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INCREASE IN RESOURCE EFFICIENCY OF MOTOR GASOLINE PRODUCTION WITH THE HELP OF MATHEMATICAL MODELS

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Abstract

In this paper, the way of increasing resource efficiency of motor gasoline production by integration of heptane isomerization process was performed. The estimation of the efficiency of isomerization process integration to the oil refinery structure was carried out by using the performed models. These models are sensitive to changes in hydrocarbon composition and physical-chemical properties of the processed feedstock and operation conditions of industrial units. Integration to the finished motor gasoline process the technology of C_7 isomerization allows to decrease in high cost flows (alkylate, toluene, MTBE) due to a significant increase in RON of low octane flows of the plant.

Keywords: *mathematical modeling; isomerization; blending; resource efficiency.*

1. Introduction

One of the effective ways of production of high octane gasoline, which meets modern ecological restrictions, is the development of integrating complexes of high octane flows with low benzene and sulfur content. However, integration of these complexes in the structure of operative oil refinery leads to a number of complicated technological problems, for example providing desirable quality and quantity of the feedstock, supporting the optimal catalyst activity and supplying of the optimal operating conditions of every unit, taking into account the energy and resource efficiency of the production. The most effective solution of these similar complicated chemical-technological problems is to use forecasting mathematical models which are built on physical-chemical and macrokinetic regularities of industrial finished motor gasoline production processes.

2. Object of research

In this paper, the object of research is process flow diagram of industrial finished motor gasoline production process, including stages of catalytic conversion of hydrocarbon feedstock and blending of high octane flows. (Fig. 1).

Currently, the process of catalytic isomerization of C_7 fraction does not have any industrial application (dash line in the PFD). However, there are a number of researches that are directed on this process [1-4]. Authors have performed the kinetic model of this process in order to estimate the efficiency of the integration of this technology in the structure of the industrial plant.

3. Method of research

The design of the physical-chemical reactor model, in general, includes the next stages: analysis of experimental data from the industrial unit, studying of the reaction mechanism on the catalyst surface, formation of the reaction list, which occurs due to the process, estimation

of the thermodynamic probability of these chemical reactions, validation of the formalization level of the reaction scheme, composition of the system of differential equations of the kinetic model, estimation of kinetic parameters of the model using experimental data, calculation of the reactor and validation of the hydrodynamic model, verification of the model.

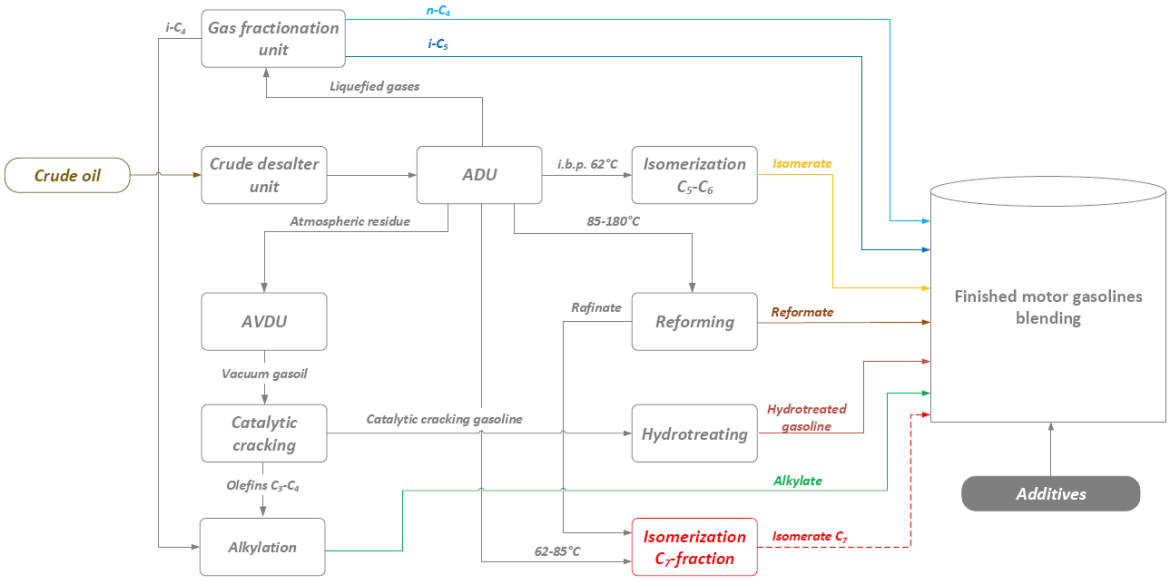

Figure 1. Block diagram of the finished motor gasoline production

Based on the experimental data from the laboratory isomerization unit the following reaction scheme was performed (Fig. 2).

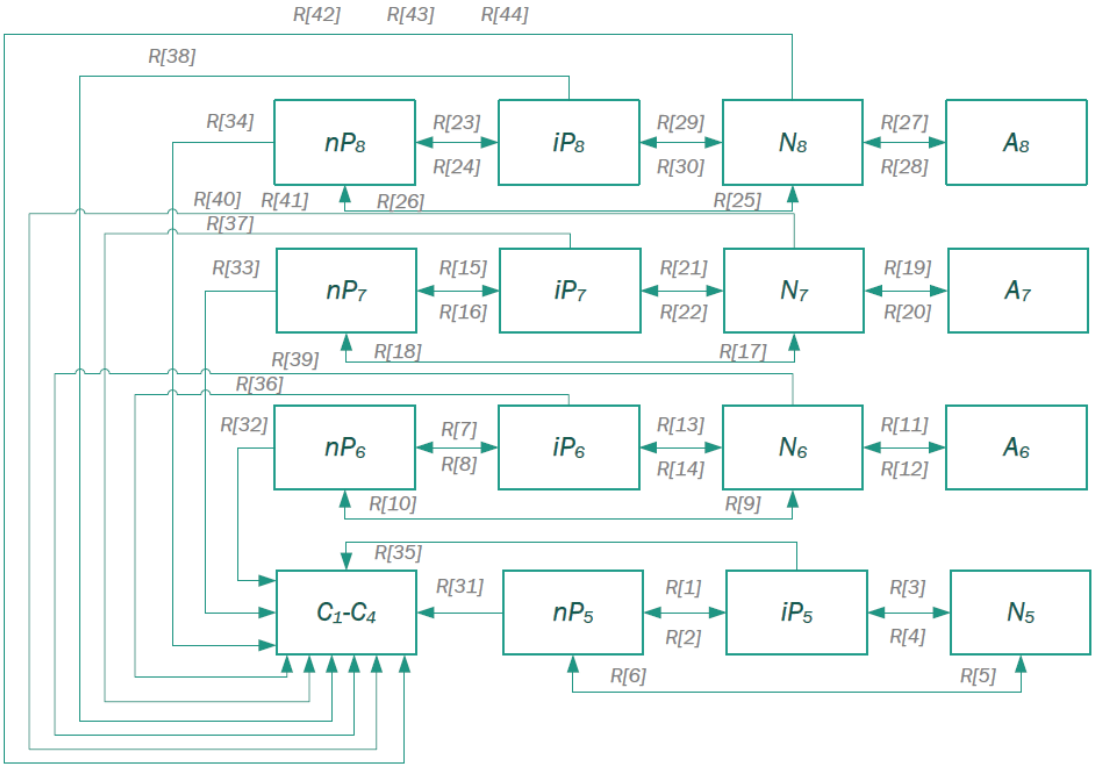

Figure 2. Formalized reaction scheme of the isomerization process

According to the law of mass action, the elementary reaction rate due to constant temperature is proportional to the concentration of the substance in the power of the stoichiometric coefficient:

$$r = k.f(C)_i \quad (1)$$

$$f(C) = C_1^{v1}.C_2^{v2} \ldots C_n^{vn} \quad (2)$$

where r – reaction rate, k – rate constant, C_i – initial concentration, v_i – stoichiometric coefficient.

In this way the kinetic model of the isomerization reactor is performed by differential equations system of material balance for every component:

$[nP_5]$ = - R[1] + R[2] - R[3] + R[4] + R[6] - R[31];
$[iP_5]$ = R[1] - R[2] - R[5] - R[35];
$[N_5]$ = R[3] R[4] + R[5] - R[6] + R[39] + R[41] + R[44];
$[H_2]$ = R[3] - R[4] + R[5] - R[6] + R[9] - R[10] + 3*R[11] - 3*R[12] + R[13] - R[14] + R[17] - R[18] + 3*R[19] - 3*R[20] + R[21] - R[22] + R[25] - R[26] + 3*R[27] - 3*R[28] + R[29] - R[30] - R[31] - R[32] - R[33] - R[34] - R[35] - R[36] - R[37] - R[38] - R[39] - R[40] - R[41] - R[42] - R[43] - R[44];
$[nP_6]$ = - R[7] + R[8] - R[9] + R[10] - R[32];
$[iP_6]$ = R[7] - R[8] - R[13] + R[14] - R[36];
$[N_6]$ = R[9] - R[10] - R[11] + R[12] + R[13] - R[14] - R[39] + R[40] + R[43] ;
$[A_6]$ = R[11] - R[12];
$[nP_7]$ = R[15] + R[16] - R[17] + R[18] - R[33];
$[iP_7]$ = R[15] - R[16] - R[21] + R[22] - R[37];
$[N_7]$ = R[17] - R[18] - R[19] + R[20] + R[21] - R[22] - R[40] - R[41] + R[42] ;
$[A_7]$ = R[19] - R[20];
$[nP_8]$ = - R[23] + R[24] - R[25] + R[26] - R[34];
$[iP_8]$ = R[23] - R[24] - R[29] + R[30] - R[38];
$[N_8]$ = R[25] - R[26] - R[27] + R[28] + R[29] - R[30] - R[42] - R[43] - R[44];
$[A_8]$ = R[27] - R[28];
$[C_1\text{-}C_4]$ = R[31] + R[32] + R[33] + R[34] + R[35] + R[36] + R[37] + R[38] + R[39] + R[40] + R[41] + R[42] + R[43] + R[44];

where R[1]-R[44] – chemical reaction rates from the formalized scheme.

Verification of the model was conducted by comparison of calculated and experimental isomerate compositions due to different temperatures (Table 1).

Table 1. Verification of the isomerization reactor model

Component	200°C		120°C	
	Experiment, wt. %	Calculation, wt. %	Experiment, wt. %	Calculation, wt. %
C_1-C_4	3.60	3.60	2.08	0.27
nC_5	0.31	0.34	0.71	0.72
iC_5	0.82	0.84	0.38	0.41
N_5	0.00	0.00	0.00	0.00
nC_6	0.67	0.42	1.66	2.00
iC_6	4.19	4.51	0.66	0.61
N_6	2.65	2.54	3.40	3.48
A_6	0.00	0.01	0.00	0.01
nC_7	15.99	16.04	26.05	26.13
iC_7	48.76	49.01	32.09	33.05
N_7	17.77	17.64	22.52	23.24
A_7	0.00	0.00	0.00	0.01
nC_8	1.14	1.18	1.14	0.86
iC_8	2.99	2.73	7.19	7.13
N_8	1.11	1.13	2.12	2.08
A_8	0.00	0.01	0.00	0.00

Model verification shows low deviations of calculated end experimental values within 1-2 %, that allows to use it for real process description.

4. Results and discussion

The composition of the isomerization feedstock can change in a wide range (for i-C_5: 8.0-20.0, for n-C_5: 17.0-32.0, for n-C_6: 14.0-25.0 wt. %), which takes influence to the products quality and cases necessity to correct technological parameters of the industrial unit. The study of the influence of the feedstock composition on isomerate quality was carried out due to constant operation conditions (Table 2). The result of the research is performed in Fig. 3.

Table 2. Operation conditions of the isomerization process

Parameter	Value
Feedstock volume flow rate, h^{-1}	90
Temperature of the reactor inlet, °C	200
Mole ratio H_2/CH	3
Reactor pressure, MPa	2.5

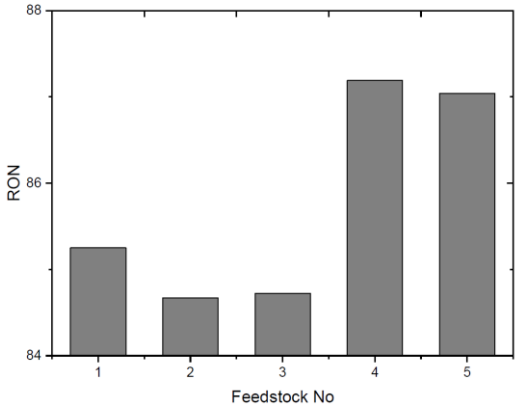

Figure 3. The influence of the feedstock composition on isomerate (calculation)

It was established, that isomerate RON changes from 2 to 2.5 points in dependence on feedstock composition.

It was found, that for C_7 isomerization process the optimal temperature is 190-210°C. The contribution of the side reaction of gas formation becomes more significant at higher temperatures (Fig. 4).

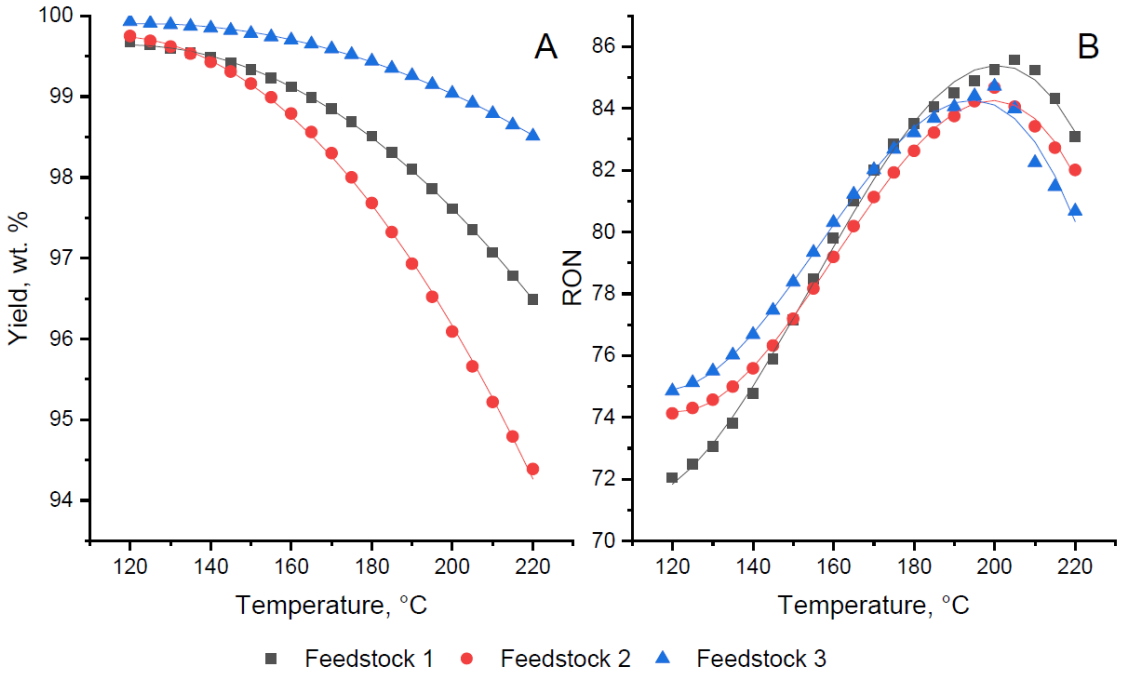

Figure 4. The temperature influence on the C_7 isomerization process: A – isomerate yield; B –isomerate RON

At low temperature, the isomerization rate is limited by a kinetic factor, which is conditioned by low values of reaction constants. At high temperature, the thermodynamic factor is manifested because isomerization is the exothermic process.

Thus there is an area of the optimal process temperature, which is determined by operation conditions, feedstock composition and equipment design of the process.

In this paper, the opportunity estimation of C_7 isomerization process integration was performed. Results of research are shown in Fig. 5.

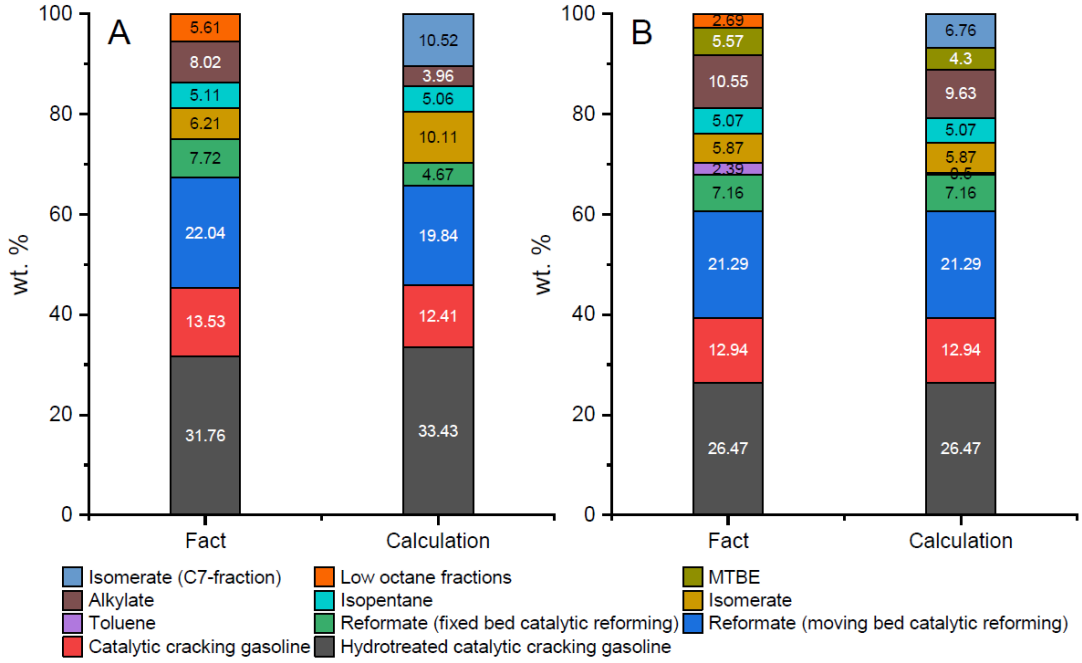

Figure 5. The estimation of the opportunity of C_7 isomerization process integration: A – gasoline RON 92; B – gasoline RON 95

The estimation of heptane isomerization process integration to the oil refinery structure was conducted due to determined quality and quantity of blending components and present production level of finished motor gasoline. Low octane blending components was used as isomerization feedstock. According to results of research, isomerization process integration allows to decrease the percent of high coast blending flows such as alkylate, toluene, MTBE by significantly increasing of low octane flows RON.

5. Conclusion

Kinetic model of C_7 isomerization process can be used for forecasting in dependence on different feedstock composition and operation conditions of the reactor: – composition and yield of the product; – products RON.

Complex application of mathematical models of isomerization and blending processes allows conducting of the estimation of the feedstock composition and operation conditions influence on hydrocarbon composition and properties of blending components and finished motor gasoline recipes.

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