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Developing of Computer Simulator of H_2SO_4-Catalyzed Benzene Alkylation with Alkenes

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Abstract

In this research, the indicators of the H_2SO_4-catalyzed benzene alkylation with alkenes were performed with use of the mathematical model, which was implemented in the industry at one of the refineries. We present the effect of the butane-butylene fraction flow rate and the isobutane concentration in the feedstock on the content of isooctane's in the alkylate. The possibility of using a mathematical model of the process of H_2SO_4-catalyzed benzene alkylation with alkenes as a training system has been shown. This will allow the oil refinery technologists to gain theoretical skills to troubleshoot industrial plants and to optimize their performance.

Keywords: *Mathematical modeling; Alkylation; Computer simulator; Optimal technological mode; Octane number.*

1. Introduction

A qualitative indicator of motor fuels is the value of their octane number, which characterizes the detonation resistance. The task of increasing the octane number of gasoline while reducing the content of aromatic hydrocarbons, sulfur, heavy metals includes the search and development of all kinds of high-octane additives that meet economic, environmental and technological criteria.

The task of optimizing the existing isobutane alkylation unit operation is extremely relevant and significant from the point of view of increasing the energy and resource efficiency of their work. The benzene alkylation with alkenes is carried out in the presence of H_2SO_4. As a rule, the use of aggressive media - acid catalysts, first of all, entails severe wear of the apparatus due to corrosion, and also increases the danger of production by several times [1-10]. A significant disadvantage is a fact that acid catalysts, having low selectivity, serve as a continuous medium for the ongoing reactions. It is scientifically proven that the target reaction proceeds at the acid-hydrocarbon interface; therefore, the volume ratio of these components plays an important role in alkylation technology.

In addition, H_2SO_4 has a high viscosity, which can be controlled under industrial conditions by changing the temperature in the reactor. Performing the process under the conditions close to optimal will reduce the likelihood of an inefficient increase in catalyst consumption (which is directly related to the energy costs of production) and increase the process selectivity.

Mathematical modeling is a convenient tool for choosing the most effective ways to optimize the operation of industrial plants. However, such problems can be solved only by mathematical models and computer modeling systems that are developed with due consideration of thermodynamic and kinetic laws of reactor processes, since they remain sensitive to changes in the raw materials flow rate and to operational properties of the catalysts.

When developing such a system, it is important to use real data obtained from an existing industrial installation in order to ensure the high adequacy of calculations.

2. Experimental

2.1. Mathematical model of H_2SO_4-catalyzed benzene alkylation with alkenes

Based on the analysis of experimental data, as well as on the results of thermodynamic calculations, a list of possible reactions reaction network (Fig. 1) of the alkylation process was developed. The found average values of the thermodynamic characteristics of the main reactions of the sulfuric acid alkylation process are presented in Table 1 (T = 279 K, pressure 0.4 MPa).

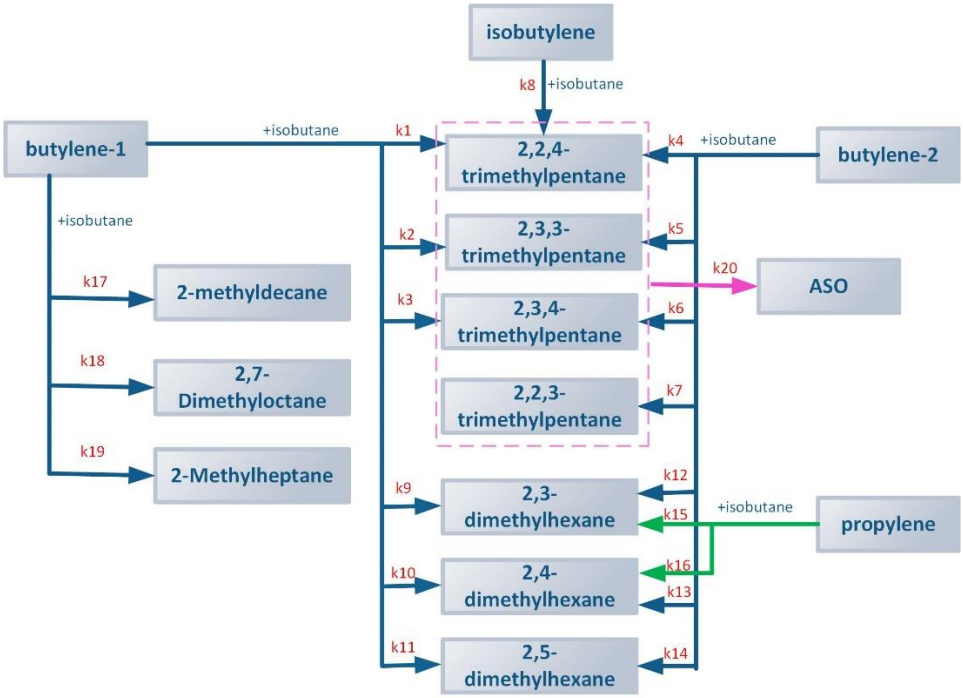

Figure 1. Reaction network of the alkylation process

Table 1. Thermodynamic parameters of alkylation process

Reaction	Δ*H*, kJ/mole	Δ*S*, J/mole·K	Δ*G*, kJ/mole
Isobutane + Butylene-1 → 2,2,4-Trimethylpentane	-75.71	-178.65	-25.15
Isobutane + Butylene -1 → 2,3,3- Trimethylpentane	-65.58	-174.18	-16.29
Isobutane + Butylene -1 → 2,3,4- Trimethylpentane	-60.73	-168.43	-13.07
Isobutane + Butylene -2 → 2,2,4- Trimethylpentane	-63.27	-173.61	-14.14
Isobutane + Butylene -2 → 2,3,3- Trimethylpentane	-53.14	-169.13	-5.28
Isobutane + Butylene -2 → 2,3,4- Trimethylpentane	-48.29	-163.39	-2.05
Isobutane + Butylene -2 → 2,2,3- Trimethylpentane	-58.73	-173.79	-9.54
Isobutane + Isobutylene → 2,2,4- Trimethylpentane	-61.11	-176.95	-11.04
Isobutane + Butylene -1 → 2,3- Dimethylhexane	-72.28	-160.60	-26.83
Isobutane + Butylene -1 → 2,4- Dimethylhexane	-76.99	-163.88	-30.61
Isobutane + Butylene -1 → 2,5- Dimethylhexane	-81.05	-162.26	-35.13
Isobutane + Butylene -2 → 2,3- Dimethylhexane	-59.83	-155.56	-15.81
Isobutane + Butylene -2 → 2,4- Dimethylhexane	-64.55	-158.84	-19.60
Isobutane + Butylene -2 → 2,5- Dimethylhexane	-68.61	-157.22	-24.11
Isobutane + Propylene → 2,3- Dimethylhexane	-75.26	-153.17	-31.91
Isobutane + Propylene → 2,4- Dimethylhexane	-85.25	-156.75	-40.89
2 Isobutane + 2Butylene -1 → 2-Methyldecane	-156.14	-321.02	-65.29
2 Isobutane + 2Butylene -1 → 2,7-Dimethyloctane	-156.06	-318.39	-65.95
Isobutane + Butylene -1 → 2-Methylheptane	-78.08	-158.50	-33.22

The developed reaction network considers the chemical transformations of hydrocarbons of raw materials with the formation of such individual components as 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, 2,3,3-trimethylpentane. At the same time, hydrocarbons with very low concentrations in the product mixture and those which do not influence the octane number significantly were combined into groups.

Based on the developed reaction network, the equations were written to describe the rates of chemical reactions that occur during the alkylation process. When developing the mathematical model, we consumed that the hydrodynamics of the alkylation contactor can be described by the ideal mixing model.

The equation of material balance, in general, can be represented as

$$\frac{dCi,j}{dt} = \frac{1}{\tau}(C_{i,j-1} - C_{i,j}) \mp W_{i,j-1} \quad (1) \qquad (1)$$

where τ – contact time, sec., C_i – concentration of the *i*-th component, W_i – reaction rate; *t* – time, sec.

The equation of heat balance, in general, can be represented as

$$\frac{dT_j}{d\tau} = \frac{1}{\tau}(T_{j-1} - T_j) + {}_j \frac{Q}{C_p^{CM}} W_{j-1} \qquad (2)$$

where Q_j – heat effect of reaction; W_j – the rate of a chemical reaction; C_p – molar heat capacity of the reaction mixture, J/K·mol; *T* – temperature, K.

To adapt the mathematical model to the industrial alkylation process in solving the inverse kinetic problem, we used data on the inlet (Table 2) and outlet concentrations of substances, as well as the technological modes for 13.05.2019. At the same time, the consumption of BBP is 59.59 m^3/h, the consumption of combined feedstock in the reactor is 41.99 m^3/h, the consumption of isobutane to the reactor is 30.08 m^3/h, the temperature of the combined feedstock at the inlet to the reactor after mixing with the isobutane fraction - 7.02 °C, pressure in the reaction zone 0.42 MPa; the temperature of the emulsion from the contactor is 11.07 °C.

Table 2. Alkylation feedstock composition for 13.05.2019

Flows	Component	wt%.	Flows	Component	wt%.
Butane-butylene fraction	∑C2	0.31	Circulating isobutane	∑C2	0
	Propane	0.05		Propane+Propylene	1.99
	Propylene	0.66		Isobutane	88.01
	Propane+Propylene	0.71		n-Butane	9.75
	Isobutane	41.42		∑ Butylenes	0.03
	n-Butane	8.14		∑ C5	0.22
	Butylene	15.39	Isobutane from separator*	∑ C2	0
	Isobutylene	5.1		Propane+Propylene	1.99
	Trans- Butylene	17.11		Isobutane	88.01
	Cis- Butylene	11.88		n-Butane	9.75
	divinyl	0.24		∑ Butylenes	0.03

** assumption that the composition is identical to that of circulating isobutane*

When performing the model calculations, the calculated output data were compared with the experimental values of the concentrations of the components of the product mixture, then minimizing the deviation. The optimal kinetic parameters were selected. As a result of numerical studies, the kinetic parameters of the main chemical reactions that occur during the alkylation were determined (Table 3).

As can be seen, the main contribution to obtaining the target product is made by reactions 1, 3, 13, 14, and 15. An analysis of the obtained and published data allows us to conclude that all ongoing reactions in the contactor are fast, since their activation energies are in the range of 40–50 kJ /mole, while slow reactions have an activation energy of 100–120 kJ/mole. According to the results of model verification, the average calculation error is 3.98 %.

Table 3. Kinetic parameters of the reactions occurring in the alkylation process (T=283.7 K)

№	Reaction	Ea, kJ/mole	k_0, sec-1
1	Isobutane + Butylene-1 → 2,2,4-Trimethylpentane	67.03	$2.09 \cdot 10^{12}$
2	Isobutane + Butylene -1 → 2,3,3- Trimethylpentane	64.50	$1.25 \cdot 10^{12}$
3	Isobutane + Butylene -1 → 2,3,4- Trimethylpentane	63.28	$1.38 \cdot 10^{12}$
4	Isobutane + Butylene -2 → 2,2,4- Trimethylpentane	63.92	$2.09 \cdot 10^{12}$
5	Isobutane + Butylene -2 → 2,3,3- Trimethylpentane	61.39	$1.25 \cdot 10^{12}$
6	Isobutane + Butylene -2 → 2,3,4- Trimethylpentane	60.17	$1.38 \cdot 10^{12}$
7	Isobutane + Butylene -2 → 2,2,3- Trimethylpentane	62.78	$4.56 \cdot 10^{4}$
8	Isobutane +Isobutylene → 2,2,4- Trimethylpentane	63.38	$1.10 \cdot 10^{12}$
9	Isobutane + Butylene -1 → 2,3- Dimethylhexane	66.17	$7.74 \cdot 10^{11}$
10	Isobutane + Butylene -1 → 2,4- Dimethylhexane	67.35	$8.04 \cdot 10^{11}$
11	Isobutane + Butylene -1 → 2,5- Dimethylhexane	68.36	$8.04 \cdot 10^{11}$
12	Isobutane + Butylene -2 → 2,3- Dimethylhexane	63.06	$7.74 \cdot 10^{11}$
13	Isobutane + Butylene -2 → 2,4- Dimethylhexane	64.24	$8.04 \cdot 10^{11}$
14	Isobutane + Butylene -2 → 2,5- Dimethylhexane	65.25	$8.04 \cdot 10^{11}$
15	Isobutane + Propylene → 2,3- Dimethylhexane	66.91	$6.02 \cdot 10^{11}$
16	Isobutane + Propylene → 2,4- Dimethylhexane	69.41	$8.29 \cdot 10^{11}$
17	2 Isobutane + 2Butylene -1 → 2-Methyldecane	87.13	$1.46 \cdot 10^{3}$
18	2 Isobutane + 2Butylene -1 → 2,7-Dimethyloctane	87.11	$2.05 \cdot 10^{3}$
19	Isobutane + Butylene -1 → 2-Methylheptane	67.62	$6.11 \cdot 10^{4}$

3. Results and discussion

3.1. Training of technology personnel of the industrial alkylation unit

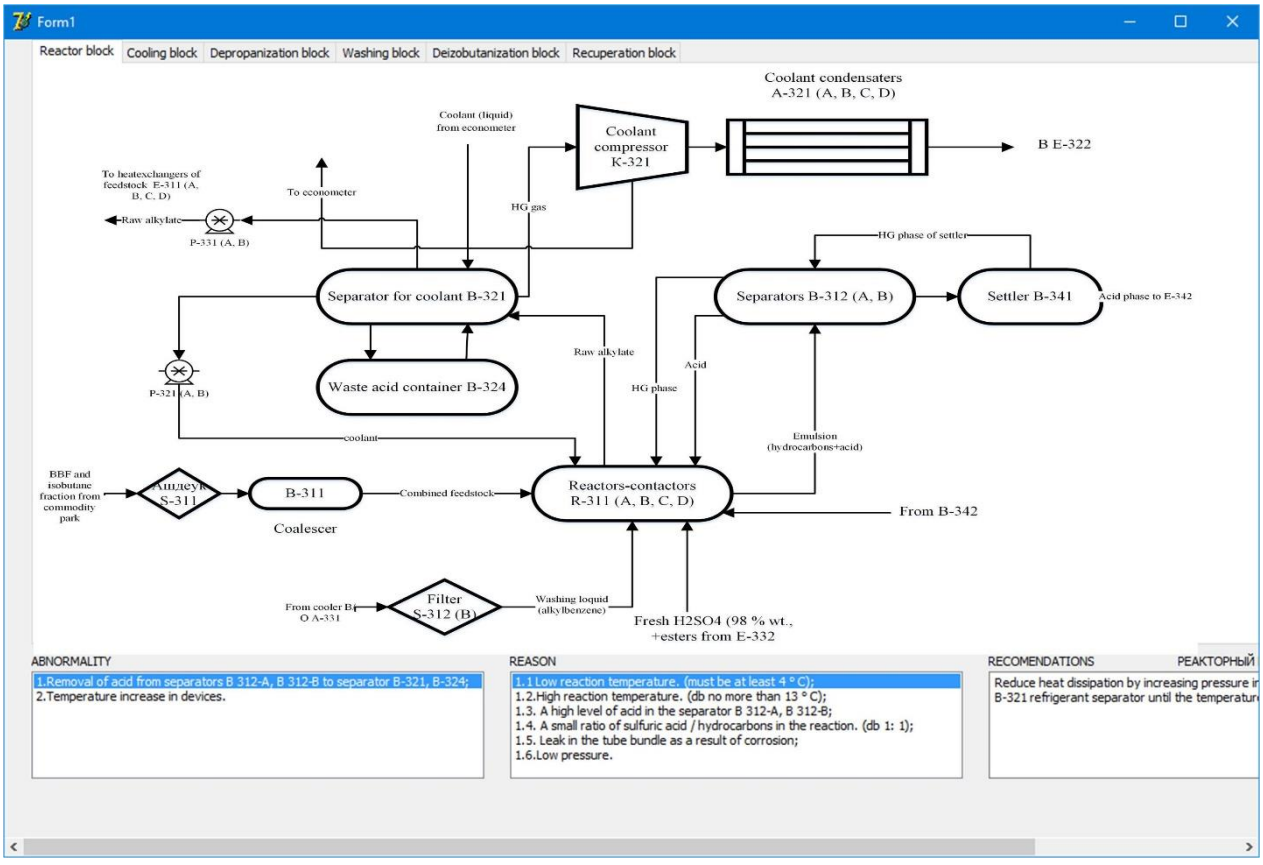

Figure 2. «Simulator» active window of the alkylation unit calculation program

The developed mathematical model of the process of sulfuric acid alkylation of isobutane with olefins, implemented in the form of a training system, allows oil refinery technologists to gain theoretical skills to troubleshoot an industrial installation, as well as to find a technologically correct solution to the problem of establishing a quantitative dependence of the octane value numbers from various operating parameters of the alkylation process, for example, from the consumption of isobutane.

The simulator is started using the "To simulator" button on the "Control" panel. After clicking the button, a window is launched in which the main blocks of the alkylation workshop are presented on the tabs. By hovering the mouse, you can display the main deviations observed in the selected devices. Further, after selecting the appropriate deviations, their main causes will be revealed. Also, after left-clicking on the alleged cause, the program will display recommendations for troubleshooting (Fig. 2).

The module "Test Tasks" is available in the "Control" panel. After clicking the button, a window is launched in which questions are displayed to test knowledge of the alkylation process. In order to start the test, it is necessary to select "Start Test" in the File menu, after which questions with four possible answers will be displayed on the main panel. The teste selects the answer using the radio button and clicks "Reply". If the answer is correct, a dialog box appears with the message "You answered correctly", otherwise - with the message "You answered incorrectly."

The simulator allows you to determine the dependence of the output parameters on temperature and isobutane flow (Fig. 3).

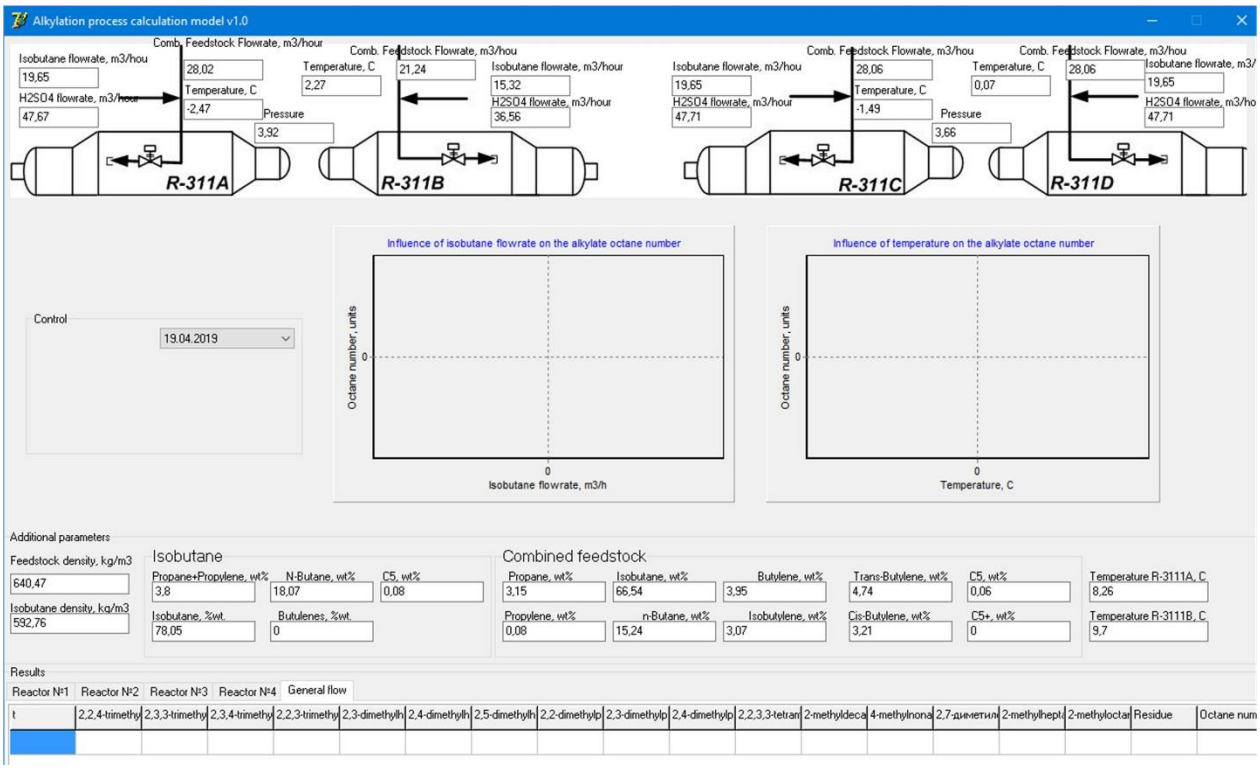

Figure 3. Active window of the alkylation unit calculation program

Scenario 1. Determination of the octane number of alkylate when changing the composition of the feed

The task. To determine how the composition of key components and the octane number of alkylate will change during the processing of raw materials of various compositions. Explain the reason.

Example. We will carry out calculations on the model subject to the processing of raw materials of different compositions (Table 4) to find out how the composition of raw materials

affects the composition of the resulting alkylate and its octane number. To do this, select a date, for example, 19.02.2019 (Fig. 4).

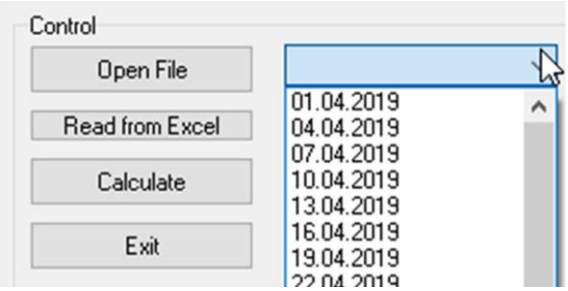

Figure 4. Choosing the data for calculation

Analyzing the composition of raw materials (1, 2, and 3) in Table 4, we conclude the main difference is in the isobutane content. Then we press the «Calculation» button and get the calculation results (Table 5).

According to Table 5, we see that the content of isooctanes is higher for feedstock composition 3. The octane number of the alkylate is also given in the «Results» table of the main program window. To view the output of alkylate, press the button «Material balance».

Table 4. Alkylation feedstock composition for 19.02.2019

Flows	Component	Feedstock composition 1, wt%.	Feedstock composition 2, wt%.	Feedstock composition 3, wt%.
Butane-butylene fraction	∑C2	3.05	2.21	1.67
	Propane	0.28	0.02	0.01
	Propylene	68.23	69.23	70.83
	Propane + Propylene	10.87	10.91	10.65
	Isobutane	4.93	5.00	5.11
	n-Butane	2.67	2.65	2.37
	Butylene	5.94	5.87	5.58
	Isobutylene	4.18	3.93	3.64
	Trans- Butylene	0.13	0.17	0.15
	Cis- Butylene	0.00	0.00	0.00
	divinyl	3.58	3.00	2.29
	∑ C5+	84.22	84.80	85.78
Circulating isobutane	∑C2	11.99	11.92	11.70
	Propane + Propylene	0.01	0.01	0.00
	Isobutane	0.20	0.27	0.23
	n-Butane	3.05	2.21	1.67
	∑ Butylenes	0.28	0.02	0.01
	∑ C5	68.23	69.23	70.83
	∑ C2	10.87	10.91	10.65
Isobutane from separator *	Propane + Propylene	4.93	5.00	5.11
	Isobutane	2.67	2.65	2.37
	n-Butane	5.94	5.87	5.58
	∑ Butylenes	4.18	3.93	3.64
	∑ C5	0.13	0.17	0.15

** assumption that the composition is identical to that of circulating isobutane*

Let us analyze the influence of the composition of raw materials. In the alkylation of isobutane with olefins, the ratio of isobutane to butylene plays an important role, and the larger it is, the higher the content of isooctanes.

To suppress the polymerization reaction, the alkylation process is carried out by diluting the olefin feed with a stream of isobutane continuously circulating in the system. Excess isobutane also prevents a dealkylation side reaction. If there is an insufficient amount of circulating isobutane in the reaction zone, alkenes interact with each other, resulting in the formation of heavy hydrocarbons that reduce the quality of the alkylate.

Table 5. Content of main components in the alkylation product flow (model calculation), wt%

Component	Feedstock composition 1, wt%.	Feedstock composition 2, wt%.	Feedstock composition 3, wt%.
2,2,4- Trimethylpentane	22.561	29.333	30.714
2,3,3- Trimethylpentane	13.139	16.509	16.292
2,3,4- Trimethylpentane	14.499	18.073	17.643
2,2,3- Trimethylpentane	3.34	4.102	4.04
2,3- Dimethylhexane	3.529	4.421	4.483
2,4- Dimethylhexane	3.743	4.631	4.61
2,5- Dimethylhexane	1.201	1.476	1.453
2,3- Dimethylpentane	0.824	0.076	0.04
2,4- Dimethylpentane	0.575	0.053	0.028

Alkylates obtained from raw materials with a lower mass fraction of isobutane have a lower octane number value. Moreover, the difference in the composition of the processed raw materials makes a significant contribution to the knock resistance by 0.85 points. The yield of alkylate also increases with increasing isobutane content in the feed.

4. Conclusions

The mathematical model of the alkylation process was developed with due consideration of the feedstock composition and main technological parameters. The model calculations allowed us to establish the laws of the isobutane with alkenes alkylation process when changing the composition of raw materials and technological parameters of the installation. In particular, it was shown that a change in the flow rate of the butane-butylene fraction does not significantly affect the content of 2,3,3-trimethylpentane in the product, while for 2,4,4-trimethylpentane, its effect is antibate. The mass fraction of 2,3,4-trimethylpentane in the alkylate, on the contrary, increases with an increase in the consumption of the butane-butylene fraction. An increase in the volume ratio of isobutane circulating to butane-butylene fraction leads to an increase in the content of 2,2,4-trimethylpentane and 2,3,3-trimethylpentane, which leads to an increase in the quality of the resulting alkylate.

Moreover, the developed mathematical model of the H_2SO_4-catalyzed benzene alkylation with alkenes, implemented in the form of a training system, allows oil refinery technologists to gain theoretical skills to troubleshoot an industrial plant and optimize its operation.

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References

[1] Bartholomew H. Mechanisms of Catalyst Deactivation. Applied Catalysis A: General. 2012; 12 (1–2): 17–60.

[2] Berenblyum AS, Ovsyannikova LV, Katsman EA, Zavilla J, Hommeltoft SI, Karasev YuZ. Acid Soluble Oil, by-Product Formed in Isobutane Alkylation with Alkene in the Presence of Trifluoro Methane Sulfonic Acid: Part I Acid Soluble Oil Composition and Its Poisoning Effect. Applied Catalysis A: General, 2002; 232 (1–2): 51–58.

[3] Berenblyum AS, Katsman EA, Karasev YZ. The Nature of Catalytic Activity and Deactivation of Chloroaluminate Ionic Liquid. Applied Catalysis A: General. 2006; 315: 128–34.

[4] Bui T, Korth W, Jess A. Alkylation of Iso-Butane with 2-Butene Using Highly Acidic Ionic Liquids. DGMK Tagungsbericht; 2007: 297–304.

[5] Davenport W, King M, Rogers B, Weissenberger A. Sulphuric Acid Manufacture. Southern African Pyrometallurgy, 2006; March: 5–8: 1-16.

[6] Petru D, and Bîldea C. Process Optimization of a Butane-Butene Alkylation Plant. UPB Scientific Bulletin, Series B: Chemistry and Materials Science, 2014. 76 (1): 71–84.

[7] Elavarasan P, Kondamudi K, Upadhyayula S. Statistical Optimization of Process Variables in Batch Alkylation of P-Cresol with Tert-Butyl Alcohol Using Ionic Liquid Catalyst by Response Surface Methodology. Chemical Engineering Journal, 2009; 155 (1–2): 355–60.
[8] Fellows PJ. 2 - Raw Material Preparation. Food Processing Technology (Third Edition), 2009: 99–124.
[9] Kirgina MV, Ivanchina ED, Dolganov IM, Chekantsev NV, Kravtsov AV, Fu F. Computer Program for Optimizing Compounding of High-Octane Gasoline. Chemistry and Technology of Fuels and Oil, 2014. 50(1): 17-27.
[10] Yvonne T, Weitkamp J. Alkylation of Isobutane with Light Alkenes on Solid Catalysts. Handb. Heterog. Catal. (2nd Ed.). 2008.

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