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Predicting Alkylate Yield and its Hydrocarbon Composition for Sulfuric Acid Catalyzed Isobutane Alkylation with Olefins Using the Method of Mathematical Modeling

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Abstract

The article provides the results of applied mathematical model of isobutane alkylation with olefins catalyzed by sulfuric acid to predict yield and hydrocarbon composition of alkylate caused by the changes in the feedstock composition and process parameters. It is shown that the alkylate produced from feedstock with less mass fraction of isobutane has lower octane value. Wherein the difference in composition of the feedstock contributes to antiknock index by the amount of 1.0-2.0 points.

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Keywords: alkylation; isobutane; isobutylene; sulfuric acid; mathematical modeling; octane number.

1. Introduction

Qualitative indicator of gasoline is the value of the octane number, which characterizes the knock resistance. The problem of increasing the octane number of gasoline accompanied by reducing the content of aromatics, sulfur and heavy metals includes exploration and development of all kinds of high-octane additives to meet the economic, environmental and technological criteria¹.

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Russian gasoline market is inferior in quality to European markets. Composition analysis of the gasoline showed that the proportion of alkylate in the Russian market is about 5%, when in the EU – it is up to 16%, and the average octane RON is 90.2 and 95.0 points respectively². To achieve significant indicators of environmentally safe gasoline output and quality it is necessary to develop and introduce new technologies in the industry, catalysts, reactor devices, which provide an increase in the production of high octane alkylate³.

The task of increasing the operation efficiency of existing plants of isobutane alkylation with olefins is very urgent and important in terms of improving energy and resource efficiency of their work.

The process of isobutane alkylation with olefins is carried out in the presence of sulfuric acid or HF. Generally, the use of corrosive media - acid catalysts primarily entails considerable wear due to corrosion of devices and also increases the plant danger several times. A significant disadvantage is also the fact that the acid catalysts having low selectivity are ongoing medium for the reactions. However, most industrial facilities in Russia and in the world use liquid mineral acids as catalysts in the alkylation process⁴. In Russia, all plants of isobutane alkylation with olefins use sulfuric acid.

It is proved that the target reaction occurs at the phase interface of hydrocarbons and acid, that's why optimization volume ratio of the acid and hydrocarbon phases depending on the composition of the feedstock plays an important role in the alkylation technology.

At the same time catalyst attraction to the reaction zone spends more resources, which in turn entails needs of many tanks made of corrosion-resistant materials; service life reduction of reaction vessels; increase in the cost of major installation repairs; much energy for acid pumping from one vessel to another; costs for catalyst regeneration; costs for stirring the mixture with the catalyst and butane-butylene fraction; increase in material consumption.

Carrying out the process under conditions close to the optimum reduces the possibility of inefficient increase in catalyst consumption (which is directly related to the energy costs of production) and increases selectivity of the process.

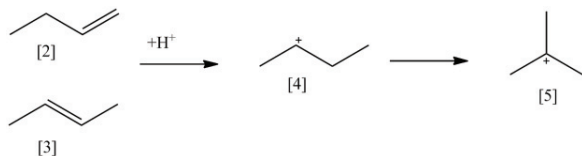
Mathematical modeling is a useful tool for selecting the most effective ways to optimize the industrial equipment performance⁵. However, such tasks can be solved with the mathematical model developed by taking into account the thermodynamic and kinetic laws of reactor processes since they are sensitive to changes in feed composition and catalyst properties [6-9].

The aim of this work is the prediction of yield and hydrocarbon composition of alkylate produced by isobutane alkylation with olefins in presence of sulfuric acid with the method of mathematical modeling.

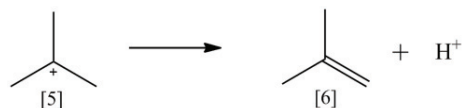
2. Object of research

Alkylation of isobutane by butene is a catalytic process accompanied by the release of a small amount of heat. The reaction of isobutane with butene flows through electrophilic substitution mechanism^{10,11,12}.

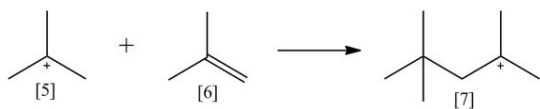
The alkylation reaction of isobutane (1) with butene-1 (2) and with butylene-2 (3) means that in the presence of sulfuric acid butyl (2), (3) via secondary butylcarbocation (4) intermediate isomerizes to tert-butylcarbocation (5):



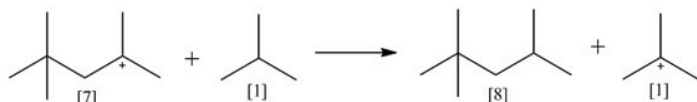
The resulting tert-butylcarbocation (5) loses a proton in the presence of a catalyst, forming isobutene (6):



Isobutene (6) reacts with a new tert-butylcarbocation (5) forming an iso-octyl-ion (7):



The isoocetyl-ion (7) reacts with a molecule of isobutane (1) to form 2,2,4-trimethylpentane (isooctane) (8) and tert-butylcarbocation (5), which continues chemical interaction with isobutene (6):



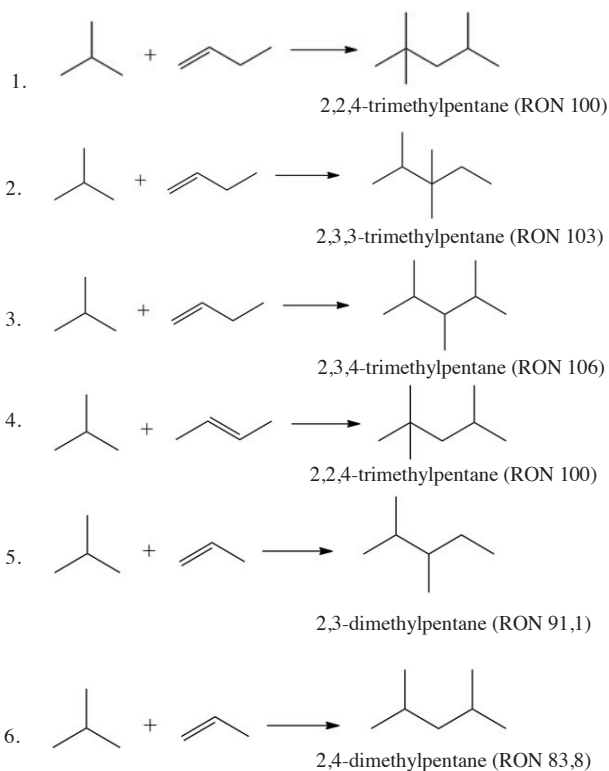
In addition to the main reaction of alkylation side reactions take place, the products of these reactions reduce the quality of the alkylate (the alkylation of propylene and ketones, polymerization).

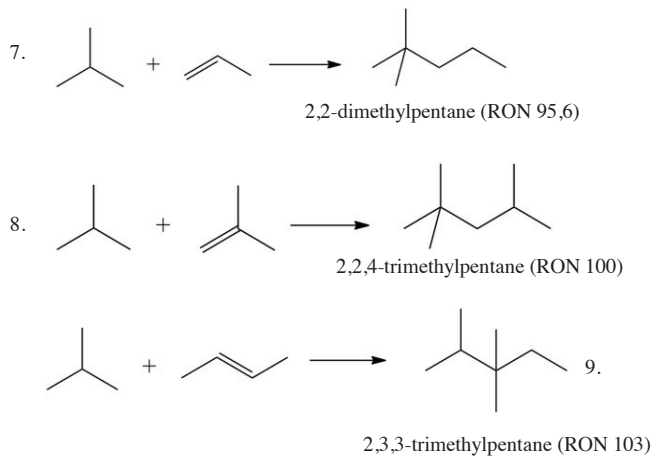
Propylene and ketones react with isobutane to form products with a low octane number. This increases the isobutane fraction spending.

If recycle isobutane in the reaction zone is in insufficient amount, the interaction of olefins between each other take place, the last results in formation of heavy hydrocarbons that reduce the alkylate quality.

To suppress the polymerization reaction of the sulfuric acid, alkylation process is carried out by diluting the olefin feed stream with isobutane, which continuously circulates through the system. The isobutane excess also prevents side reaction of dealkylation.

The main contribution to the overall antiknock rate of alkylates is made by branched hydrocarbons produced during the following reactions:





The principal scheme of the alkylation process implemented in industry is presented in Figure 1.

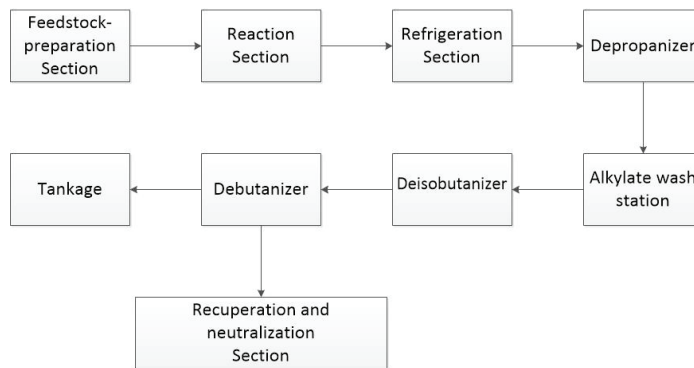


Fig. 1. The principal scheme of the alkylation process.

In large power plants effective cascade type horizontal alkylation reactors are enforced. The reactor is a hollow horizontal cylinder divided by partitions into sections (stages) with stirrers, which provide intensive contact between acid and raw material (Figure 2).

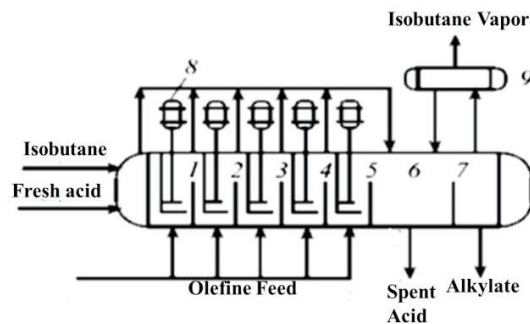


Fig. 2. The principal scheme of the horizontal cascade reactor for sulfuric acid alkylation.

The penultimate section serves as a separator in which the acid is separated from the hydrocarbons. Reaction heat is removed by partial evaporation of circulating isobutane and complete evaporation of propane contained in the raw material. Application of cascade reactors operating on the principle of "auto-refrigeration" simplifies and reduces the cost of installation of C-alkylation as it eliminates the need for the refrigerant^{13,14}.

Typically there are several reactors, which are involved as a part of the alkylation industrial plant in industry, and the temperature of the emulsion in the reactor is 4-13°C, the feed rate ranges from 24 to 74 m³/h, the flow rate of butane-butylene fraction (BBF) varies from 30 to 74,5 m³/h, the reactor pressure is kept within 0,35-0,47 MPa, the volume ratio of isobutane to olefin volume in the hydrocarbon stream entering the reaction is about 7/1-12/1.

The composition of raw alkylation process is shown in Table 1.

Table 1. Feed composition, % mas.

Feed	Component	Concentration
BBF	C2 sum	0.00–1.00
	Propane	0.20–1.30
	Propylene	0.17–1.20
	Propane + Propylene	1.00–1.60
	Isobutane	37.00–42.00
	n-Butane	7.80– 8.50
	Butylene	14.50–15.50
	Isobutylene	6.50–9.00
	Trans-butylene	16.50–17.90
	Cis-butylene	11.00–12.00
	Divinyl	0.2–0.3
Circulating Isobutane	C5+sum	0.00–0.18
	Propane + Propylene	2.30–3.20
	Isobutane	83.00–85.00
	n-Butane	10.20–13.60
	C5 sum	0,30–0,50

3. Methods

While compiling the mathematical model of so complicated chemical process, such as alkylation, there is no objective need and technical possibilities to take into account all transformations of the individual components.

Based on the analysis of experimental data as well as on the results of thermodynamic calculations, a list of possible reactions of the alkylation process and formalized scheme of substances transformations were compiled and composed (Fig. 3) The found average thermodynamic characteristics of the basic process of sulfuric acid alkylation reactions are presented in Table 2 (T=279 K, the pressure is 4 kgf/cm²).

Table 2. Thermodynamic characteristics of some main reactions of alkylation process

Reaction	ΔH , kJ/mole	ΔG , kJ/mole	ΔS , kJ/mole K
Isobutane + Butylene -1 \rightarrow 2,2,4-trimethylpentane	-72.5	-19.3	-190.8
Isobutane + Butylene -1 \rightarrow 2,3,3-trimethylpentane	-134.1	-78.2	-200.4

Butylene -2 + Butylene -2 → 2,2,4-trimethylpentene	-98.2	-41.9	-201.7
Isobutane + Butylene -1 → 2,4-dimethylhexane	-79.2	-28.7	-181.5
Isobutane + Butylene -1 → 2,3-dimethylhexane	-76.7	-25.4	-184.2
Isobutane + Butylene -2 → 2,5-dimethylhexane	-63.6	-11.7	-186.4
Isobutylene + Propylene → 2,4-dimethylpentane	-60.5	-0.8	-116.4
Butylene -1+ Propylene → 2,3-dimethylpentane	-140.1	-91.1	-175.8
Butylene -1 + Propane → 2,2-dimethylpentane	-84.1	-33.6	-181.2
Propylene + Propylene → Isohexene	-140.7	-92.9	-171.4
Isobutylene + Isohexane → Isodecane	-111.3	-36.5	-170.3
Isobutane + Butylene -1 → 2-methylheptane	-77.1	-26.0	-184.3

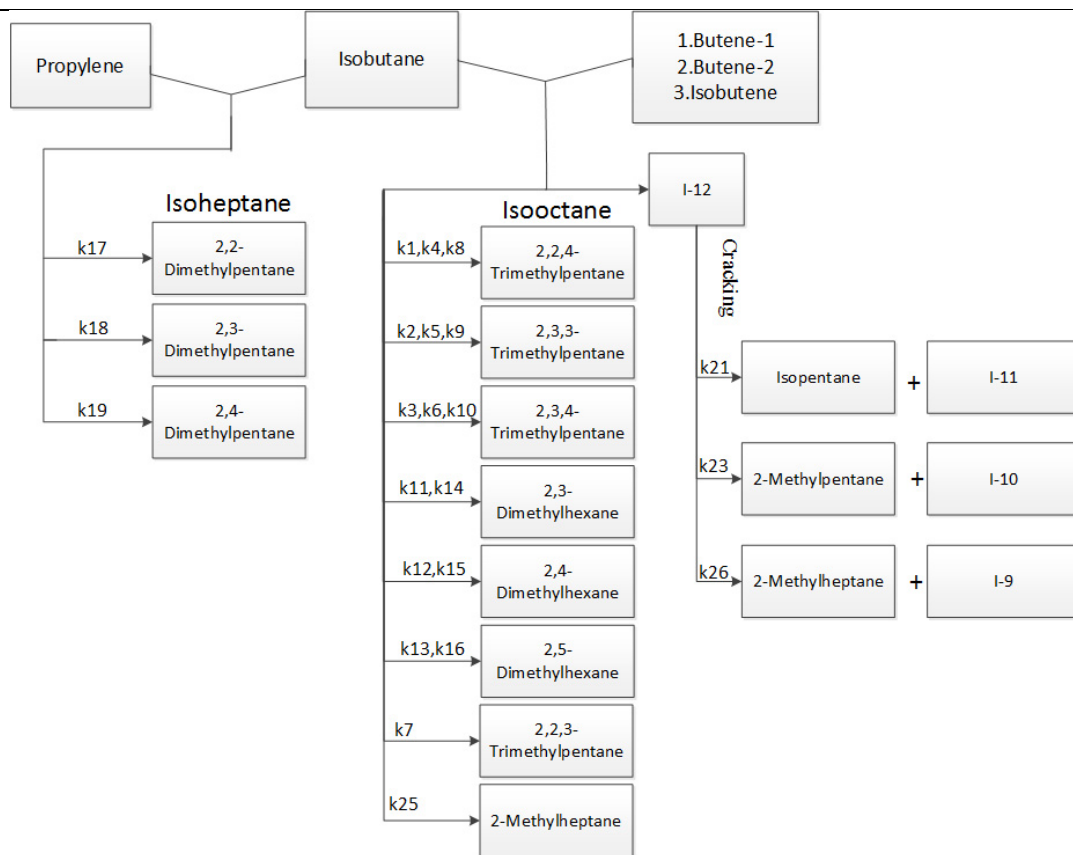


Fig. 3. The formalized scheme of substances transformations in the process of sulfuric acid alkylation of isobutane with olefins: k_i is a constant speed of respective reaction.

Chemical conversions of hydrocarbon feedstock to form the individual components, such as 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, and 2,3,3-trimethylpentane, are considered in the above formalized scheme. At the same time, hydrocarbons, which contents in the product mixture of the alkylation reactor is insignificant and their contribution to the alkylate octane number is negligible, were grouped.

On the basis of the developed reaction scheme, the equations describing the rates of chemical reactions in the isobutane alkylation process were compiled.

The kinetic model of the process includes a component-wise material balance equation. For components, such as isobutane, butene-1 and butene-2, kinetic model equation according to formalized reactions scheme has the form:

$$\begin{aligned} \frac{dC_{isobutane}}{d\tau} = & -k_1 \cdot C_{isobutane} \cdot C_{butylene-1} - k_2 \cdot C_{isobutane} \cdot C_{butylene-1} - k_3 \cdot C_{isobutane} \cdot C_{butylene-1} - k_4 \\ & \cdot C_{isobutane} \cdot C_{butylene-1} - k_5 \cdot C_{isobutane} \cdot C_{butylene-1} - k_6 \cdot C_{isobutane} \cdot C_{butylene-2} - k_7 \\ & \cdot C_{isobutane} \cdot C_{propylene} - k_8 \cdot C_{isobutane} \cdot C_{propylene} - k_9 \cdot C_{isobutane} \cdot C_{propylene} - k_{10} \\ & \cdot C_{isobutane} \cdot C_{butylene-2}^2 - k_{12} \cdot C_{isobutane} \cdot C_{butylene-1} - k_{13} \cdot C_{isobutane} \cdot C_{isobutylene} - k_{14} \\ & \cdot C_{isobutane} \cdot C_{butylene-2} - k_{15} \cdot C_{isobutane} \cdot C_{butylene-2} \end{aligned}$$

$$\begin{aligned} \frac{dC_{butylene-1}}{d\tau} = & -k_1 \cdot C_{isobutane} \cdot C_{butylene-1} - k_2 \cdot C_{isobutane} \cdot C_{butylene-1} - k_3 \cdot C_{isobutane} \cdot C_{butylene-1} - k_4 \\ & \cdot C_{isobutane} \cdot C_{butylene-1} - k_5 \cdot C_{isobutane} \cdot C_{butylene-1} - k_{12} \cdot C_{isobutane} \cdot C_{butylene-1} \end{aligned}$$

$$\frac{dC_{butylene-2}}{d\tau} = -k_6 \cdot C_{isobutane} \cdot C_{butylene-2} - k_{14} \cdot C_{isobutane} \cdot C_{butylene-2} - k_{15} \cdot C_{isobutane} \cdot C_{butylene-2}$$

Initial conditions:

$$\tau = 0 \quad C_i(0) = C_{i,0}$$

i – hydrocarbon.

The resulting kinetic model is formalized and quasi-homogeneous.

While developing the model of the reactor it was assumed that the fluid dynamics model describes the alkylation contactor as continuous stirred-tank reactor.

The material balance equation can be generally represented as

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

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

Heat balance equation of the alkylation reactor is:

$$\frac{dT_j}{d\tau} = \frac{1}{\tau} (T_{j-1} - T_j) + \frac{Q_j}{C_p} W_{j-1}$$

where Q_j – standard enthalpy of formation, W_j – velocity of chemical reaction, C_p – heat of the reaction mixture, J/(mol·K), T – temperature.

The activation energy and pre-exponential factor in the Arrhenius equation were determined on the basis of the theory of absolute rates of chemical reactions (Transition State Theory):

1. Pre-exponential factor is determined using the following equation:

$$k_0 = \chi \frac{k \cdot T}{h} e^{\frac{\Delta S_0^\ddagger}{R}}, \quad (1)$$

χ – transmittance (transmission coefficient); k – the Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K); T – temperature, K; h – the Planck's constant ($6.62 \cdot 10^{-34}$ J/s), ΔS_0^\ddagger – enthalpy of activation, kJ/mol, R – the gas constant (8.314 J/(mol K)).

Enthalpy of activation is calculated according to the following formula:

$$\Delta S_0^\ddagger = S_0^{TS} - \sum S(R_i),$$

For bimolecular reaction:

$$k_0 = \chi \frac{k_b \cdot T}{h} e^{\frac{RT}{RT}} = \chi \frac{k_b \cdot T}{h} e \quad (2)$$

2. Activation energy calculation:

$$E_a = \Delta H^\ddagger + nRT \quad (3)$$

ΔH^\ddagger – activation enthalpy.

The calculations were performed using density functional theory (DFT) at the B3LYP level of theory. This method was chosen for its high accuracy in relation to experimental results. Since this is the highest level of theory for DFT calculations that Gaussian uses, and some of the reactions of interest here involve many atoms, a basis set is needed to be selected that was of a small enough size to keep the calculations manageable, but still allow accurate description of the physical situation. Finally, the basis selected for these calculations is the 6-31++G(d,p) basis. The polarization functions were necessary since every step in the reaction pathway involves at least one polar molecule.

The basis with diffuse functions is used for a more accurate description of anions as well as systems with lone electron pairs. Adding these features can more accurately describe the behavior of electrons at large distances from the nucleus.

Processes accompanied by a decrease in the number of lone pairs of electrons, such as protonation, are also better simulated with the inclusion of diffuse functions.

Calculations were performed for reactions in the liquid phase, so it was necessary to include effects in the potential felt from the nearby molecules. For this purpose, the Thomas limited polarization model was used (Integral Equation Formalism (IEFPCM)).

It defines a cavity (or space) as the series combination of blocked atomic spheres. As the solvent sulfuric acid was applied because the ratio of sulfuric acid to the hydrocarbons is maintained at 1: 1.

In order to take into account physico-chemical properties of sulfuric acid it is necessary to set parameters, such as the static (ϵ_s) and optical (ϵ_{opt}) dielectric constants in the method; for sulfuric acid they are respectively 101 and 2.042. For searching transition state we used method of quadratic synchronous transit based on the fact that on the PES (potential energy surface) the program can make a family of parabolas, which connect the point of reactant and the point of product. The vertices of these parabolas are approaching the point TS. If you vary the parameters of parabolas minimizing the norm of the gradient (this requires the calculation of the energy and gradient at points on the parabola), the search process can converge at the true TS^{15,16,17}.

Table 3. The kinetic parameters of the main reactions of the alkylation process, 283.7 K

№	Reaction	E_a , kJ/mole	The pre-exponential factor in the Arrhenius equation, sec ⁻¹
1	Isobutane + Butylene -1 → 2,2,4-trimethylpentane	40.56	$9.86 \cdot 10^{17}$
2	Isobutane + Butylene -1 → 2,3,3-trimethylpentane	40.67	$4.10 \cdot 10^7$
3	Isobutane + Butylene -1 → 2,3,4-trimethylpentane	23.10	$1.26 \cdot 10^{13}$
4	Isobutane + Butylene -1 → 2,4-dimethylhexane	28.40	$7.95 \cdot 10^{15}$
5	Isobutane + Butylene -1 → 2,3-dimethylhexane	29.01	$2.40 \cdot 10^{16}$
6	Isobutane + Butylene -2 → 2,5-dimethylhexane	32.92	$7.0 \cdot 10^{17}$
7	Isobutylene + Propylene → 2,4-dimethylpentane	30.60	$9.86 \cdot 10^{17}$
8	Butylene -1+ Propylene → 2,3-dimethylpentane	33.50	$1.15 \cdot 10^{22}$
9	Butylene -1 + Propane → 2,2-dimethylpentane	15.80	$4.50 \cdot 10^7$
10	3 Butylene -2 + Isobutane → Isodecane + 2-methylheptane	29.16	$5.10 \cdot 10^{15}$
11	Isobutylene + Isohexane → Isodecane	35.56	$9.86 \cdot 10^{17}$
12	Isobutane + Butylene -1 → 2-methylheptane	13.01	$9.70 \cdot 10^6$
13	Isobutylene + Isobutane → 2,2,4-trimethylpentane	22.24	$2.50 \cdot 10^{12}$
14	Isobutane + Butylene -2 → 2,2,4-trimethylpentane	31.01	$2.16 \cdot 10^{16}$
15	Isobutane + Butylene -2 → 2,3,3-trimethylpentane	30.90	$9.86 \cdot 10^{17}$

The main contribution to obtain the desired product is made by the reactions of 1, 3, 13, 14 and 15.

The analysis of the obtained data and literature data allows concluding that all of the reactions in the contactor are fast since their activation energies are in the range of 40-50 kJ/mol, the reaction may slow till the activation barrier of 100-120 kJ/mol.

Table 4 shows the results of comparison between the calculated and experimental values of the main components concentrations of the alkylation product mixture.

Table 4. Comparison of the calculated and experimental values of the concentrations of the main components of the alkylation product mixture

Component	Calculated concentration value % mas.	Experimental concentration value % mas.	Accuracy, %
2,2,4-trimethylpentane	30.12	30.15	0.13
2,3,3-trimethylpentane	17.72	17.42	1.76
2,3,4- trimethylpentane	14.52	14.77	1.66
2,4-dimethylhexane	2.56	2.90	12.99
2,3-dimethylhexane	2.67	2.80	4.69
2,5-dimethylhexane	3.52	3.43	2.65

The average value of accuracy was 3.98%.

4. Results and discussion

In order to assess the effect of the composition of raw materials to the octane number of alkylate, the calculations were made in the model, and the alkylates compositions were obtained (Table 6) provided processing of raw materials of different composition (Composition of raw materials №1 and composition of raw materials №2), Table. 8, under the same process conditions (Table 5).

Table 5. Composition of feed streams (experimental data)

Feed	Component	Composition of feed №1	Composition of feed №2	
Combined feed composition, % mas.	C2 sum	0.00	0.11	
	Propane	2.69	1.54	
	Propylene	0.08	0.23	
	Isobutane	64.38	71.56	
	n-Butane	17.30	9.18	
	Butylene	3.59	5.45	
	Isobutylene	4.06	1.80	
	Trans-butylene	4.55	6.04	
	Cis-butylene	3.31	4.19	
	Divinyl	0.03	0.08	
	C5 sum	0.08	0.14	
	C5+ sum	0.03	0.02	
	Isobutane from the separator, % mas.	C2 sum	0.00	0.00
		Propane + Propylene	3.12	1.99
Isobutane		75.52	88.01	
n-Butane		21.25	9.75	
Sum of butylenes		0.00	0.03	
	C5 sum	0.11	0.22	

Table 6. The contents of key components in the alkylate (calculated using model), % mas.

Component	№1	№2
2,2,4-trimethylpentane	26.20	30.12
2,3,3-trimethylpentane	15.43	17.73
2,3,4- trimethylpentane	14.43	14.52
2,4-dimethylhexane	6.66	2.56
2,3-dimethylhexane	6.77	2.67
2,5-dimethylhexane	2.99	3.52
2,4-dimethylpentane	1.00	2.67
2,3-dimethylpentane	1.77	1.49
Isodecane	0.11	0.21
2-methylheptane	0.22	0.11

As can be seen, in isobutane alkylation with olefins a big role is played by ratio of isobutane to butene, and the bigger it is, the higher the octane number of the obtained alkylate is (Tab. 7).

Using the mathematical model of the gasoline blending implemented in the computer simulation system Compounding, the basic properties of alkylate were calculated.

Table 7. The properties of the resulting alkylate calculated using the model

Parameter	№1	№2
RON	95.22	97.28
Vapour pressure, kPa	34.33	34.77
Density, kg/m ³	679.23	678.59

5. Conclusions

The studies established the mathematical model of isobutane alkylation with olefins and investigated the dependence of anti-knock properties of alkylate on the composition and process conditions.

As a result of studies it was found that the anti-knock properties of the alkylate are directly dependent on the feed composition, particularly on the content of isobutane. Alkylates produced from feedstock with less isobutane mass fraction have a smaller value of RON. Wherein the difference in composition of the feedstock contributes to antiknock index by the amount of 1.0-2.0 points.

Acknowledgements

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