Modeling and Optimization of the Catalytic Isomerization of the Pentane-Hexane Fraction with Maximization of Individual High-Octane Components Yield

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Introduction

The object of this research is the process of catalytic isomerization of the pentane-hexane fraction. The catalytic isomerization is applied to increase the petrol octane number via structural changing of a carbon skeleton of linear paraffins. Hydroprocessed petrol fractions at 62 – 70 ^{0}C, the raffinates of catalytic reforming, etc. are used as a raw material. The process takes place under a hydrogen atmosphere in presence of bifunctional catalysts [1 – 3].

It is known that the octane number is very important operational characteristic of a petrol. It mostly depends on the origin of petrol individual components. Among target individual components of the catalytic isomerization of the pentane-hexane fraction, dimethyl-substituted hydrocarbons (2,2-dimethyl butane, 2,3-dimethyl butane) and isopentane possess the largest octane numbers. Thus, maximization of their content is a crucial task. The final octane number of a petrol also depends on the degree of conversion of n-pentane and n-hexane that possess small octane numbers, and the larger the degree the more effective the whole process.

The goal of this research is to perform multi-criteria optimization (MCO) of the reactor section of the pentane-hexane fraction catalytic isomerization process with the use of a kinetic model aimed at increasing the content of high-octane individual components, degree of conversion of n-pentane and n-hexane, and lowering the yield of hydrocracking products (methane, ethane, propane, and butane) based on the Pareto approximation.

The object of research is the reactor section of the pentane-hexane fraction catalytic isomerisation unit represented by a column consisting of three reactors. For full transformation of raw material, recycling of the non-trandformed hydrocarbons is provided. Hydroprocessed petrol fraction served as a raw material. Characteristics of hydroprocessed petrol fraction are given in Table 1. Raw material input was 39206.71 kg/h. Consumption of fresh hydrogen-containing gas (HCG) was 1054.62 kg/h. Pressure in the reaction zone was 3.2 MPa. Inlet temperatures at the first, second and third reactors were 147.7 0C, 164.8 0C, and 146.2 ^{0}C, respectively. Outlet temperatures were 164.8 ^{0}C, 177.6 ^{0}C, and 148.1 ^{0}C, respectively. The bifunctional catalyst SI-2 was used as the process catalyst. Catalyst mass in each reactor was 9000 kg.

References

[1] S.A. Akhmetov Technology of deep oil and gas processing. Textbook for universities. Ufa: Gilem, 2002. - 672 p. (in Russian).

[2] K. Pather and D. Lokhat Gas-phase Hydroisomerization of n-Hexane Over Pt/SO4-ZrO2: Kinetic Modeling and Reactor Simulation.

[3] K. Pather and D. Lokhat Gas-phase Hydroisomerization of n-Hexane Over Pt/SO4-ZrO2: Kinetic Modeling and Reactor Simulation.

Transformation scheme of the catalytic isomerization

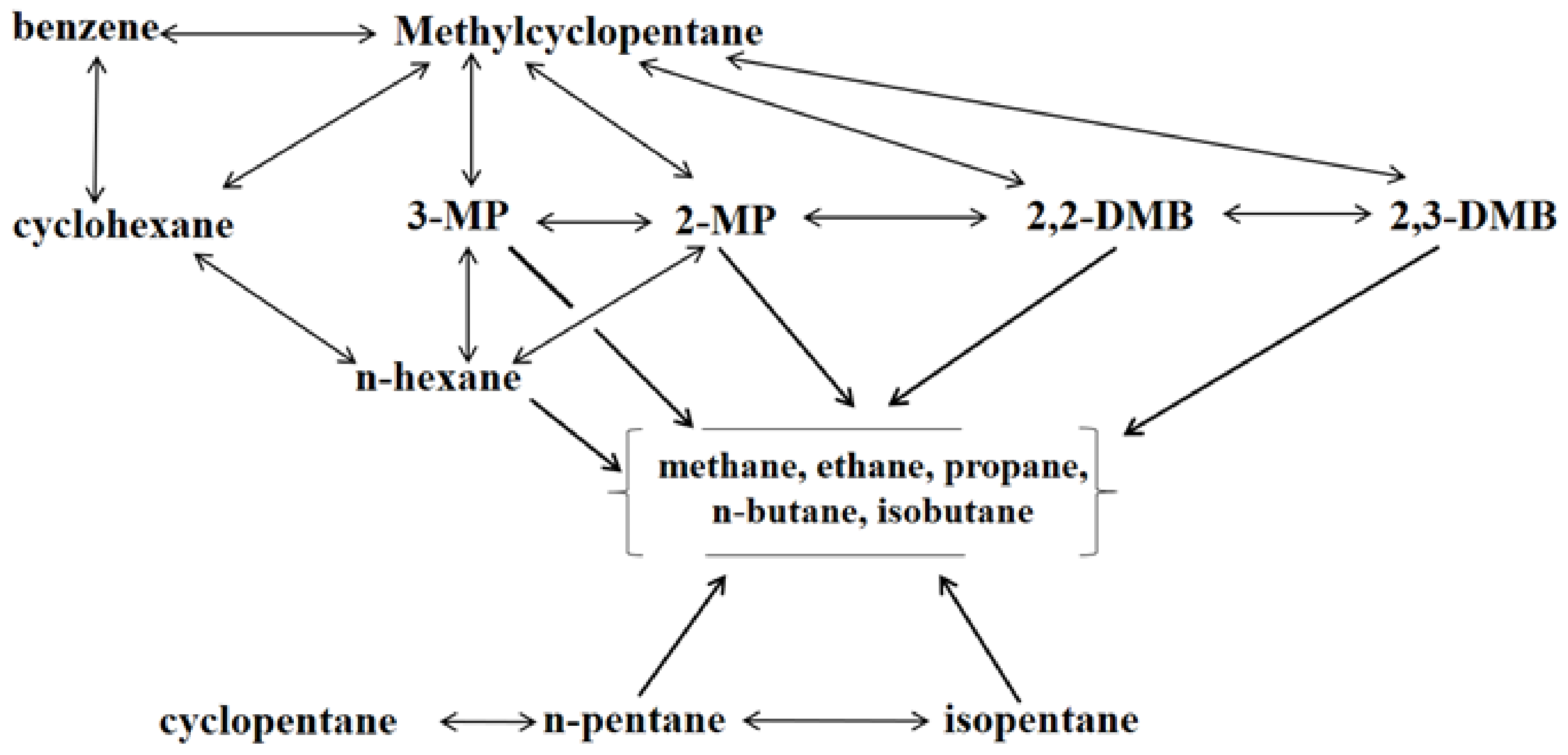

Fig. 1. Transformations of the catalytic isomerization of the pentane-hexane fraction (2-MP — 2-methyl pentane; 3-MP — 3-methyl pentane; 2,2-DMB — 2,2-dimethyl butane; 2,3-DMB — 2,3-dimethyl butane

The first step of mathematical description of the object is to elaborate the scheme of hydrocarbon transformations within the process. It is worth to mention that accuracy of the calculations and mathematical model adequacy are directly related to the detail degree of chemical transformations. Thus, the transformation scheme must sufficiently reflect the physico-chemical essence of the process [9].

Figure 1 represents the scheme of transformations of the elaborated model.

According to Figure 1, benzene in the content of the raw material, due to the presence of hydrogen, completely hydrates to cyclohexane or methyl cyclopentane. Naphthene hydrocarbons also undergo hydration with breaking of the cyclic structure. Hydrocarbons n-pentane and n-hexane (as well as their corresponding isomers) also undergo hydrocracking with the yield of methane, ethane, propane, n-butane and isobutane.

Therefore, the elaborated model includes 17 components which mutually isomerize, hydrogenize/dehydrogenize and undergo hydrocracking.

The reaction rates included in the kinetic model were recorded according to the mass action law. Mathematical model of the process represents a system of non-linear differential equations:

$$\frac{dx}{d\tau} = \sum_{i=1}^{J} \nu_{ij} w_j, i = 1, \dots, I,$$

$$w_j = k_j \prod_{i=1}^{J} \left(\frac{x_i}{F}\right)$$

$$k_j = k_j^0 \exp\left(-\frac{E_j}{RT}\right)$$

with initial conditions: at $\tau = 0, x_i(0) = x_i^0$;.

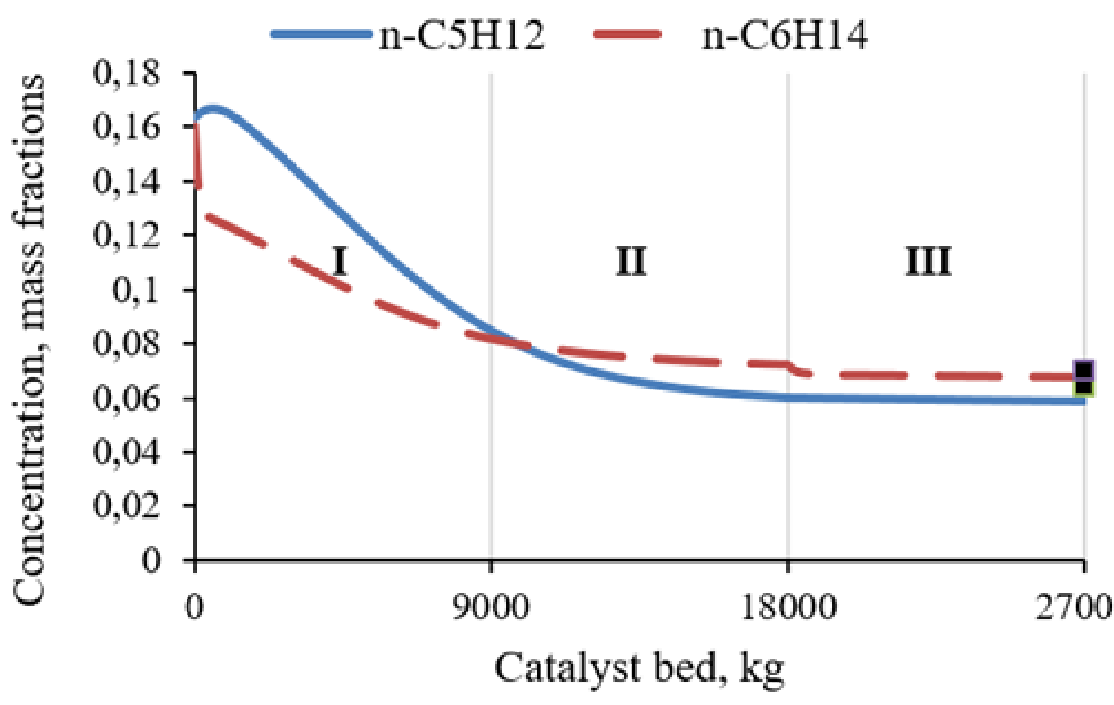

Fig. 2. N-penthane and n-hexane concentrations profile. Vertical lines correspond to the reactor section zones I-III

Multi-criteria optimization

The variable parameters of the pentane-hexane fraction catalytic isomerization MCO are the inlet temperatures at the first T_1 and third T_3 reactors, because in manufacturing the temperatures are changed in these particular facilities of the reactor section, and thus the technological mode is maintained. The optimality criteria are: isopentane selectivity f_1, 2,2-dimethyl butane and 2,3-dimethyl butane selectivity f_2, n-pentane fractional conversion ratio f_3, n-hexane fractional conversion ratio f_4 – maximization and sum of gases yield f_5 – minimization.

It is necessary to detect optimal values of the variable parameters T_1, T_2 which values change in the range of 130-155 ^{0}C (corresponds to the normal technological mode) and provide for the optimality criteria achievement of the extreme point.

$$\underset{X \in D_X}{extr} F(X) = F(X*) = F*$$

Results

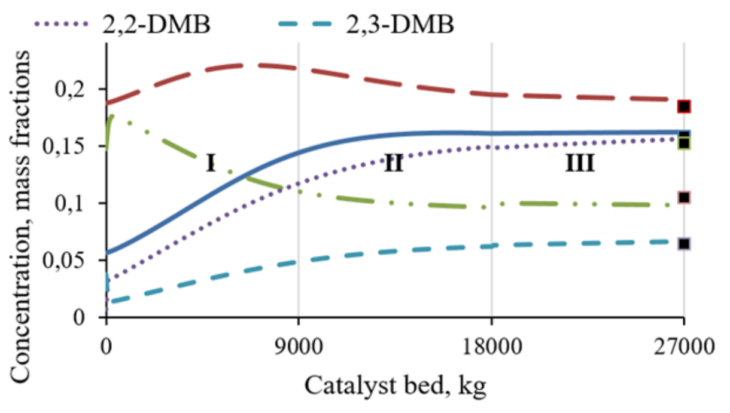

Fig. 3. Isopentane, 2-methyl pentane (2-MP), 3-methyl pentane (3-MP), 2,2-dimethyl butane (2,2-DMB) and 2,3-dimethyl butane (2,3-DMB) concentrations profile.

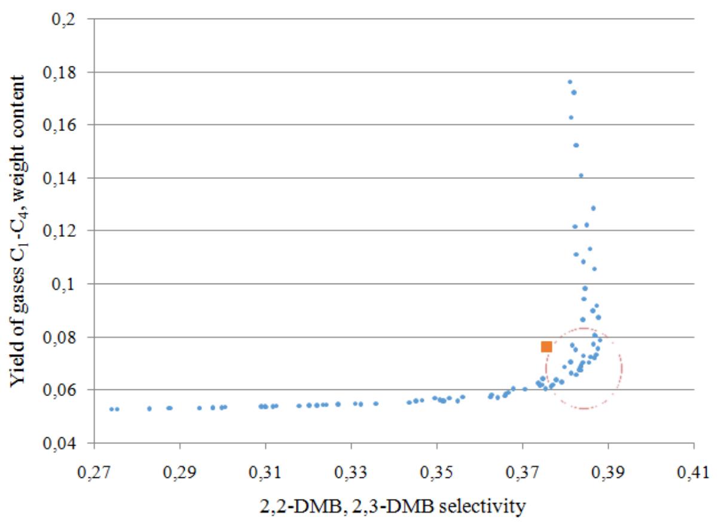

Fig. 4. 2,2-dimethyl butane and 2,3-dimethyl butane selectivity dependence on the yield of C1-C4 gases