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Increasing the efficiency of liquid phase alkylation of benzene with propylene using the method of mathematical modeling

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Abstract

In this study the existing problems of liquid-phase alkylation of benzene with propylene problems are indicated. The paper describes the stages alkylation of benzene with propylene mathematical model development. The model allows to define the composition of the product stream under changing of plant process parameters: temperature, benzene/propylene molar ratio and feed space velocity. The error of the model does not exceed 7.5%. «Alkylation» computer modeling system is developed in Borland Delphi 7 and the optimization module of the process parameters is called «Optimization». In Aspen HYSYS the technological scheme of rectification products alkylation of benzene with propylene using aluminum chloride catalyst was developed. Integration of computer models allowed to determine the technological modes of production, providing isopropylbenzene outlet with higher quality.

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Keywords: alkylation; benzene; propylene; isopropylbenzene; mathematical modeling.

1. Introduction

The most important petrochemical products are alkylates [1-3]. In the Russian Federation, liquid catalytic systems are usually used. The use of such catalysts leads to equipment corrosion and formation of significant quantities of environmentally hazardous and difficulty recyclable drains. However, the change of existing

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production on the modern solid catalysts [4-5] requires the radical plants reconstruction, which is characterized by long production downtime.

Today there is an acute problem for alkylate production as an efficiency increasing of existing facilities corresponded to strict standards of ecological safety. The problem of chemical-technological systems optimization in general is successfully solved using the mathematical modeling method.

One of the productions for which the solution of multi-factor problem is desirable is the production of isopropylbenzene (cumene). Currently, existing mathematical models of isopropylbenzene production cannot solve the problem of efficiency increasing for the operating plant. Presently, the evidence-based approach for the optimization of alkylation production that uses toxic and corrosive catalyst was proposed. Thus, the purpose of this study is to improve the efficiency of liquid-phase alkylation of benzene with propylene by the process optimum conditions ensuring with the use of mathematical modeling.

To achieve this goal the following tasks were solved:

1. The development, software implementation and verification of mathematical model adequacy of liquid phase alkylation of benzene with propylene.
2. Determination of reactor optimum technological modes that depend on the feedstock composition for the isopropylbenzene production corresponded to premium quality requirements.
3. Development of optimal scheme of process streams direction for the fractionation products block in liquid phase alkylation of benzene with propylene to create the conditions for a clearer alkylation products separation.

2. Object of research

Technological installation scheme of isopropylbenzene (cumene) production consists of six process units: the preparation of catalytic complex; catalytic column reactor; catalyst decomposition and catalytic complex washer; benzene trapping from absorption gases and their neutralization; benzene azeotropic drying units and rectification of product separation.

Process conditions are characterized by the top and bottom reactor temperature, pressure, raw and catalyst flows: $T = 100 - 130^{\circ}\text{C}$; $P = 0.11 - 0.19 \text{ atm.}$; benzene/propylene molar ratio: $2.5/1 \div 4/1$; feed space velocity: 5.1 h^{-1} .

The input raw flow in the alkylator has the following composition, % wt.: propane-propylene fraction (PPF) (propane 2.03 – 11; propylene 89.00 – 97.97); dried benzene containing fraction (DBF) (60.29 benzene – 87.41; IPB 1.11 – 9.43; hexene 1.67 – 3.98; toluene 0.02 – 2.13; ethylbenzene (EB) 0.1 – 1.56; xylene 0.01 – 1.13; n-propylbenzene (NPB) 0.01 – 0.13; 3-butylbenzene (3-BB) 0.05 – 0.65; 2-butylbenzene (2-BB) 0.13 – 1.06; cymene 0.08 – 1.36; n-butylbenzene (NBB) 0.08 – 0.47; polyalkylbenzene (PAB) 6.54 – of 24.19). The reaction mass of alkylation reactor (RMA) has the following composition, % wt.: hexane 0.84 – 3.15; benzene 40.94 – 57.81; IPB 26.27 – 39; toluene 0.38 – 3.8; EB 0.08 – 1.32; xylene 0.01 – 1.13; NPB 0.05 – 0.15; 3-BB 0.05 – 0.44; 2-BB 0.1 – 0.65; cymene 0.15 – 0.75; n-BB 0.08 – 0.32; PAB 6.84 – 18.07; xylene 0.01 – 0.05; the rest - 2.0.

The mechanism of the target alkylation reaction includes four stages [6]. The first stage is the reaction of propylene with hydrogen chloride resulting propyl formation and easily dissociates into ions. The second stage is the formation of carbocation. And the third stage is the electrophilic benzene attack by carbocation and intermediate or σ -complex with a high energy value formation. This stage is limited. The last stage involves hydrogen elimination from the intermediate, catalyst recovery and product formation.

3. Research methods

To evaluate the thermodynamic possibility of reactions quantum chemistry methods [7-9] were used.

Numerical studies were carried out with the use of density method of functional theory (DFT) at the B3LYP level. 6-31 ++ G (d, p) parameters were chosen in such a way to keep the controllability of calculations and do not reduce the accuracy of physical description. As a result, the basis set has been selected. The above reactions proceed in a liquid phase, so it is necessary to include the effect of solvation. For this model the limiting Thomas polarization (polarized continuum model (C-PCM)) has been used. It defines a cavity (space) as a combination of blocked atomic spheres series. The benzene solvent was chosen because benzene to propylene ratio in industry is at 3 - 10:1.

The first stage was carried out by optimization of molecular electronic structures of products and reactants at each stage for each of considered reactions, and vibrational frequencies are calculated, as well as enthalpy, entropy and Gibbs energy of benzene with propylene alkylation reactions in industry conditions.

Using features in Gaussian 09W software it became possible to examine the mechanism of reaction process as a series of successive stages and determination of limited one. It was also possible to relate thermodynamic functions and kinetic parameters from the transition state characteristics of the activated complex.

Thermodynamic parameters were determined for each transition state of considered reactions.

As a result of numerical studies the initial approximations were obtained. These approximations are used to solve the inverse kinetic problem and to determine the kinetic parameters of the target and side reactions in alkylation of benzene with propylene in the presence of aluminum chloride. Then they have been clarified by comparing the defined results with the experimental installation data.

Mathematical model development of alkylator includes the steps of material and heat balances equations generating according to the hierarchical principle of chemical processes modeling [10-11].

For the software implementation of the mathematical model equations *Borland Delphi 7* programming language was used.

The methods of multi-dimensional optimization considering the simultaneous influence of all technological parameters on reactor operation are applied to definite the conditions for alkylation process carrying out that provide the maintenance of desired concentration values of EB, n-propylbenzene and butylbenzene, and also the maximal concentration value of isopropylbenzene during various structure raw processing. In this case the scheme of optimization was based on parameter choice from N – parameters from a to b range, where b – is the optimum parameter. The offered algorithm includes determination of such N – parameters combinations as at which each of them as much as possible approaches b , but does not exceed the limit of a - b range [12-13].

4. Results and discussion

Results of defined thermodynamical parameters for the main reactions in alkylation process under industrial conditions are presented in Table 1.

Table 1. The calculated thermodynamic characteristics of benzene with propylene alkylation (T = 395 K, P = 1.6 atm.)

Reaction	ΔH , kJ/mol	ΔS , J/mol·K	ΔG , kJ/mol
$C_6H_6 + C_3H_6 \rightarrow C_6H_5CH(CH_3)_2$	-71.00	-167.17	-4.97
$C_6H_5CH(CH_3)_2 + C_3H_6 \rightarrow C_6H_4(CH(CH_3)_2)_2$	-70.39	-166.27	-4.71
$C_6H_4(CH(CH_3)_2)_2 + C_6H_6 \rightarrow 2$ $C_6H_5CH(CH_3)_2$	-0.62	-0.89	-0.26
$C_6H_4(CH(CH_3)_2)_2 + C_3H_6 \rightarrow$ $C_6H_3(CH(CH_3)_2)_3$	-8.21	-305.27	112.37
$C_6H_3(CH(CH_3)_2)_3 + C_6H_6 \rightarrow$ $C_6H_4(CH(CH_3)_2)_2 + C_6H_5CH(CH_3)_2$	-62.79	138.10	-117.34
$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$	-73.12	-162.59	-8.90
$C_6H_5CH_3 + C_3H_6 \rightarrow C_6H_4CH_2CH(CH_3)_2$	-70.35	-163.61	-5.73
$2 C_3H_6 \rightarrow C_6H_{12}$	-77.33	-166.38	-11.61
$2 C_2H_4 \rightarrow CH_2=CH-C_2H_5$	-93.54	-136.91	-39.46
$2 C_2H_4 \rightarrow CH_3-CH=CH-CH_3$	-107.23	-157.22	-45.12
$2 C_2H_4 \rightarrow CH_2=C(CH_3)_2$	-109.25	-142.66	-52.90
$C_6H_6 + CH_3-CH=CH-CH_3 \rightarrow$ $C_6H_5CHCH_3C_2H_5$	-67.98	-167.10	-1.98
$C_6H_6 + CH_2=C(CH_3)_2 \rightarrow C_6H_5C(CH_3)_3$	-48.13	-173.30	20.33
$C_6H_6 + CH_2=CH-C_2H_5 \rightarrow C_6H_5C_4H_9$	-74.28	-155.80	-12.74
$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$	-87.76	-148.48	-29.11
$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2$	-87.10	-147.93	-28.66
$C_6H_4(C_2H_5)_2 + C_2H_4 \rightarrow C_6H_3(C_2H_5)_3$	-75.16	-153.25	-14.63
$C_6H_6 + C_6H_3(C_2H_5)_3 \rightarrow C_6H_4(C_2H_5)_2 + C_6H_5C_2H_5$	-12.59	4.77	-14.48

$2 C_6H_6 + C_3H_6 \rightarrow C_6H_5CH_3 + C_6H_4(CH_3)_2$	-93.63	203.51	-174.02
$2 C_6H_6 + C_2H_4 \rightarrow 2 C_6H_5CH_3$	-99.68	185.17	-172.82
$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2 C_6H_5C_2H_5$	-0.66	-0.55	-0.44

The list of reactions was compiled on the basis of literature data [14], as well as component composition data of input and output alkylate streams obtained according to monitoring.

To assess the adequacy of defined thermodynamic parameters they were compared to the reference. So for the target alkylation reaction: $C_6H_6 + C_3H_6 \rightarrow C_6H_5CH(CH_3)_2$ the reference thermodynamic parameters at $T=400$ K and $P=1$ atm: $\Delta H = -98.65$ kJ / mol, $\Delta S = -155.42$ J / (mol*K) and $\Delta G = -21.21$ kJ / mol.

Calculated with the use of quantum chemistry methods thermodynamic parameters of alkylation reaction are different from the reference data. It must be noted that an actual process conditions differ from the conditions that describe the state of an ideal gas. So it is necessary to determine the thermodynamic characteristics of the main alkylation reactions with the use of quantum chemistry methods.

The calculated results showed that all considered reactions are reversible, except the formation of triisopropylbenzene ($\Delta G = 112.37$ kJ / mol), transalkylation of triisopropylbenzene in isopropylbenzene and diisopropylbenzene ($\Delta G = -117.34$ kJ / mol), xylene, toluene obtaining ($\Delta G = -174.02$ kJ / mol), alkylation of benzene with propylene to form two molecules of toluene ($\Delta G = -172.82$ kJ / mol).

Based on the thermodynamic probability of reactions in alkylation target and side reactions were identified. Formalized scheme of substances transformations was developed (Fig. 1). The kinetic model takes into account all reactions and for the simplification of mathematical description [15] such components as: diisopropylbenzene, triisopropylbenzene, diethylbenzene, triethylbenzene are combined into one PAB (polyalkylbenzenes) group with high molecular weight. The combining into one group of butylbenzenes (BB) is justified by common chemical structure (isomers principle), and based on particular component structure and that the component content of group is negligible at the outlet.

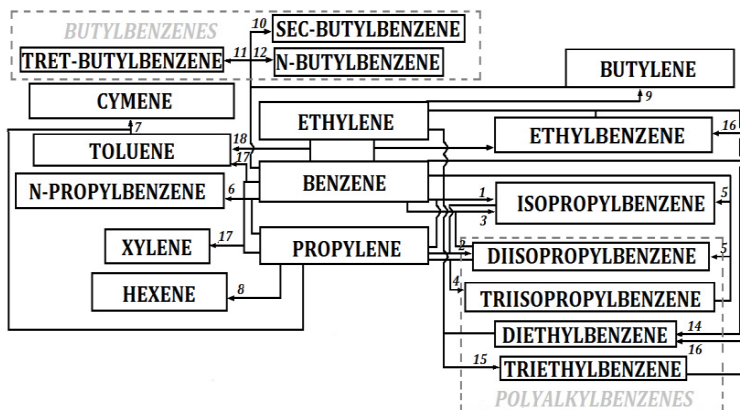


Fig. 1. Formalized scheme of reaction substances

The equations of chemical reaction rates for each component were drawn up according to the law of mass action while taking into account the assumption of quasi-homogeneous kinetic alkylation model. The initial conditions: $\tau = 0, C_i = C_{0i}$, where i - corresponded hydrocarbon, C_i - concentration of i -substance, mol / m³). The next kinetic equation describes the rate of IPB formation:

$$\begin{aligned} \frac{dC_{IPB}}{dt} = & k_1 \times C_B \times C_P + k_1 \times C_B \times C_{DIIPB} + k_1 \times C_{DIIPB} \times C_B \times C_P + k_1 \times C_B \times C_P + k_1 \times C_B \times C_{DIIPB} + k_1 \times C_{DIIPB} \\ & k_2 \times C_{IPB} \times C_P + k_2 \times C_{IPB}^2 + k_2 \times C_{TIIPB} + k_2 \times C_{IPB} \times C_P + k_2 \times C_{IPB}^2 + k_2 \times C_{IPB} + 2k_3 \times C_{DIIPB} \times C_P \\ & + 2k_3 \times C_{DIIPB} \times C_P + k_5 \times C_T \times C_P + k_5 \times C_T \times C_P \end{aligned} \quad (1)$$

where B - benzene; P - propylene; DIIPB - diisopropylbenzene; TIIPB - triisopropylbenzene; T - toluene, k_j - rate constant of j - reaction.

Kinetic model of transformation for other components was developed similar.

The obtained kinetic model is formalized and quasi-homogeneous and rate constants k_j are effective, i.e. are a combination of constants at all intermediate stages. The determination of kinetic parameters was carried out by solving of inverse kinetic problem on the basis of experimental data obtained from industrial alkylation installation.

It was determined that the alkylation reaction has the lowest activation energy compared to transalkylation reaction (for alkylation activation energy equals 150.94 kJ/mol and pre-exponential factor of the Arrhenius equation equals $1.58 \cdot 10^5 \text{ s}^{-1}$ and for transalkylation alkylation activation energy equals 156.13 kJ/mol and pre-exponential factor of the Arrhenius equation equals $5.34 \cdot 10^4 \text{ s}^{-1}$, respectively) [16]. Calculations have shown that the rate of transalkylation is significantly reduced with a gradual catalyst deactivation. As a result, PAB accumulates in the reaction mixture and cannot be transalkylated. To avoid this, it is important to restrict the reactants flow and the possibility of process intensification is limited by the slow transalkylation reaction. It is shown that secondary reactions of transalkylation that formed di - and trisopropylbenzene at the previous stages have the greatest contribution to the main product yield (isopropylbenzene). The defined constants of the main process reactions are given in Table 2.

The rate constants values of isopropylbenzene polyalkylbenzenes formations [14] as well as transalkylation polyalkylbenzenes formations are in the range of $(1.09 - 3.54) \cdot 10^{-4} \text{ s}^{-1}$, and show that the target reaction rate for this process is several orders higher than rates of side reactions ($2.09 \cdot 10^{-6} \text{ s}^{-1}$ to $1.65 \cdot 10^{-10} \text{ s}^{-1}$).

These kinetic parameters were used as a basis for the development of mathematical model [17], which will allow to predict the quality of alkylate, depending on raw composition, temperature regime of the process and contact time of reactants in reactor. The mathematical description of the considered process in the reactor comprises both kinetic and hydrodynamic parts.

Taking an assumption of plug flow model applicability, taking into account the structural features of alkylation reactor, kinetic equation models were supplemented by the hydrodynamic component. This assumption has been proved by the diffusion Peclet number evaluation. The value of thermal Peclet criterion $Pe_T = 8693.4$. The value of Reynolds number $Re = 7936.1$. According to the literature data the relationship between diffusion (PeD) and thermal criteria Peclet is 1.05-1.5. Consequently, PeD ranges from 9128.0 to 13040.0. Since $Pe_D \geq 200$, and $Pe_T \geq 1$ the hypothesis that in the reactor hydrodynamic mode is close to the ideal displacement is confirmed.

Therefore, for the i -substance the material balance equation:

$$\frac{dC_i}{dt} = u \frac{dC_i}{dl} \pm W_i \quad (2)$$

where u - linear flow rate; W_i - reaction rate of i -component; C_i - concentration of i -component; t - time; l - length of reactor [17].

Mathematical model of the steady state is given by (3):

$$\frac{dC_i}{d\tau} = W_i \quad (3)$$

where τ - residence time of reagents in the reaction zone and equal to contact time.

Overall material balance alkylation reactor is as follows (4):

$$G_{DBF} + G_{PPF} + G_{FCC} + G_{RCC} + G_{recycled\ benzene} = G_{ARM} + G_{waste\ gas} \quad (4)$$

where DBF - dry benzene fraction; PPF - Propane-propylene fraction; FCC - fresh catalyst complex; RCC - recycled catalyst complex; ARM - alkylation reaction mass.

The reactor is adiabatic, the heat balance equation is written as follows (5):

$$\rho^{mix} C_p^{mix} \frac{\partial T}{\partial \tau} = \pm \sum_{j=1}^N (-\Delta H_j) \cdot W_j, \quad (5)$$

where W_j - the velocity of j - chemical reaction; ΔH_j - thermal effect of j - chemical reaction, kJ / mol; C_p^{mix} - molar heat capacity of reaction mixture, J / (mol*K); ρ^{mix} - density of reaction mixture, kg / m³; T - temperature, K; N - number of reactions.

Table 2. Comparison of calculated and experimental data

Date	IPB output, kg/h		Δ , %	PAB output, kg/h		Δ^* , %
	Calc.	Exp.		Calc.	Exp.	
Jun.13	5774.0	5398.7	6.5	1752.0	1642.5	6.25
Jul.13	5003.1	4683.9	6.38	1162.8	1091.5	6.13
Aug.13	5419.6	5134.5	5.26	1698.3	1613.2	5.01
Sep.13	5848.2	5544.1	5.2	2190.7	2082.3	4.95
Oct.13	6281.2	6026.8	4.0	2165.8	2083.5	3.8
Nov.13	5408.0	5056.5	6.5	1582.0	1483.1	6.25
Dec.13	5704.2	5339.1	6.4	2270.8	2131.2	6.15
Jan.14	6985.0	6558.9	6.1	2563.0	2413.1	5.85
Feb.14	6186.6	5853.8	5.38	2173.5	2062.0	5.13

*Here Δ is the error of calculation, %.

The developed mathematical model was complemented by a mathematical function of optimization, that ensure strict adherence to the side components of alkylation reaction mass: n-propylbenzene (NPB), ethylbenzene (EB) and butylbenzenes (BB) (not more than 0.05, 0.02 and 0.05% wt., respectively). Error in mathematical model calculations for the main components (Table 2), such as IPB and PAB does not exceed 7%, which is comparable with error in method of gas chromatography (maximum 10%). Therefore, it was concluded that the model is adequate and is suitable for a variety of technological calculations.

It was found that the optimum values of productivity and catalyst consumption in isopropylbenzene production can be achieved at $T \approx 120-130$ °C when the transalkylation proceeds at high speed, and the concentration of polycyclic compounds that deactivate the catalyst is still small. It is shown that the optimum catalyst flow rate will be such type that will provide not only high-speed of target alkylation of benzene with propylene reaction but also transalkylation reaction rate of PAB, which contributes significantly to the IPB formation. Using the developed optimization module the flow of complex catalyst was determined in which isopropylbenzene increases the yield and reduces the amount of undesirable components - PAB.

The concentration of isopropylbenzene in the reaction mass of alkylation reactor by optimization is increased by 1 000 - 1 500 kg/h. The yield of PAB reducing the selectivity is decreased by 200-700 kg/h. It was defined to achieve high selectivity of the process (concentration of IPB equals 99.99% wt.) the output of PAB should be equal 7-10 % of the product mixture volume (not more than 1 500 kg/h at cumene yield equaled 6 000 kg/h) for transalkylation reactions.

Forecast calculations for each set of independent variables were made using the developed model. From different options of calculation a mode that satisfies the optimality criteria has been defined. According to this criteria: the maximum of IPB output is not less than 30 wt. %; minimum output NPB not more than 0.05% wt.; EB minimum yield is not more than 0.02% wt.; BB minimum yield is not more than 0.05% wt.

The first criterion is responsible for the yield, the following three - for the quality of the product. The optimum technological mode is that in which these criteria will be carried out.

It was proposed to change the alkylation reactor product separation order by successive separation in columns K-22/1 and K-22/2 (Fig. 2).

For the preliminary conclusion about the effectiveness of the flowing direction changing a computer model of the technological scheme of the reactor products separation in alkylation process using aluminum chloride catalyst was developed in *Aspen HYSYS*.

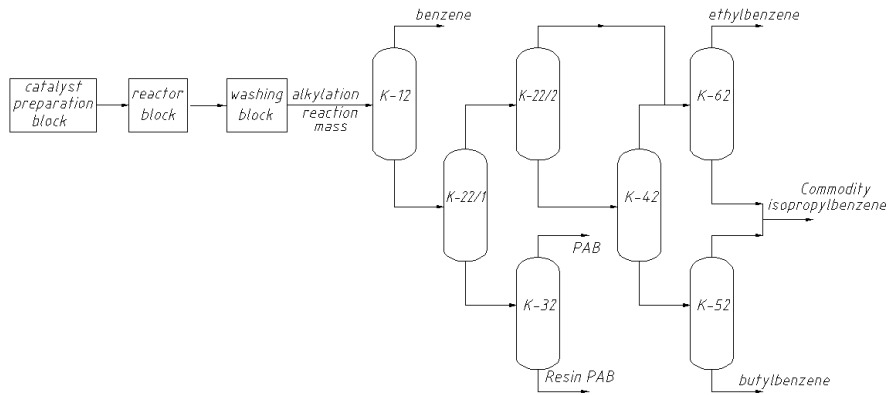


Fig. 2. Simplified flow scheme on IPB production using chloride aluminum catalyst. Where ARM - alkylation reaction mass, EB - ethylbenzene, PAB - polyalkylbenzenes, BB – butylbenzene, IPB commercial isopropylbenzene.

The accuracy of concentration calculations for the main components with the use of mathematical models does not exceed 10%, which let to conclude that the model is adequate and suitable for the use in process determination, for example to simulate device operations during the technological scheme of separation unit changing.

As a result the values of technological parameters of the devices were obtained. These values provide more effective products separation in distillation unit for IPB production and allow to succeed IPB quality according to superior quality of TU 38.402-62-140-92 and requirements of consumers in the amount of 7 840 kg / h.

However, achieving a superior quality of commercial product is not possible with a high content of undesirable components in reaction alkylation mass, such as NPB. Due to proximity of IPB and NPB boiling temperatures it is difficult to separate them at the rectification stage, so it is necessary to optimize the operating mode of alkylation reactor, providing a minimum output of secondary components.

Therefore, the next stage of this work was an implementation of mathematical model of the reactor alkylation in *Aspen HYSYS*.

Combined mathematical model of IPB production integrated with module in *Aspen HYSYS* provided the performance of alkylation reactor determination in conjunction with modified products separation unit and the determination of such unit modes that will provide minimum side components outlet corresponded to the highest grade of IPB, suitable for the production of not only phenol and acetone but also a-methylstyrene (a-MS) which is an intermediate for a-methylstyrene rubber production. It is shown that possible cause of quality deterioration in products obtained from IPB is NPB formation. NPB is used for the production of a-MS with the feed, the content of which ranges from 0.1 to 0.2% wt. under acceptable range that do not exceed 0.05% wt.

Reducing the content of NPB is only possible by changing the technological mode of alkylation reactor operation unit. The minimum content of NPB (0.05 % wt.) for a given composition of raw is achieved at high feed space velocity (4 h^{-1}) and low temperature (114-115°C) and the minimum molar ratio of benzene:propylene (2.5:1) [18]. This mode in the reactor is taken to be optimal.

At such reactor modes IPB was obtained (10 750 kg/h), the structures of process streams given in Table 3.

Table 3. Structures of process streams for commercial IPB production

Component name	Concentration in ARM, % wt.	Concentration in commercial IPB, % wt.
Hexane	0.0002	-
Benzene	40.2681	-
IPB	34.7440	99.9395
Toluene	0.0072	-
Ethylbenzene	1.6300	0.0267
NPB	0.0047	0.0222
BB	0.0210	0.0117
PAB	23.3160	-
Propane	0.0100	-

The calculations showed that in IPB production block under required parameters of technological modes of the reactor and distillation columns commercial IPB can be obtained up to 99.94% wt. (10 750 kg / h).

5. Conclusion

1. The mathematical model alkylation of benzene with propylene (model error does not exceed 7%) allows to quantify the conversion rate of hydrocarbons in a wide range of reactor temperature change from 110 °C to 137 °C, feed space velocity from 2.0 to 4.0 h⁻¹, and the raw material composition (molar ratio of benzene:propylene is from 2.5:1 to 7:1).

2. Cumene concentration in the product mixture reaches 34.5 wt.% instead of 27-30% wt. when the temperature decreases from 128-132 °C to 114-115 °C, the molar ratio of benzene:propylene is from 7:1 to 2.5:1 and increasing of feed space velocity from 2.5-3.0 h⁻¹ to 4.0 h⁻¹. At this mode the recommended minimum polyalkylbenzenes concentration is reached (8.65 %wt.).

3. The proposed variant of technological changes in separation sequence in the product distillation block provides an incensement of isopropylbenzene concentration up to 99.9% by weight. The integration of implemented mathematical model of alkylation reactor with a computer model of separation unit in *Aspen HYSYS* provides determination of technological process modes for isopropylbenzene production units that are required for high quality production (99.94% wt.) without loss of output.

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