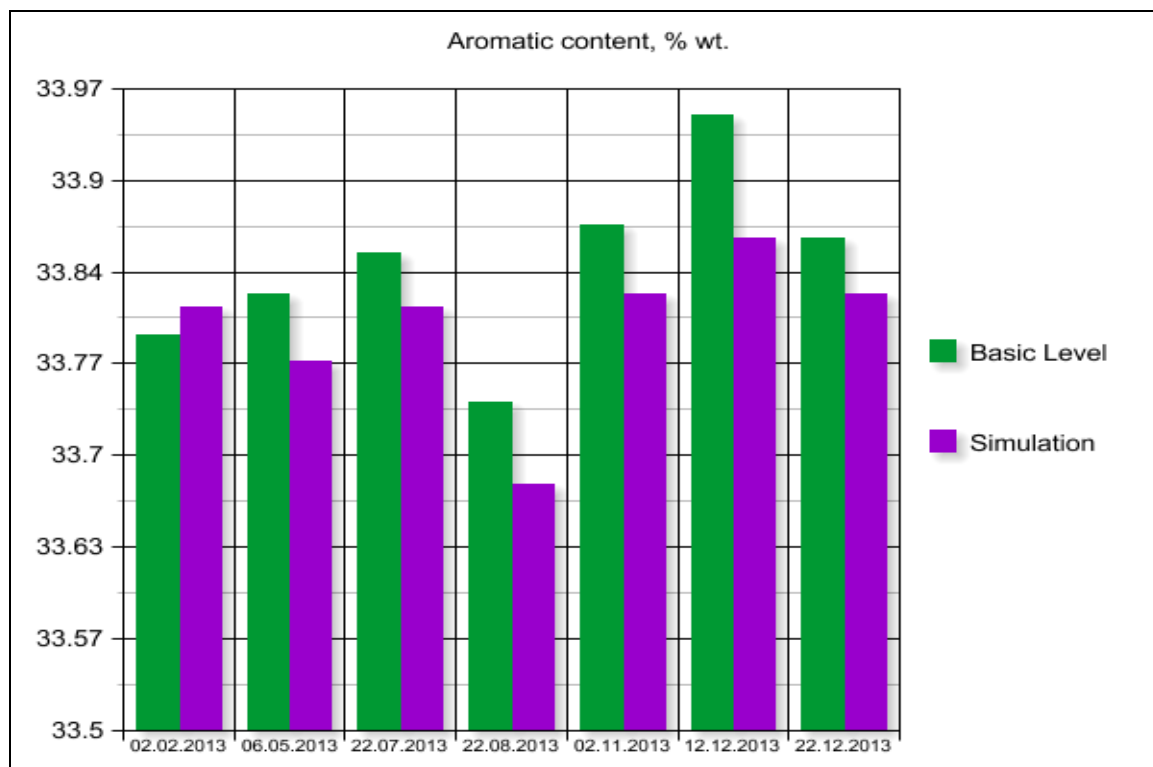


Fig. 5. Aromatic content in product

With optimization of the fraction of NK-62 ° C, the composition of fractions 62-105 ° C - raw catalytic reforming unit changes, however, the calculation results in changes in the content of aromatic hydrocarbons in the catalyst and is slightly less than 1% (Fig. 5).

References

1. Smith R.B. Kinetic analysis of naphtha reforming with platinum catalyst. *Chem. Eng. Prog.* 1959; **55**: 6, p. 76-80
2. Ostrovsky N.M. Kinetic of catalyst deactivation: Mathematical models and its application. *M.: Science*. 2001; 334 p.
3. Gyngazova M.S., Kravtsov A.V., Ivanchina E.D., Korolenko M.V., Chekantsev N.V. Reactor modeling and simulation of moving-bed catalytic reforming process, *Chem. Eng. J.* 2011; **176-177**: 134-143.
4. Sharova E.S., Poluboyartsev D.S., Chekantsev N.V., Kravtsov A.V., Ivanchina E.D. Monitoring of the commercial operation of reforming catalysts using a computer simulation system. *Catalysis in Industry*. 2009; **1**: 2, p. 128-133.
5. Gyngazova M.S., Kravtsov A.V., Ivanchina E.D., Korolenko M.V., Uvarkina D.D. Kinetic model of the catalytic reforming of gasolines in moving-bed reactors. *Catalysis in Industry*. 2010; **2**: 4, p. 374-380.
6. Kocsag C.I., Tutun I.A., Safta C. Study of C5/C6 isomerization on Pt/H-zeolite catalyst in industrial conditions, *Ovidius Univ. Annal. Chem.* 2011; **22**: 2, p. 102-106.
7. A. van de Runstraat, J. van Grondelle, R.A. van Santen, Microkinetics modelling of the hydroisomerization of n-hexane, *Ind. Eng. Chem. Res.* 1997; **36**: 3116-3125.
8. Ahari J.S., Khorsand K., Hosseini A.A., Farshi A. Experimental study of C5/C6 isomerization in light straight run gasoline (LSRG) over platinum mordenite zeolite, *Petroleum Coal*. 2006; **48**: 3, p. 42-50.
9. Li C.L., Zhu Z.L. Network of n-hexane isomerization over Pt/Al₂O₃ and Pd/HIV catalysts.
10. Liu H., Meng X., Zhang R., Liu Z., Meng J., Xu C. Reaction performance and disappearance kinetics of n-pentane isomerization catalyzed bichloroaluminate ionic liquid, *Catal. Commun.* 2010; **12**: 180-183.

11. Volkova G.G., Reshetnikov S.I., Shkuratova L.N., Budneva A.A., Paukshtis E.A. n-hexane skeletal isomerization over sulfated zirconia catalysts with different Lewis acidity, *Chem. Eng. J.* 2007; **134**: 106-110.
12. Ono Y. A survey of the mechanism in catalytic isomerization of alkanes, *Catal. Today*. 2003: **81**: 3-16.