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Influence of Technological Parameters of the Alkylation Reactor Operation on the Concentration of n-Propylbenzene in the Product Mixture

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Abstract

This paper describes the problem of a high content of n-propylbenzene as an undesirable component of the product mixture in the process of liquid-phase alkylation of benzene with propylene at one of the Russian refineries. The unit was monitored and technological parameters influencing the content of n-propylbenzene were identified. A mathematical model of the alkylation process has been developed and, on its basis, a computer modeling system "Alkylation" in the Borland Delphi 7 environment, which allows calculating the composition of the product flow when the most important technological parameters of the reactor change (temperature, benzene: propylene molar ratio, feedstock flowrate).

Keywords: *Alkylation; n-propylbenzene; Mathematical model; Benzene; Propylene.*

1. Introduction

Today there are six units to produce the isopropylbenzene (IPB) by alkylation of benzene with propylene in Russia [1–4]. All these units use aluminum chloride as a catalyst. In addition to its main disadvantages (highly corrosive environment and toxicity of effluents), aluminum chloride has a number of significant advantages: high selectivity for the main product, "mild" process conditions

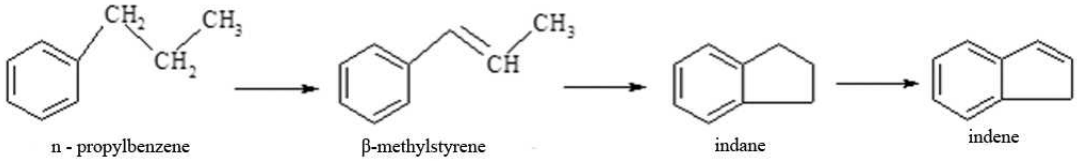
At present, leading scientific institutes are developing and offering for industrial implementation various modifications of zeolite-containing catalysts for the implementation of the gas-phase process of benzene alkylation with propylene. Zeolites are highly selective, their use in the domestic petrochemical industry would eliminate the problem of harmful emissions and equipment corrosion. At the same time, such catalysts imply carrying out the process at sufficiently high temperatures (about 250–350ºC), as well as the presence of a regeneration stage, therefore, require high energy consumption. In addition, for the transition to zeolite-containing catalysts, a long time is required for the reconstruction of reactor blocks designed for liquid-phase alkylation [1--12].

Thus, today there is a need to solve the problem of increasing the efficiency of production of IPB on aluminum chloride, including using the modern method of mathematical modeling.

At the studied refinery, IPB serves as a raw material for production of not only phenol and acetone, but also of α-methylstyrene (*α-MS*), which in turn is used to produce alpha-methyl styrene rubber. In the shop for the production of *α-MS*, in the commercial product in the early 2000s, the so-called X-component was discovered, which is not separated at the rectification stage and leads to a decrease in the quality of *α-MS*.

For more than 10 years, research has been carried out in the plant laboratory to determine the composition of the X-component and to establish the reasons for its formation. By mass spectrometry, it was determined that the composition of the product mixture of the alkylation

reactor contains compounds such as indan and indene, presumably being X-components, the formation of which is most likely associated with the dehydrogenation reaction of n-propylbenzene (NPB), through the stage of formation of an unstable compound - beta-methylstyrene:



Thus, the reason for the formation of the X-component is n-propylbenzene, which is supplied to the production of *a-MS* together with the raw material - IPB; its content ranges from 0.1 to 0.2 wt%. with permissible limits not exceeding 0.05% wt. It is possible to achieve a decrease in the airbag content only by changing the operating mode of the alkylation reactor unit.

The purpose of this work was to determine the technological parameters of the alkylation reactor, providing a decrease in the concentration of n-propylbenzene in the product mixture by the method of mathematical modeling.

2. Experimental

The first stage of the work was the analysis of experimental data from an industrial plant for the production of isopropylbenzene in the presence of aluminum chloride during its operation in January - July 2019.

The alkylation reactor is a column-type apparatus, where reagents (PPF - propane-propylene fraction, DBC - dried benzene charge) and a catalyst complex (returnable and regenerated) are fed through the mixing chamber. The technological regime of the process is characterized by the temperature of the top and bottom of the reactor, pressure and consumption of raw materials and catalyst. The composition of the input stream to the alkylation reactor (alkylator) is shown in Table 1.

Table 1. Component composition of the alkylator input stream

Component	Concentration, wt%.
Propane-propylene fraction (PPF)	
Propane	2.03 – 11.00
Propylene	89.00 – 97.97
Dried benzene charge (DBC)	
Benzene	60.29 – 87.41
iso-propylbenzene	1.11 – 9.43
Hexene	1.67 – 3.98
Toluene	0.02 – 2.13
Ethylbenzene	0.1 – 1.56
Xylene	0.01 – 1.13
n-propylbenzene	0.01 – 0.13
3- butylbenzene	0.05 – 0.65
2- butylbenzene	0.13 – 1.06
p-cymene	0.08 – 1.36
n-butylbenzene	0.08 – 0.47
Polyalkylbenzenes (PAB)	6.54 – 24.19

The product mixture has the following mass composition: hexane (0.84-3.15), benzene (40.94-57.81), toluene (0.38-3.8), ethylbenzene (0.08-1.32), isopropylbenzene (26.27 - 39.00), n-propylbenzene (0.05 - 0.15), 3-butylbenzene (0.05 - 0.44), 2-butylbenzene (0.10 - 0, 65), cymene (0.15 - 0.75), n-butylbenzene (0.08 - 0.32), polyalkylbenzenes (PAB) (6.84 - 18.07), xylene (0.01 - 0.05), the residue (about 2.00).

The temperature of the top of the reactor in the period under consideration varied within the range from 115 to 124ºC depending on the temperature of the still to maintain the isothermal regime.Thus, the temperature drop across the reactor did not exceed 1.0-1.5ºC, the pressure in the system was maintained at the level of 0.11-0.19 MPa. With a decrease in the temperature in the reactor, a slight decrease in the content of n-propylbenzene was observed (Fig. 1), which is most likely explained by a decrease in the rate constant of the reaction for the formation of NPB from benzene and propylene.

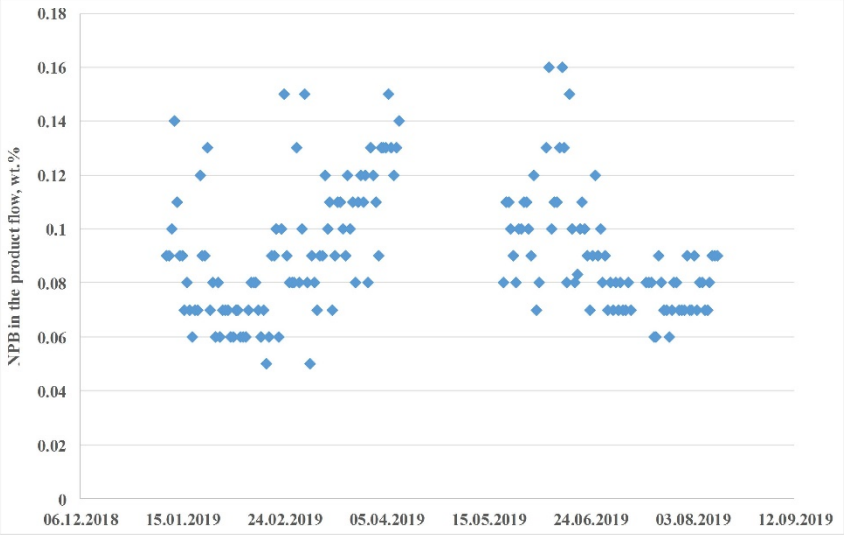


Figure 1. Change in the NPB content in the product during the plant operation in January – July 2019

At the moment, the alkylation reactor maintains low values of pressure and temperature (115 - 118 °C; 0.11 MPa), which makes it possible to achieve the lowest possible concentration of NPB. Along with the temperature of the process, the composition of the output stream is significantly influenced by the feedstock flowrate, which determines the contact time of liquid reagents and in an industrial alkylation unit varies from 1.28 to 3.12 h^{-1}.

The analysis of experimental data showed that the content of NPB decreases with a decrease in the molar ratio of benzene: propylene and the volumetric feed rate. The minimum concentration of NPB is 0.04 wt.% is achieved with a benzene: propylene ratio of 4: 1 (Fig. 2) and feedstock flowrate of 1.97 h^{-1}.

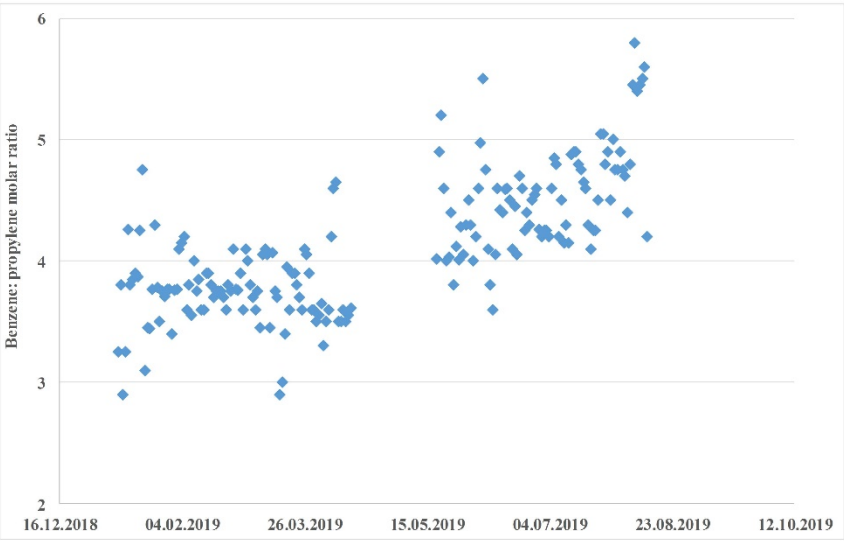


Figure 2. Change in the benzene: propylene molar ratio

The monitoring of industrial alkylation plant operation made it possible to extract information on those parameters that affect the airbag output. As shown by the analysis of experimental data, it is possible to achieve a decrease in the content of n-propylbenzene by lowering the temperature and pressure in the reactor, lowering the molar ratio of feed streams (DBC: PPF), as well as reducing the volumetric feed rate. In order to avoid significant material and time costs when searching for the optimal values of these parameters, we developed a mathematical model of the process, which requires only a computational experiment on a computer.

3. Mathematical modeling

Based on the analysis of the composition of the input stream into the reactor, a hydrocarbon conversion scheme was developed. The calculation and analysis of the thermodynamic functions of the main components, such as enthalpy, entropy and Gibbs energy for all reactions of the alkylation process, was carried out. In this work, to determine them, we used the ab initio quantum-chemical DFT method. The calculations were performed using the Gaussian 09W software package. The results of calculating the thermodynamic parameters for the main reactions of the alkylation process are shown in Table 2 (the parameters of the reactions of ethylene and propylene dimerization, benzene alkylation with the formation of ethylbenzene, butylbenzenes, cymene, xylene and toluene were determined in a similar way).

Table 2. Thermodynamic and kinetic characteristics of main reactions of the alkylation process (T=395 K, P=0.16 MPa)

Reaction	ΔH, kJ/mol	ΔS, kJ/mol·K	ΔG, , kJ/mol	DFT-determined kinetic parameters		The rate constants determined via solving the inverse kinetic problem, k_{fw}, m^3/mol·sec
				A_0, m^3/mol·sec	E_a, kJ/mol	
$C_6H_6 + C_3H_6 \leftrightarrows C_6H_5CH(CH_3)_2$	-71.00	-167.17	-4.97	$1.58\cdot10^5$	150.94	$3.94\cdot10^{-4}$
$C_6H_5CH(CH_3)_2 + C_3H_6 \leftrightarrows C_6H_4(CH(CH_3)_2)_2$	-70.39	-166.27	-4.71	$2.26\cdot10^5$	128.81	$1.09\cdot10^{-4}$
$C_6H_4(CH(CH_3)_2)_2 + C_6H_6 \leftrightarrows 2\ C_6H_5CH(CH_3)_2$	-0.62	-0.89	-0.26	$5.34\cdot10^4$	156.13	$3.05\cdot10^{-2}$
$C_6H_3(CH(CH_3)_2)_3 + C_6H_6 \leftrightarrows C_6H_4(CH(CH_3)_2)_2 + C_6H_5CH(CH_3)_2$	-62.79	138.10	-117.34	$1.01\cdot10^4$	154.71	$1.11\cdot10^{-2}$
$C_6H_6 + C_3H_6 \leftrightarrows C_6H_5C_3H_7$	-73.12	-162.59	-8.90	$1.28\cdot10^5$	130.41	$2.09\cdot10^{-5}$

The calculated values of the Gibbs energy made it possible to conclude that all reactions are reversible and proceed under the given conditions [13–17]. When developing a kinetic model, all reactions included in the transformation scheme were taken into account, and such components as diisopropylbenzene, triisopropylbenzene, diethylbenzene, triethylbenzene were combined into one group of pseudo-components with high molecular weights. Another reason for this was that in the experimental data under study there is no information on the content of these individual components, and they are presented as PAB. Butylbenzenes (BB) are also combined into one group, since the content of an individual component of the group in the output stream is insignificant. Combining the components into groups made it possible to simplify the mathematical description of a complex multicomponent process. A formalized scheme for the conversion of hydrocarbons during alkylation is shown in Fig. 3.

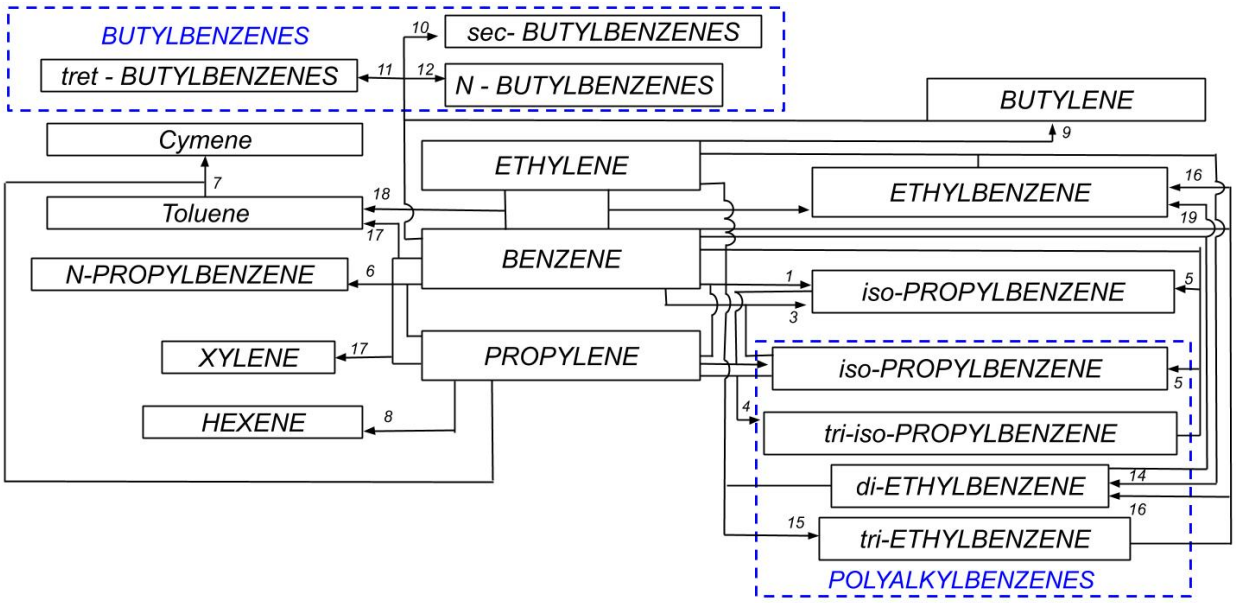


Figure 3. Formalized reaction network

The developed kinetic model of the benzene with propylene alkylation according to the formalized reaction network has the following form:

$$\begin{cases}
\frac{dC_{benzene}}{d\tau} = -W_1 + W_{-1} - W_3 + W_{-3} - W_5 + W_{-5} - W_6 + W_{-6} - W_{10} + W_{-10} - W_{11} + W_{-11} - W_{12} + W_{-12} - \\
-W_{13} + W_{-13} - W_{16} + W_{-16} - 2W_{17} + 2W_{-17} - 2W_{18} + 2W_{-18} - W_{19} + W_{-19}; \\
\frac{dC_{propylene}}{d\tau} = -W_1 + W_{-1} - W_2 + W_{-2} - W_4 + W_{-4} - W_6 + W_{-6} - W_7 + W_{-7} - 2W_8 + 2W_{-8} - W_{17} + W_{-17}; \\
\frac{dC_{IPB}}{d\tau} = W_1 - W_{-1} - W_2 + W_{-2} + 2W_3 - 2W_{-3} + W_5 - W_{-5}; \\
\frac{dC_{NPB}}{d\tau} = W_6 - W_{-6}; \\
\frac{dC_{toluene}}{d\tau} = -W_7 + W_{-7} + W_{17} - W_{-17} + 2W_{18} - 2W_{-18}; \\
\frac{dC_{cymene}}{d\tau} = W_7 - W_{-7}; \\
\frac{dC_{hexene}}{d\tau} = W_8 - W_{-8}; \\
\frac{dC_{ethylene}}{d\tau} = -2W_9 + 2W_{-9} - W_{13} + W_{-13} - W_{14} + W_{-14} - W_{15} + W_{-15} - W_{18} + W_{-18}; \\
\frac{dC_{butylene}}{d\tau} = W_9 - W_{-9} - W_{10} + W_{-10} - W_{11} + W_{-11} - W_{12} + W_{-12}; \\
\frac{dC_{ethylbenzene}}{d\tau} = W_{13} - W_{-13} - W_{14} + W_{-14} + W_{16} - W_{-16} + 2W_{19} - 2W_{-19}; \\
\frac{dC_{xylene}}{d\tau} = W_{17} - W_{-17}; \\
\frac{dC_{PAB}}{d\tau} = W_2 - W_{-2} - W_3 + W_{-3} + W_{14} - W_{-14} - W_{19} + W_{-19}; \\
\frac{dC_{BB}}{d\tau} = W_{10} - W_{-10} + W_{11} - W_{-11} + W_{12} - W_{-12};
\end{cases}$$

Initial conditions: $at\ \tau = 0 \quad C_i(0) = C_{i,0}$, where *i* – corresponding hydrocarbon.

Here: W_i and W_{-i} – forward and reverse reaction rates, mol/(m^3·sec).

Thus, the equations of reaction rates for the formation of isopropylbenzene and n-propylbenzene were drawn up according to the law of effective masses:

$$W_{IPB} = k_{0(1)} \cdot e^{-\frac{Ea(1)}{RT}} \cdot C_{benzene} \cdot C_{propylene} + k_{0(2)} \cdot e^{-\frac{Ea(2)}{RT}} \cdot C_{benzene} \cdot C_{diisopropylbenzene} + +k_{0(3)} \cdot e^{-Ea(3)/RT} \cdot C_{diisopropylbenzene};$$

$$W_{NPB} = k_{0(4)} \cdot e^{-Ea(4)/RT} \cdot C_{benzene} \cdot C_{propylene};$$

where: W_n – rate of the n-th reaction, mol/(m^3·sec); k_i – n-th reaction rate constant; E_{ai} – activation energy of the n-th reaction, J/mol; R – universal gas constant, J/(mol·K); T – temperature, K; C_i – concentration of the i-th component, mol/m^3. Expressions for the rates of reactions with the participation of other components were composed in a similar way.

The resulting kinetic model is formalized and quasi-homogeneous. The kinetic parameters were determined by solving the inverse kinetic problem based on experimental data obtained from an industrial alkylation plant, while the initial approximation was chosen based on the results of quantum chemical simulation of reactions and determination of the thermodynamic parameters of the transition state of intermediate stages. The activation energy and the preexponential factor in the Arrhenius equation were determined on the basis of the theory of absolute rates of chemical reactions (the theory of the transition state). The kinetic parameters of the main reactions of the alkylation process, determined when solving the inverse kinetic problem, as well as the values of the preexponential factor and activation energies, selected as initial approximations, are given in Table 2.

The calculated values of the components concentrations of the alkylation reactor product mixture were compared with the experimental data from the industrial plant during the period of its stable operation (January - July 2019), and the calculation error did not exceed 7.5% (Fig. 4). The developed model was programmatically implemented in the Borland Delphi 7 programming language.

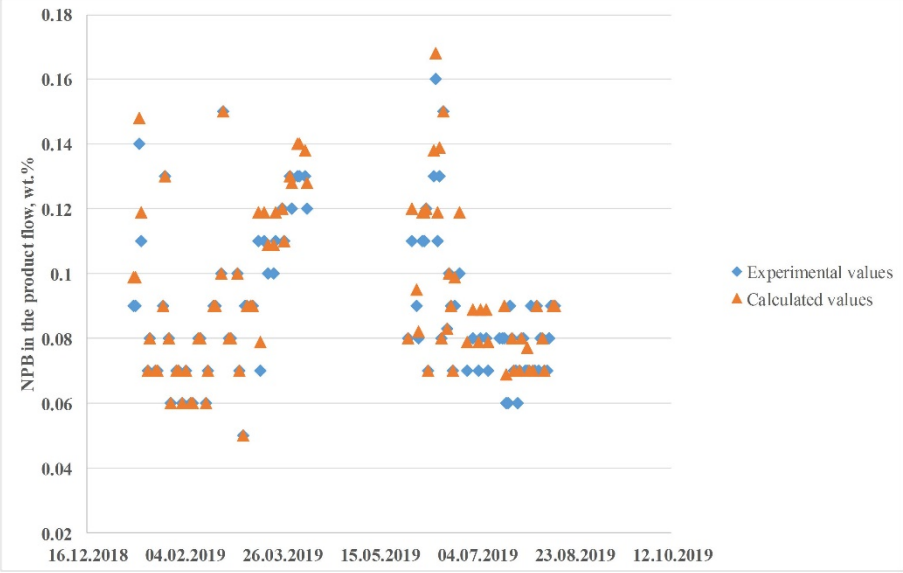


Figure 4. Comparison of calculated and experimental data on the NPB content in the product mixture

Using the developed program, calculations were carried out on the effect of temperature, the benzene: propylene molar ratio, and the volumetric feed rate of the raw material on the NPB content. The calculation was carried out for the mass composition of the feed mixture of the alkylation reactor on July 2, 2019: benzene (81.01), hexane (3.79), toluene (0.97) ethylbenzene (1.04), isopropylbenzene (6.75), n-propylbenzene (0.02), butylbenzenes (0.25), cymene (0.08), polyalkylbenzenes (PAB) (6.09), residue (2). The NPB concentration was 0.13% by weight. Flow rates: PPF - 2.1 t/h, DBC - 20 t/h, catalyst complex - 11.36 t/h.

4. Results and discussion

Carrying out a numerical experiment on a model with varying temperature and the benzene: propylene ratio (Fig. 5), made it possible to achieve the minimum value of the NPB content (0.08 wt%) with a minimum ratio of 2.5: 1 and the temperature in the reactor (115°C).

Further, at a constant benzene: propylene ratio equal to 2.5: 1, studies were carried out on the effect of temperature and feedstock flowrate on the concentration of NPB in the product mixture of the alkylation reactor (Fig. 6).

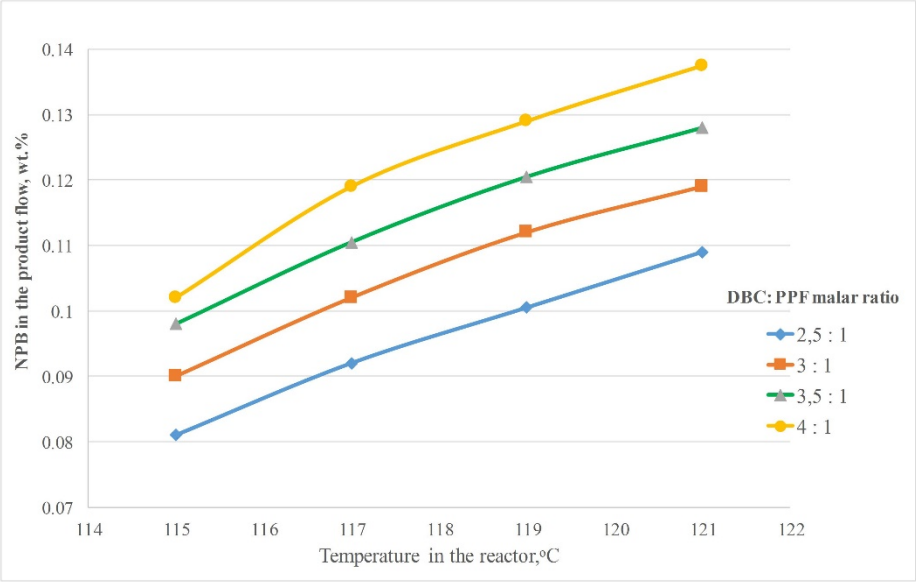


Figure 5. Content of NPB depending on temperature and molar ratio of reagents

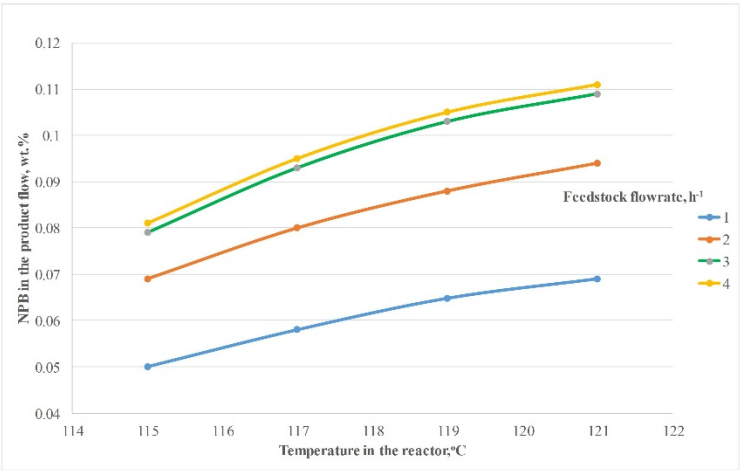


Figure 6. Content of NPB depending on temperature and feedstock flowrate

The minimum content of n-propylbenzene (0.05 wt.%) for a given selected feedstock composition is achieved at a low feedstock flowrate (1 h^{-1}), low temperature (114-115°C), and a minimum benzene: propylene molar ratio of 2. 5: 1. To determine the conditions for carrying out the alkylation process, ensuring the maintenance of the required value of NPB concentration (less than 0.05 wt.%), as well as the maximum value of the IPB concentration during the processing of raw materials of various compositions, in the future, methods of multidimensional optimization will be applied, considering simultaneous influence of all technological parameters on the operation alkylation reactor.

5. Conclusions

The monitoring of the benzene with propylene alkylation unit operation was carried out and the technological parameters influencing the content of n-propylbenzene, as the main undesirable component of raw materials for the production of α-methylstyrene, were revealed.

A mathematical model of the alkylation process has been developed and, on its basis, a computer modeling system "Alkylation" in the Borland Delphi 7 environment, which allows calculating the composition of the product flow when the most important technological parameters of the reactor change (temperature, benzene: propylene molar ratio, feedstock flowrate).

Using the developed model, the conditions were determined that ensure the minimum possible value of the concentration of n-propylbenzene in the product mixture of the alkylation reactor during processing of this type of feedstock.

The developed model, supplemented by an optimization function, will be used in the future to conduct a numerical experiment to determine the technological parameters of the alkylation reactor, which ensure the maintenance of the required value of the NPB concentration (0.05 wt%), as well as the maximum value of IPB concentration during various raw materials processing.

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