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MATHEMATICAL MODELING OF THE PROCESS CATALYTIC ISOMERIZATION OF LIGHT NAPHTHA

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Abstract

The aim of this work is to study the process of catalytic isomerization of light naphtha by the method of mathematical modelling. The influence of temperature and feedstock flow rate on octane number and yield of the product (branched alkanes) was studied depending on the feedstock composition. The temperature mode of the process was optimized depending on the composition and feedstock flow rate.

Keywords: *catalytic isomerization; branched alkanes; octane number; method of mathematical modelling.*

1. Introduction

Motor fuel is one of the most demanded products of the oil refining industry. The demand for motor fuel is constantly increasing all over the world [1-5]. Currently, the tendency towards increasing the demand for motor fuel of meeting EURO standards is observed [6-10]. Isomerization of gasoline fractions is the process of obtaining a high-octane component of gasoline fuels by converting linear hydrocarbons into isomers. The studies on oil refining processes using the method of mathematical modelling are relevant these days. The models, developed based on the thermodynamic and kinetic regularities of the processes, allows making recommendations for control of the technological parameters of industrial processes, which ensures meeting specifications for product quality and achieving an optimal yield of the product in the conditions of constantly changing the composition of the feedstock. The aim of this work is to study the process of catalytic isomerization by the method of mathematical modelling.

2. Object and method of research

The object of the current research is the industrial process of catalytic isomerization, which is aimed to produce gasoline fuel of meeting EURO standards.

Development of new and intensification of existing catalytic processes is effectively performed by the method of mathematical modeling, the methodology and foundations of which were described in the classical works of the Academician of the Russian Academy of Sciences GK Boreskov and the Corresponding Member of the Russian Academy of Sciences MG Slinko in 1960-1970s [11] at the Boreskov Institute of Catalysis Siberian Branch of the Russian Academy of Sciences (Boreskov and Slinko [12-14]).

Further works of Slinko [15] are devoted to the theory of catalytic reactions, processes and reactors. Significant contribution to the development of mathematical modeling of catalytic processes and reactors was made by the followers of MG Slinko: VS Beskov [16], Matros [17],

GS Yablonsky [18], AS Noskov [19], ED Ivancina [20-24], and foreign researchers: R Aris [25], GF Froment [26].

The feedstock for the process of catalytic isomerization light naphtha passes through two successive reactors with a catalyst, then enters the stabilization column. The sequential arrangement of the reactors allows the process to be carried out continuously, while in one reactor the catalyst regeneration takes place; in the second one, the isomerization process takes place. This method of operation allows for economical use of the catalyst without interrupting production. This scheme is the simplest variant of isomerization. To describe the process of isomerization by mathematical modeling, the following steps are required:

- thermodynamic analysis of the process;
- evaluation of the kinetic parameters of the possible reaction;
- model of the reactor;
- construction of the technological scheme.

Isomerization reactions are reversible processes in which the system tends to a thermodynamic equilibrium between n-paraffins and isoparaffins. The main reactions occurring in the reactor are shown in Fig. 1 with the indication of octane numbers according to the research method.

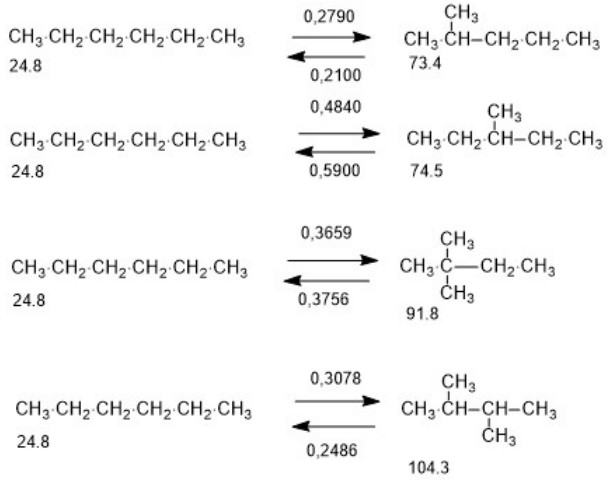


Figure 1. Main reactions of the isomerization process at T = 130°C, P = 3 MPa, on Pt/$SO^{4-}ZrO_2$ catalyst

Experimental data of industrial run of the isomerization unit were used in the construction of a mathematical model. Changes in the composition of raw materials used for the calculation are shown in Table 1.

Such change in the feedstock composition requires constant correction of the mode of the isomerization reactor operation, determination and maintenance of optimal technological parameters for the exact feedstock composition in order to obtain the maximum yield of the product meets required quality. In this work, the influence of temperature and feedstock flow rate on the yield was studied, as well as a technological mode for the two variants of unit operation was optimized using the developed mathematical model.

Table 1. Changes in raw material composition

Component	wt. %	Component	wt. %
isopentane	7.3 – 15.4	3- methylpentane	6.7 – 13.3
n-pentane	14.9 – 28.9	n-hexane	7.1 – 17.1
2,2 - dimethylbutane	0.3 – 1.1	Methylcyclopentane	2.6 – 11
cyclopentane	5 – 13.3	Benzene	0.7 – 1.6
2,3- dimethylbutane	1.6 – 3.1	Cyclohexane	0.4 – 7.2
2- methylpentane	13.9 – 20.7		

The model is written as a system of material and heat balances as follows:

$$\begin{cases} G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^{m} a_j \cdot W_j \\ G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^m} \sum_{j=1}^{m} Q_j \cdot a_j \cdot W_j \end{cases} \quad (1)$$

Initial and boundary conditions are as follows: z=0: C_i=$C_{i,0}$; T=T_0; V=0: C_i=$C_{i,0}$; T=T_0, where z is the volume of refined feedstock from the moment of fresh catalyst load, m^3; G is the feedstock flow rate, m^3/h; $z = G \cdot t$ (t is the catalyst operating time from the moment of fresh catalyst load, h); C_i is the content of i^{th} component, mol/l; V is the catalyst bed volume, m^3; a_j is the catalyst activity in j^{th} reaction; ρ is the density of mixture, kg/m^3; C_p^{mix} is the specific heat capacity of the mixture, J/(kg·K); Q_j is the heat effect of j^{th} reaction, J/mol; T is the temperature, K; W_j is the rate of j^{th} reaction, mol/(l·s); m is the number of reactions. In the above system of equations, the residence time of the reagents in the reaction zone, which depends on the hourly flow rate of the feedstock G and the volume of the catalyst V, under the conditions of the unstable load of the industrial plant for feedstock is replaced by the "reduced time" z = G·t, equal to the total volume of the processed feedstock during the time t.

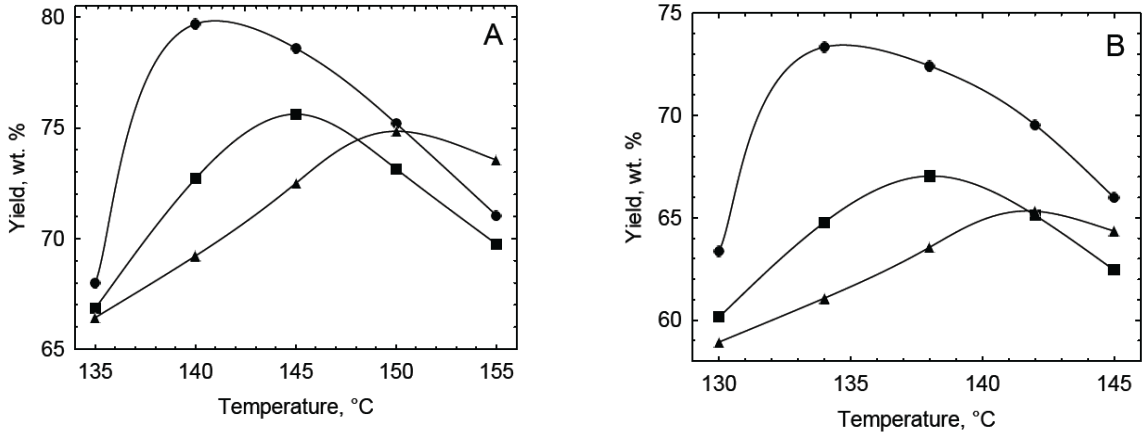
The system of differential equations is solved by the difference method and is implemented in the object-oriented Delphi environment.

3. Experimental

3.1. Studying the influence of temperature on the izomerization process

The process of isomerization of light gasoline is equilibrium, and the quality of the resulting product depends on the equilibrium position between the target and side reactions. At low temperatures, the process slows down the kinetic factor due to the low values of the isomerization rate constants of normal alkanes. At high temperatures manifests the thermodynamic factor of the deceleration of the process: because isomerizes normal paraffins are favorable to low temperature because of its exothermic. The results of predictive calculations are shown in Fig. 2.

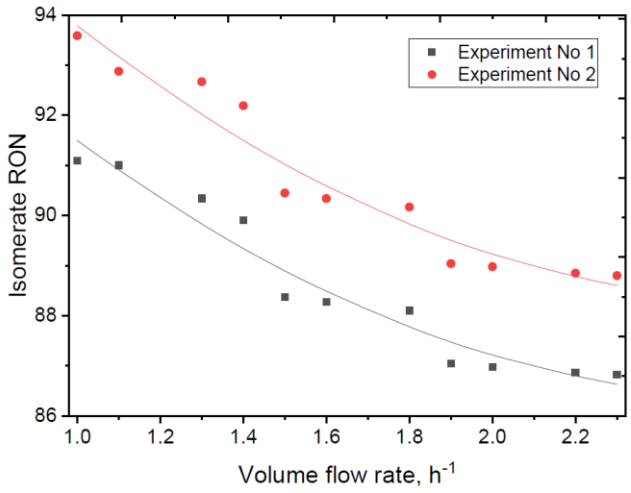
An increase in the isomerization temperature above the optimum (138-142°C for raw materials with a low content of naphthenic and aromatic hydrocarbons, 145-147°C for raw materials with a high content of naphthenic, 148-155°C for raw materials with a high content of aromatic and naphthenic hydrocarbons) leads to a decrease in the yield of isomerizate due to an increase in the contribution of adverse reactions.



A-sulfated catalyst B-chlorinated catalyst

Figure 2. Yield of C5-C6 isoalkanes depending on temperature: (●) – composition No. 1, (■) – composition No. 3, (▲) – composition No. 6

3.2. Studying the influence of feedstock flow rate on the izomerization process



As the load on the raw material increases on the isomerization reactor unit, the contact time of the raw material with the catalyst decreases, and the octane number of the isomerizate obtained decreases. The forecast is based on models of the influence of feed loading on the octane number of the isomerized product to the isomerization with recycling of n-C_5-C_6 and the low-branched hexanes presented in Fig. 3.

Figure 3 Octane number(RON) isomerizate depending on the volumetric feed rate of raw materials for isomerization technology with n-C_5-C_6 recycle and low-branched hexanes

4. Conclusions

The influence of temperature and feedstock flow rate in the rages 320–360 C and 290–330 m^3/h respectively on the cold flow properties and yield of the product (diesel fuel) was studied depending on the feedstock composition. The temperature mode of the process was optimized depending on the composition and feedstock flow rate.

The optimal temperature range in reactors is determined by the technological mode of the process, the composition of the processed raw materials, as well as the hardware design of the process. The high content of naphthenic and aromatic hydrocarbons in raw materials leads to inhibition of transformation of normal alkanes into isoalkanes. Depending on the type of catalyst, the optimum temperature lies in the range of 138-142°C for raw materials with a low content of naphthenic and aromatic hydrocarbons, 145-147°C for raw materials with a high content of naphthenic, 148-155°C for raw materials with a high content of aromatic aR

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