

16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

Application of cumene technology mathematical model

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Abstract

The work describes the existing problems of the technological systems for cumene synthesis catalyst AlCl_3 . The paper describes the stages of development of the mathematical model of benzene alkylation with propylene. The model allows the calculation of composition of the product stream when changing process parameters of the plant: temperature, molar ratio of benzene/propylene, feed space velocity. The error of the model does not exceed 7.5%. The computer modeling system «Alkylation» is developed in Borland Delphi 7, and the module optimization of the process parameters is called «Optimization». The calculations allowed reducing the catalyst consumption in the alkylation reactor (to 10-15%) and increasing the cumene concentration in the product mixture (to 25% wt.). The concentration of n-propylbenzene in the output stream is 0.05 wt%. The recommendations for optimization of the industrial alkylation unit are presented for implementation at OJSC «Omsky Kautchuk».

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Peer-review under responsibility of Tomsk Polytechnic University

Keywords: cumene, alkylation, mathematical modelling, aluminum chloride, optimization.

1. Introduction

Production of cumene is one of the most large-scale productions in the world, which is among the five largest industries - ethylene, propylene, benzene, ethylbenzene, and cumene. Thus 90% of the resulting cumene is used for the production of phenol and acetone and about 10% in the production of α -methylstyrene as a valuable component of rubbers¹.

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In the world 44% of phenol is used to produce bisphenol A and diphenyl carbonate for the production of polycarbonates, polysulfones, polyacrylates, polyamides, and epoxy resins. About 40% of phenol produced in Russia is exported to Finland, China, and Latvia. In Russia production capacity of α -methyl styrene and rubber on its base will reach 1.8 million tons per year by 2016. Global demand for acetone increases by an average of 4.2 - 5.3% per year, and in 2012-2016, the demand for acetone in Russia is forecast ² to grow by an average of 1.2% per year, and will reach 164.5 thousand tons in 2016.

On the Russian phenol plant cumene preparation using complex compound of aluminum chloride as catalyst has undergone minor changes compared to the original ^{3,4}, which have the same technical level, engineering design, and technological scheme.

The technology has a one-step character, sufficient efficiency, propylene conversion is 99%, differential selectivity of cumene reaches 91%, benzene conversion per pass is 30-40% ^{5,6}.

Although debugging technology and long experience in plant operation of liquid phase alkylation the conversion efficiency of benzene to cumene is not high, benzene overrun is more than 250 kg. per one ton of cumene.

Cumene output is $35 \pm 1\%$, more than 15% of the amount of produced cumene is waste.

The production instability manifests itself in the increased volume of heavy impurities (polyalkylbenzenes and tar) in the reaction mixture of alkylation.

Current problems in the cumene technology are product quality and alkylation temperature reduction below the regulatory values, aluminum chloride overruns, and catalyst complex resinification.

The alkylation reactions (transalkylation) slowed during the gradual deactivation of the catalyst.

The rate of transalkylation reactions of polyalkylbenzenes is especially reduced because there is no time for reversible reaction. To avoid this, we increase the flow of benzene with a view to intensify the process of the slowest transalkylation reaction.

Accumulation of some side products effects on alkylation catalyst deactivation. Such substances can bind strongly with $AlCl_3$ or form stable σ -complexes, which hardly gave its proton to the olefin molecule. These substances are polyalkylbenzenes at low temperatures when the reaction speed is low and at high temperatures they are polycyclic aromatic compounds and resins ⁷.

At present, Russian companies are producing 6 - 15 kg of the residue - aluminum hydroxide as wet slurry containing significant amounts of organic impurities (sometimes up to 20 - 25%) per one ton of cumene.

Improved quality and reduction of cumene production waste is a challenge for the industry that can be successfully achieved through the production optimization with the use of advanced information technologies such as computer modeling systems with high prognostic potential ^{8,9,10}.

The purpose of the work is to increase the production efficiency by the alkylation reactor operation optimization using the method of mathematical modeling.

2. Objectives

In this paper we have the tasks:

1. Reduction of the catalytic complex flow;
2. Improvement of the main product – cumene;
3. Reduction of the impurities concentration such as n-propylbenzene, butylbenzenes, and ethylbenzene to 0.05, 0.02 and 0.05mass% respectively;
4. Reduction of the amount of by-products – polyalkylbenzenes.

3. Mathematical modeling

Mathematical modeling includes the following steps:

- Study of the technological scheme and experimental data obtained by the alkylation of benzene with propylene at OJSC «Omsky Kautchuk»;
- Thermodynamic analysis of multicomponent chemical process.
- Formalization of hydrocarbon conversions mechanism, formal scheme drafting of substance transformations.

- Development of process kinetic model according to the selected formalized scheme.
- Solution of the inverse kinetic problem.
- Mathematical description of the reactor.
- Creation of the algorithm for solving a system of differential equations.
- Software implementation of the mathematical model equations.
- Checking the created model for adequacy.
- Further research of the process using the developed mathematical model;
- Optimization of the process and making recommendations to improve the efficiency of cumene production.

3.1. Cumene technology

The drained benzene fraction from the cube of the column 3 in the heat exchanger 2 warms up the fraction for drainage (Fig. 2). This fraction runs to the collector 8, from where it is continuously pumped to the alkylator 9, the fraction of propylene is also supplied here. The catalytic complex is prepared in the apparatus 6 with the mixer. The drained benzene fraction (the mixture of benzene, polyalkylbenzenes, and other components), aluminum chloride (concentration of pure substance is not more than 10 mass %), the water (1-2 mass % of the weight of the loaded AlCl_3) are fed and mixed.

The prepared complex is periodically supplied to the alkylator. The reaction occurs in the alkylator 9 filled with the liquid reaction mixture, reflux condenser 10 for vaporized benzene return and heat dissipation.

To capture the benzene from exhaust gases the gases are sent to the absorber 13. The hydrocarbon layer withdrawn after the separator 12 is composed of benzene, mono- and polyalkylbenzenes.

In the synthesis of isopropylbenzene the reaction mass contains 45 ... 55% of benzene, 35 ... 40% of cumene, 8 ... 12% of dialkylbenzene, 3% of some by-products and tars.

Processes for this technological parameters are: $T = 100 - 130^\circ \text{C}$; $P = 0.11 - 0.16 \text{ atm}$; molar ratio of benzene ÷ propylene = $2.5 : 1 \div 4 : 1$; feed space velocity = $1 - 5 \text{ h}^{-1}$.

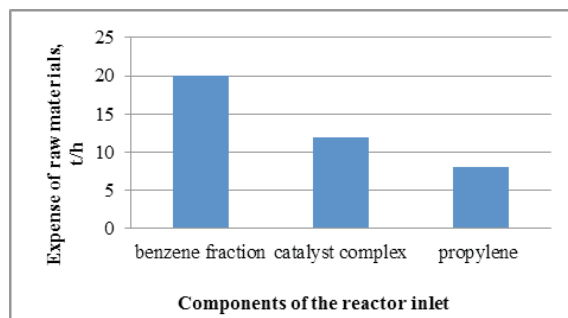


Fig. 1. Raw materials consumption in the reactor

All this mixture passes through the water cooler 15 and further settles in the cold separator 16, where the catalyst complex is periodically returned to the alkylator. The alkylate is then directed for removal of dissolved hydrogen chloride and aluminum chloride.

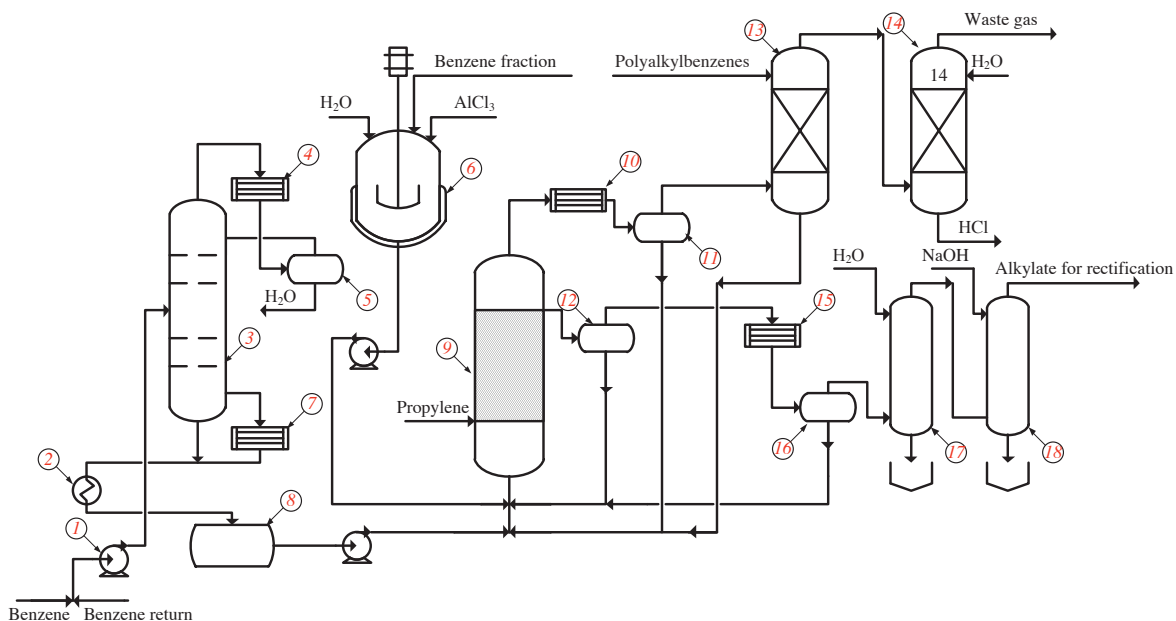


Fig. 2. Technological scheme of isopropylbenzene: 1 - pump; 2 - heat exchanger; 3 - column azeotropic dehydration of the benzene charge; 4, 10 - capacitors; 5 - separator; 6 - unit for catalytic complex; 7 - heater; 8 - collector; 9 - alkylator; 11 - gas separator; 12, 16 - separators; 13 - absorber; 14 - water scrubber; 15 - refrigerator; 17, 18 - scrubbing column.

To this end, the mixture is washed in the counter current columns 17 and 18 first with water, then – with aquatic alkali. The mixture is sent for distillation, and ethylbenzene, cumene, butylbenzenes, polyalkylbenzenes are consistently obtained. The yield of the desired product with all the losses is 94 ... 95% at the flow of 3 ... 7 AlCl_3 kg per one ton of cumene. The experimental data of streams and compositions are given in Fig. 1, 3 (a, b).

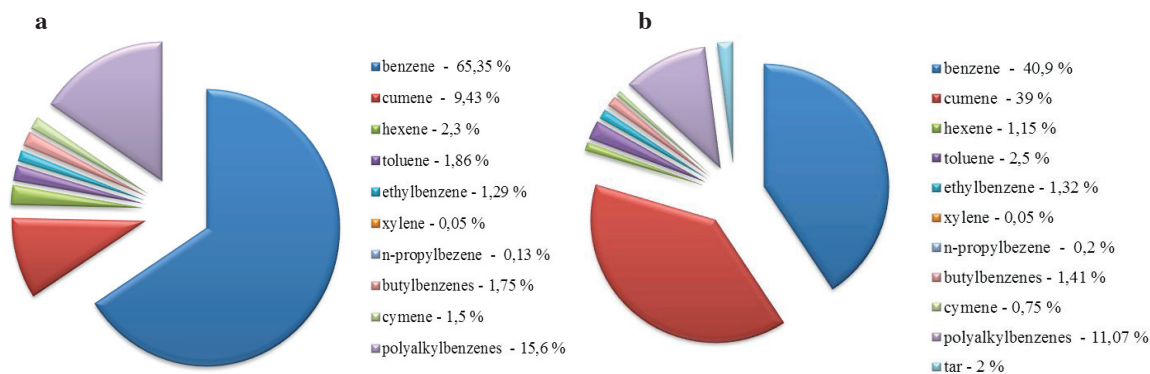


Fig. 3. (a) The component composition of the inlet and (b) outlet streams of the alkylator, % wt.

3.2. Determination of thermodynamic parameters

Chemical reactions were determined on the basis of the structure analysis of the reactor input and output streams.

For calculation of the thermodynamic functions of the main components, such as enthalpy, entropy and Gibbs energy the density functional theory (DFT) method was used.

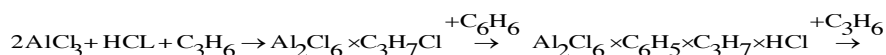
The calculations were performed using the software package Gaussian 09W¹¹, the results of calculations are shown in Table 1.

Table 1. The thermodynamic and kinetic parameters of the main reactions (the process conditions: T=395 K, P=1.6 atm).

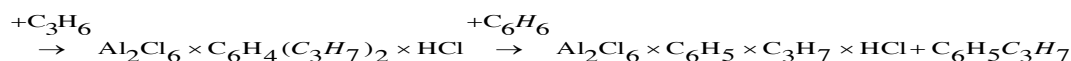
№	Reaction	ΔG , kJ / mol	$\cdot 10^5, A_0$	Ea, kJ / mol
1	$C_6H_6 + C_3H_6 \rightarrow C_6H_5CH(CH_3)_2$	-4.97	1.580	150.94
2	$C_6H_5CH(CH_3)_2 + C_3H_6 \rightarrow C_6H_4(CH(CH_3)_2)_2$	-4.71	2.260	128.81
3	$C_6H_4(CH(CH_3)_2)_2 + C_6H_6 \rightarrow 2 C_6H_5CH(CH_3)_2$	-0.26	0.534	156.13
4	$C_6H_4(CH(CH_3)_2)_2 + C_3H_6 \rightarrow C_6H_3(CH(CH_3)_2)_3$	112.37	0.180	140.64
5	$C_6H_3(CH(CH_3)_2)_3 + C_6H_6 \rightarrow C_6H_4(CH(CH_3)_2)_2 + C_6H_5CH(CH_3)_2$	-117.34	0.101	154.71
6	$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$	-8.90	1.280	130.41
7	$C_6H_5CH_3 + C_3H_6 \rightarrow C_6H_4CH_2CH(CH_3)_2$	-5.73	1.360	143.83
8	$2 C_3H_6 \rightarrow C_6H_{12}$	-11.61	1.970	116.20
9	$2 C_2H_4 \rightarrow CH_2=CH-C_2H_5$	-39.46	16.50	166.98
10	$C_6H_6 + CH_2=CH-C_2H_5 \rightarrow C_6H_5CHCH_2C_2H_5$	-1.98	54.50	159.90
11	$C_6H_6 + CH_2=C(CH_3)_2 \rightarrow C_6H_5C(CH_3)_3$	20.33	5.650	158.23
12	$C_6H_6 + CH_2=CH-C_2H_5 \rightarrow C_6H_5C_4H_9$	-12.74	14.20	147.95
13	$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$	-29.11	7.160	137.48
14	$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2$	-28.66	0.290	129.58
15	$CH_4(C_2H_5)_2 + C_2H_4 \rightarrow C_6H_3(C_2H_5)_3$	-14.63	3.510	177.98
16	$C_6H_6 + C_6H_3(C_2H_5)_3 \rightarrow C_6H_4(C_2H_5)_2 + C_6H_5C_2H_5$	-14.48	0.420	165.09
17	$2 C_6H_6 + C_3H_6 \rightarrow C_6H_5CH_3 + C_6H_4(CH_3)_2$	-174.02	14.20	216.11
18	$2 C_6H_6 + C_2H_4 \rightarrow 2 C_6H_5CH_3$	-172.82	14.20	216.11
19	$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2 C_6H_5C_2H_5$	-0.44	0.323	238.27

3.3. Investigation of the reaction mechanism

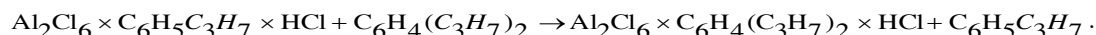
The first step of the process is the addition of aluminum chloride to the olefin in the presence of hydrogen chloride, benzene, and then a ternary complex is formed:



The olefin joins after formation of a triad complex. Further the reaction of exchange occurs between the complex and initial hydrocarbon (benzene) with formation of alkylbenzene:



The mechanism of transalkylation:



3.4. Kinetic model

All reactions from Table 1 were considered for creation of the kinetic model, and components such as diisopropylbenzene, triisopropylbenzene, diethylbenzene, triethylbenzene were merged into one group of pseudo-high molecular weights which are named PAB.

Butylbenzenes are also united in one group as the maintenance of a separate component of the group in the output stream is insignificant. Ingredients combination in the groups allows us to simplify the mathematical description of the complex multi-component process¹².

The rate equation of alkylation, transalkylation and dimerization reactions were composed according to the law of mass action, the equations for the remaining components are similar, see Table 2.

Table 2. The rate equation of alkylation, transalkylation and dimerization reactions.

Alkylation	$W_1 = k_1 \cdot C_{benzene} \cdot C_{propylene}$ $W_3 = k_3 \cdot C_{diisopropylbenzene} \cdot C_{benzene}$
Transalkylation	$W_5 = k_5 \cdot C_{triisopropylbenzene} \cdot C_{benzene}$ $W_{16} = k_{16} \cdot C_{triethylbenzene} \cdot C_{benzene}$
Dimerization	$W_8 = k_8 \cdot C_{propylene}^2$ $W_9 = k_8 \cdot C_{ethylene}^2$

The kinetic model of alkylation of benzene with propylene according to the formal scheme of transformations is as follows:

$$\left\{ \begin{array}{l} \frac{dC_{benzene}}{d\tau} = -W_1 - W_3 - W_5 - W_6 - W_{10} - W_{11} - W_{12} - W_{13} - W_{16} - 2W_{17} - 2W_{18} - W_{19}; \\ \frac{dC_{propylene}}{d\tau} = -W_1 - W_2 - W_4 - W_6 - W_7 - 2W_8 - W_{17}; \\ \dots\dots\dots \end{array} \right.$$

Initial conditions: $\tau = 0$, $C_i = C_{0i}$, where i – hydrocarbon.

W_n — rate of n -th reaction, mol/(m³·sec), k – the reaction rate constant, E_a – activation energy, J/mol, R – the universal gas constant, J/(mol·K), T – temperature, K, C_i – concentration of i -th component, mol/m³.

3.5. Solution of the inverse kinetic problem and the determination of the kinetic parameters (activation energy and pre-exponential factor in the Arrhenius equation).

The kinetic model is formalized and quasi-homogeneous. The kinetic parameters were determined by the solution of the inverse kinetic problem on the basis of the experimental data obtained from the alkylation plant. The initial approximation was chosen from the results of quantum and chemical modeling of reactions and determination of the thermodynamic parameters of the transition state of the intermediate stages¹¹.

A_0 and E_a in the Arrhenius equation were determined on the basis of the theory of absolute rates of chemical reactions^{12, 13, 14}. The reactions kinetic parameters of the process are shown in Table 1. The rate constants of the chemical reactions are determined by solving the inverse kinetic problem by minimizing the differences between the calculated and the experimental data obtained by concentrating the components of the product mixture of the alkylation reactor, see Table 3.

Table 3. The kinetic parameters of the main alkylation reactions by solving the inverse kinetic problem

Reaction	k, mol/(m ³ ·sec)
$C_6H_6 + C_3H_6 \rightarrow C_6H_5CH(CH_3)_2$	$3.94 \cdot 10^{-4}$
$C_6H_5CH(CH_3)_2 + C_3H_6 \rightarrow C_6H_4(CH(CH_3)_2)_2$	$1.09 \cdot 10^{-4}$
$C_6H_4(CH(CH_3)_2)_2 + C_6H_6 \rightarrow 2 C_6H_5CH(CH_3)_2$	$3.05 \cdot 10^{-4}$
$C_6H_3(CH(CH_3)_2)_3 + C_6H_6 \rightarrow C_6H_4(CH(CH_3)_2)_2 + C_6H_5CH(CH_3)_2$	$1.11 \cdot 10^{-4}$
$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$	$2.09 \cdot 10^{-6}$
$C_6H_6 + CH_2=CH-C_2H_5 \rightarrow C_6H_5C_4H_9$	$7.69 \cdot 10^{-6}$
$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$	$3.39 \cdot 10^{-7}$
$C_6H_6 + C_6H_5(C_2H_5)_3 \rightarrow C_6H_4(C_2H_5)_2 + C_6H_5C_2H_5$	$9.65 \cdot 10^{-8}$
$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2 C_6H_5C_2H_5$	$1.60 \cdot 10^{-4}$

3.6. Material and heat balance

$$G_{DBF} + G_{PPF} + G_{FCC} + G_{RCC} + G_{returnbenzene} = G_{ARM} + G_{waste\ gas}, \quad (1)$$

Where:

DBF - Dry benzene fraction; PPF - Propane-propylene fraction; FCC - Fresh catalyst complex; RCC - Return catalyst complex; ARM - alkylation reaction mass.

The reactor is adiabatic, the heat balance equation is written as follows¹⁵:

$$\rho^{mix} C_p^{mix} \frac{\partial T}{\partial \tau} = \pm \sum_{j=1}^N (-\Delta H_j) \cdot W_j \quad (2)$$

$-\Delta H_j$ - thermal effect of j-th chemical reaction kJ / mol;

C_p^{mix} - molar heat capacity of the reaction mixture, J / (mol K);

ρ^{mix} - density of the reaction mixture, kg / m³;

N - number of reactions.

3.7. Verification of the mathematical model

The calculated values for the components of the product mixture of the alkylation reactor were compared with the experimental data from the industrial plant, wherein the calculation error does not exceed 7.5%, see in Fig. 4 (a, b).

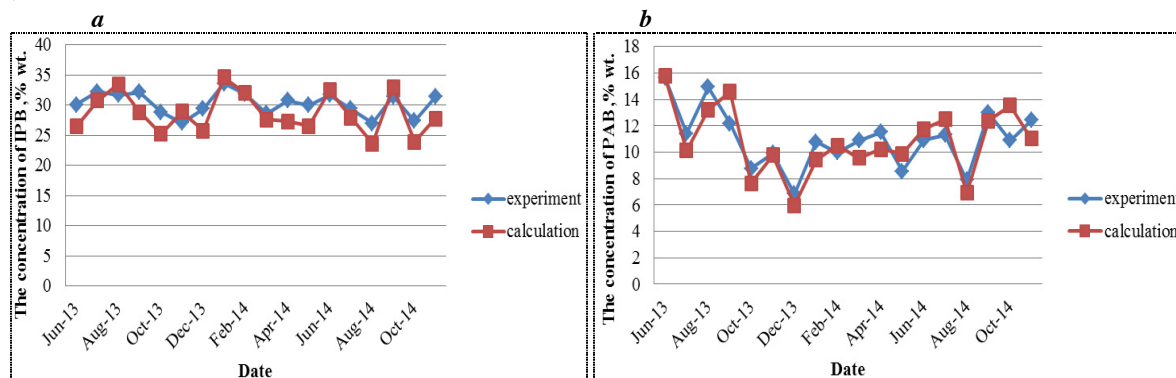


Fig. 4. (a) Comparison of the calculated and experimental data content of IPB and (b) PAB in the product mixture.

The model is implemented in the programming language Borland Delphi 7 and supplemented by the optimization mathematical function to ensure strict compliance of the values of the components of the alkylation reaction mass: n-propylbenzene, ethylbenzene, and butylbenzenes, (not more than 0.05, 0.02, and 0.05 mass%, respectively).

Differential equations of the model are solved with Euler's method, optimization method developed by Nelder-Mead, also known as the flexible polyhedron's method¹⁵.

4. Results and discussions

Using the developed model the study on the effect of reducing the consumption of the catalyst complex in the target outputs (IPB) and secondary components (PAB) was conducted. Research was conducted with use of the developed model on influence of decrease in an expense of a catalytic complex on exits of main component (IPB), and co-product (PAB), see in Fig. 5 (a, b).

Optimization of process parameters to reduce consumption remove the catalyst complex at 10-15% (1500 - 2000 kg / h), which has a positive impact on the operation of the plant, namely the decrease in the number of secondary components of the alkylation reaction - PAB.

As can be seen in Fig. 5 (a, b), the concentration of isopropylbenzene in the reaction mass of alkylation reactor increased by an average of 2-4%, which is based on the production rate of 1000-1500 kg / h. The PAB yield reducing selectivity decreased (by an average of 2-3%). In terms of performance decline in PAB consumption ranged from 200 to 700 kg / h.

Optimization of the process parameters under reduced consumption of catalyst was carried out at varying temperatures, feed space velocity (WHSV), and the molar ratio of benzene and propylene (Table 4).

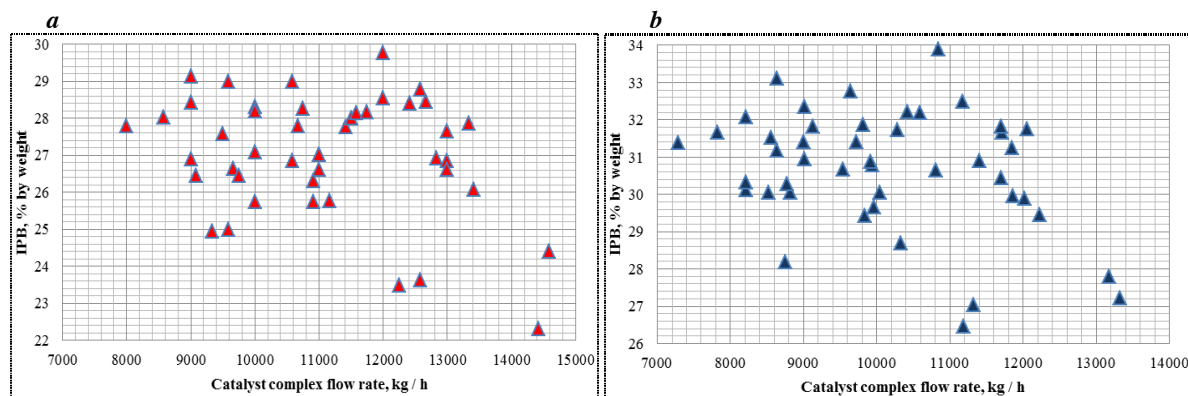


Fig. 5 (a) Catalyst complex rate in the alkylation reactor before and (b) after optimization

During the optimization the concentration of cumene in the product mixture has been found to increase as the temperature and the molar ratio of benzene/propylene decreases increasing feed space velocity. There was an increase in the concentration of cumene in the reaction mixture to 25%.

Table 4. The results of the optimization of the installation technological modes

Before optimization				After optimization				Δ IPB, %
T, K	Molar ratio	WHSV, h^{-1}	IPB, Mass %	T, K	Molar ratio	WHSV, h^{-1}	IPB, Mass %	
401	4.038	3.671	29.97	395	2.888	3.944	29.99	24.3
409	5.000	5.021	28.07	395	5.400	3.815	34.90	24.3
401	3.889	2.987	29.41	397	2.888	3.276	32.50	9.5
402	4.240	2.987	30.97	395	2.888	3.706	31.38	3.5
402	4.038	2.987	30.98	397	2.888	4.245	32.36	4.2
402	4.200	3.609	31.86	395	2.275	3.531	37.80	18.6
399	4.773	3.233	28.69	397	3.150	3.505	35.07	22.0
402	4.565	2.828	27.25	398	1.925	4.679	34.50	25.3

5. Conclusions

The mathematical model of the alkylation process of benzene with propylene is developed. It allows the calculation of the composition of the product stream when changing the critical process parameters of the plant: temperature, molar ratio of benzene/propylene, feed space velocity. Applied use of the models and software module optimization allows:

- increasing the concentration of the target product (IPB) in the reaction mass to 25 mass%;
- reducing the consumption of the catalyst complex by 10-15% with no loss of production performance;
- reducing the concentration of n-propylbenzene, ethylbenzene, and butylbenzenes to normal (0.05, 0.02 and 0.05 wt.%) in IPB product;
- reducing the amount of by-products (PAB) by an average of 2-3 mass%.

Acknowledgements

The work is performed as a part of the Russian Government Project "Science" 1.1348.2014.

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