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INCREASE OF EFFICIENCY ISOPROPYLBENZENE MANUFACTURING WITH USE OF INTEGRATED MATHEMATICAL MODELS

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Abstract

A mathematical model of isopropyl benzene obtaining reactor process on chloroaluminum catalyst was developed. With use of HYSYS software a computer model of benzene with propylene alkylation technological scheme was created. Integration of computer models allowed carrying out calculations to determine technological modes of production, allowing to obtain a marketable product of higher quality. It was shown that increasing of isopropylbenzene concentration in commercial product to 99.9% by weight can be achieved by implementing of sequence separation in distillation columns due to redistribution of ethylbenzene and n-butyl benzene loads.

Keywords: alkylation; isopropylbenzene; mathematical modeling; rectification.

1. Introduction

Isopropylbenzene (IPB) or cumene production is among the five most large-scale production of the world, along with the production of ethylene, propylene, benzene and ethylbenzene [1-2]. However, about 10% is used for production of α-methylstyrene, a main component α-methyl-styrene rubbers, and the resulting 90% of IPB - for production of phenol and acetone [3-4]. The largest enterprise-phenol and acetone by cumene technology in Russia are "Ufaorgsintez", "Kazanorgsintez", "Samaraorgsintez and" Omsk rubber "with a total capacity of phenol to 250 thousand tons per year [5-6].

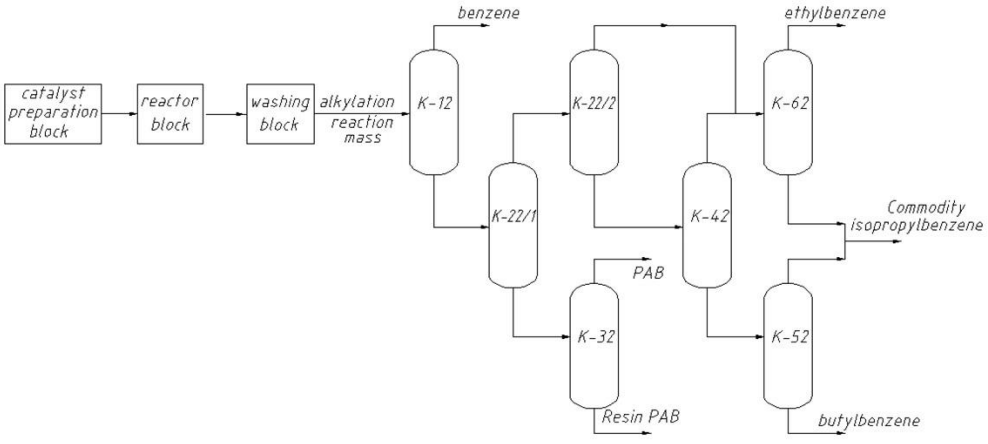

Figure 1. Simplified flow diagram of IBP production on chloroaluminum catalyst

At the moment, trade IPB of PJSC "Omsk rubber" contains 99.7% by weight of target component. IPB production is not working at full capacity, and IBP is only used as a raw

material for production of alpha-methyl styrene (a-MS). In order to use the full capacity of production it was decided to implement IPB as an independent commercial premium product with target component content of not less than 99.9% by weight.

One of the possible ways to increase IPB concentration in commercial product is "rema-nifolding" of K-22 / 1.2 columns. According to a scheduled scheme column K-22/1 and K-22/2 of distillation unit are working in parallel [7]. According to the proposed scheme, K-22/1 and K-22/2 are operated in series (fig. 1). As a tool of rectification scheme reconstruction results prediction mathematical modeling method was chosen. Thus, the aim of this work is to improve the efficiency of IPB production on chloroaluminum catalyst with use of mathematical modeling method.

2. Experimental

2.1. Development of computer model of benzene with propylene alkylation on chloroaluminum catalyst process products separation block with use of HYSYS software

HYSYS program is a reliable tool for technological calculation of mass transfer separation processes. The basis of all technological calculations is known techniques, based on the basic laws of chemical thermodynamics and phase equilibrium. "Built-in" properties calculation packages provide reliable results of calculations of hydrocarbon mixtures and non-hydrocarbon fluids used in the petrochemical and chemical industry [8].

Using scheduled data on temperature, pressure, geometric characteristics of devices, as well as IPB production plant operation monitoring results in HYSYS medium a computer model of the technological scheme was developed. The composition of dried benzene fraction (DBF) was taken as input data, wt. %: benzene 60.,29 – 87.41; OPB 1.11 – 9.43; hexene 1.67 – 3.98; toluene 0.02 – 2.13; ethylbenzene 0.1 – 1.56; xylol 0.01 – 1.13; n-propylbenzene; 0.01 – 0.13; 3-buthylbenzene 0.05 – 0.65; 2- butylbenzene 0,13 – 1,06; cymene 0.08 – 1.36; n-butylbenzene 0.08 – 0.47; PAB 6.54 – 24.19.

For further calculations with use of developed model, namely for calculation of process parameters due to change of rectification scheme the model is to be verified. Fig. 2 shows the results of comparative analysis of calculated and experimental data (secondary components, as for them the error is higher than that of the target component - IPB - error does not exceed 0.01%).

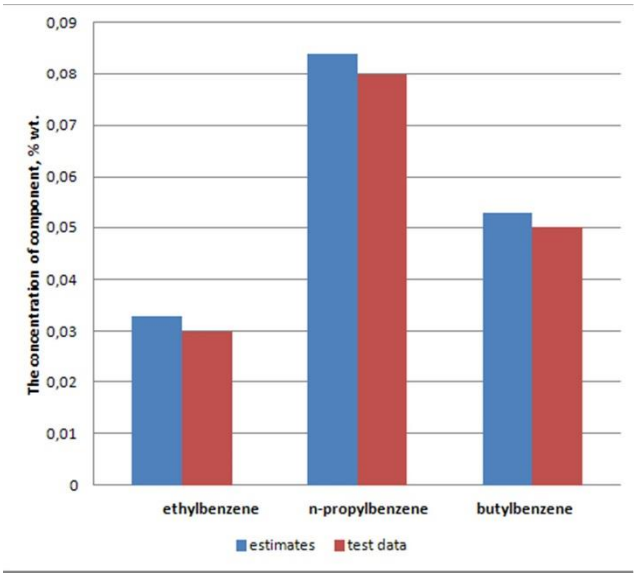

Figure 2. Comparative analysis of calculated and monitoring data on the yield of commercial IPB (in 2015 year)

Accuracy of main components concentrations calculation with use of mathematical models does not exceed 10%, which leads to conclusion that model is adequate and suitable for use in calculation process, such as to simulate devices operation when technological scheme of separation unit changing.

2.2. Changing rectification process scheme in IPB production

To change the rectification block technological scheme of IPB production is obtaining of commercial product with target component content of not less than 99.94 wt.%, The content of impurities in the product should not exceed the values corresponding to the IPB highest grade, which corresponds to ASTM standards (Tab. 1).

Table 1 Comparative characteristics of commodity IPB with the requirements to a higher grade in accordance with TC 38.402-62-140-92

Quality Indicator	Norm according to TC	Commodity IPB
Density at 20 ^{0}C, g/sm^3	0.861-862	0.862
IPM mass ratio, wt. % (not less)	99.9	99.951
Mass fraction of organic impurities, wt. % (no more)		
ethylbenzene	0.05	0.0307
n-propylbenzene	0.05	0.0181
butylbenzenes and higher hydrocarbons	0.02	0.0003
no aromatics	-	-

The next step of computer simulation model application is to calculate the efficiency of process when you change the sequence of columns in IPB production rectification block, namely changing the K-22/2 column layout. In this case, the supply circuit is provided K-22/1 distillate as for supply K-22/2column, and the bottom product of K-22/2 is sent as feed to K-42. Thus distillate K-22/2, mixed with the distillate of K-42 is sent as feed to K-62. Thus, by changing the supply of K-22/1 distillate the total load on K-42 and the load of light hydrocarbons (ethylbenzene) decreases.

Tab. 2 shows the technological parameters of rectification columns in IPB production. When calculating distillation columns following parameters were varied: feed of input plate in the column, the temperature at the top and bottom plates, pressure of top and bottom of the column, feed of distillate and bottom product. Efficiency of plates in the columns was accepted as minimum to better fit model to the real data.

Table 2. Recommended technological parameters of distillation columns in IPB production

Process parameter	Columns positions*					
	K-12	K-22/1	K-22/2	K-42	K-52	K-62
Efficiency of plates (or nozzles),%	60	55	55	55	55	55
Feed						
Feeding plate	24	24	24	36	44	20
Feed, kg/h	37050	14070	10550	10180	8450	2098
Inlet temperature, ^{0}C	125	110.6	125	90	151.2	100
Inlet pressure, kgs/m^2	1.796	2.550	1.136	2.076	2.078	1.95
Distillate						
Reflux liquid flow, kg/h	11100	73800	11400	93800	38300	50400
Selection of distillate, kg/h	22980	10550	372.6	1725	6000	257.3
Column top temperature, ^{o}C	82.2	88.6	152	155	108.2	150
Column top pressure, kgs/m^2	0.1	0.136	0.05	0.05	0.272	0.1
Bottom						
Bottom selection, kg/h	14070	3517	10180	8450	2450	1840
Column bottom temperature, ^{o}C	176.0	184.6	162	162	130.3	163
Column bottom pressure, kgs/m^2	0.650	0.272	0.28	0.28	0.544	0.31

Tab. 3 shows the compositions of streams according to calculations. Compared to a scheduled scheme, network and technological mode of rectification unit change leads to changes in composition of process streams, not only of commodity IPB, but also intermediate. For example, with the bottom product of K-22/1 heavy n-butyl benzene takes part. That has a positive effect on separation of heavy butylbenzenes in K-52.

Table 3. Compositions of flows in rectification scheme of IPB manufacturing

Component name, wt. %	K-12		K-22/1		K-22/2		K-42		K-52		K-62		Commodity IPB
	top	bottom	top	bottom	top	bottom	top	bottom	top	bottom	top	bottom	
Benzene	99.6656	0.0104	0.0139	-	0.3933	-	-	-	-	-	0.5696	-	-
IPB	0.0937	73.6944	98.2587	-	84.2584	98.7712	94.7188	99.6408	99.9705	98.8606	42.5616	99.8884	99.9512
Toluene	0.0110	0.0840	0.0112	-	0.3163	-	0.0005	-	-	-	0.4550	-	-
Ethylbenzene	0.0685	1.0490	1.3986	-	15.0186	0.9000	5.2710	0.0067	0.0095	-	56.4138	0.0998	0.0307
NPB	-	0.1580	0.2107	-	0.0133	0.2179	0.0098	0.2605	0.0200	0.8236	-	0.0117	0.0181
n-buthylbenzene	-	0.0527	0.0254	0.1346	-	0.0263	-	-	-	-	-	-	-
Sec-buthylbenzenes	-	0.0347	0.0462	-	-	0.0479	-	0.0479	-	0.1647	-	-	0.0001
tert-buthylbenzenes	-	0.0265	0.0353	-	-	0.0363	-	0.0441	0.0001	0.1511	-	-	0.002
PAB	-	24.9659	-	99.8654	-	-	-	-	-	-	-	-	-
Propane	0.1612	-	-	-	-	-	-	-	-	-	-	-	-

Thus, it can be concluded that the change in rectification unit scheme of IPB production is effective because implementation of proposed technical solutions have achieved the quality of commodity IPB responsible for higher grade of TC 38.402-62-140-92 [9] and requirements of consumer, in amount of 7840 kg/h.

However, achieving a high quality of commercial product is not possible with a high content of undesirable components, such as n-propylbenzene (NPB), in alkylation reaction mass. Due to proximity of IPB and BPB boiling temperature, it is difficult to separate them in 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 the work was integration of mathematical model of benzene with propylene alkylation on chloroaluminum catalyst reactor [10-11] into the computer model of IPB installation in HYSYS software.

3. Results and discussion

3.1. Integration of mathematical model of benzene with propylene alkylation on chloroaluminum catalyst reactor into the computer model of IPB installation in HYSYS software

The developed mathematical model of benzene with propylene alkylation process on chloroaluminum catalyst allows to estimate alkylation structure reactor reactionary mass composition. HYSYS simulation environment is a program of open type, allowing "embedding" any program modules.

Development of mathematical model of reactor process in HYSYS is complicated by the need to define values of chemical reactions rate constants, which is only possible to determine experimentally. Therefore, mathematical model of benzene with propylene alkylation reactor process was built for the task [4].

One of the most important stages in development of catalytic process mathematical model is to determine catalysts kinetic parameters (rate constants, pre-exponential factors in the Arrhenius equation and activation energy). Development of mathematical modeling methods in practice, kinetic and technological process analysis provides a measure of kinetic

parameters of various contacts by the inverse kinetic problem solving. Thus defined parameters of these reactions occurring in alkylation process can be used to develop mathematical models for different industrial environment and determine its predictive ability.

In the transition to the next stage of modeling for definite contact apparatus structural and hydrodynamic factors should be taken into account. These factors determine the choice of reactor models, as well as consideration of possible diffusion of complications during chemical reactions in it. Further refinement of mathematical model is possible by testing it on real industrial sites for different operating conditions, by permanent calculations of current indicators of the process and comparison of obtained results with experimental data [12-16].

In this case, to carry out optimization calculations IPB production parameters that depend both on bubble type catalytic reactor efficiency, and on distillation columns efficiency, software-implemented mathematical model of reactor process was introduced into HYSYS and "synthesized" with computer model of distillation unit. Thus, the output parameters of alkylation reactor mathematical model are the input parameters of rectification unit computer model.

Thus, combined mathematical model of IPB obtaining process integrated with HYSYS module, provided calculation performance of alkylation reactor together with product separation block. Determination of these devices modes will provide the lowest output of side component and yield of target product meeting the highest IPB grade. IPB and BNP have close values of boiling points are it is difficult to separate them by distillation. For obtaining of commercial product containing 99.9% by weight of target component it is necessary to minimize concentration of BNP, arriving to rectification, that is, to reduce the rate of its formation in the reactor.

To achieve reduction of NPB content is only possible by changing of alkylation reactor block mode. The numerical experiments with use of mathematical models by varying temperature and benzene/propylene molar ratio, allowed achieving the minimum NPB content.

Thus, the optimal alkylation reactor mode corresponds to the following values of process parameters: temperature of 114°C and benzene/propylene molar ratio of 2.5/1. After rectification system marketable IPB was obtained in amount of 10750 kg/h.

The calculations showed that the installation producing SP achieved while respecting the values of the parameters of a technological mode of operation of the reactor and distillation columns can be obtained trademark UPS containing 99.94% of the target component in an amount of 10750 kg / h, while the impurities will not exceed the amounts required by higher grade product.

4. Conclusions

1. It is found that change of reaction mixture separation sequence in distillation columns (K-22/1 and K-22/2), leads to increasing to increasing of SPB content up to 99.9% in comercial product concentration by weight. It is achieved by load redistribution of ethylbenzene and n-butylbenzene. A column of technical IPB obtaining (K-42) plays the role of duplicate column, which has a positive effect on commercial product purity.
2. A computer model of separation unit of IPB manufacturing production developed in HYSYS adequately describes the rectification processes in the series-connected devices. The calculation error does not exceed 10%.
3. The integrated software-implemented mathematical model of IPB production on chloroaluminum catalyst allows calculation of technological modes of process devices UPS necessary for production of high quality commercial product (99.94 wt.%). Thus, for given composition of dried benzene fraction with PAB content from 6 to 24% by weight, maximum IPB concentration is achieved in commercial product at high feed flow rate (4 h^{-1}), low temperature (114-115°C) and the lowest possible benzene/propylene molar ratio equal to 2.5/1.

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References

[1] Booming Petrochemical Industry Assures Cumene Sales to Grow by 4% / Process Worlwide; Ed. Dominic Stefan. URL: http://www.process-worldwide.com/management/markets_industries/articles/393591/.

[2] Manufacturing of acetone: production, use, market data. URL: http://www.newchemistry.ru/printletter.php?n_id=4886).

[3] Appl M. Ullmann's Encyclopedia of Industrial Chemistry. – 2006.

[4] Hock H, Lang S. Autoxidation of hydrocarbons. IX. Peroxides of benzene derivatives. Ber. Dtsch. Chem. Ges. B. 1944.V. 77: 257-264.

[5] The new directory of chemist and technologist. Raw materials and products of industry of organic and inorganic substances. Part 1 / under obsch.red. Pokonova YV; Starhova VI. – S.Pb .: ANO NGO "Peace and family", ANO NPO "Professional". –2002. - 988 p. [In Russian].

[6] Vogel AI, Tatchell AR, Furnis BS, Hannaford AJ and Smith PWG. Vogel's Textbook of Practical Organic Chemistry. 5th Edition. Prentice Hall. – 1996. – 514 p.

[7] TC 2-035-2006: permanent technological regulations for production of isopropyl benzene by alkylation of benzene with propylene [2] *PJSK «Omskiy kauchuk».* – 2011. – 259 p. [In Russian].

[8] HYSYS version 3.1 Basis. HYPROTECH. Electronic manual.

[9] TC 38.402-62-140-92 isopropylbenzene (cumene) S6H5CH (CH3). Technology, first grade [In Russian].

[10] Nurmakanova AE, Salishcheva AA, Chudinova AA, Syskina AA, Ivashkina EN. Comparison between Alkylation and Transalkylation Reactions using ab Initio Approach. Procedia Chemistry. 2014; 10: 430-436.

[11] Chudinova AA, Salishcheva AA, Ivashkina EN, Moizes O, Gavrikov AA. Application of cumene technology mathematical model. Procedia Chemistry. 2015; 15: 326-334.

[12] Ivanchina ED, Ivashkina EN, Dolganova IO, Platonov VV. Effect of Thermodynamic Stability of Higher Aromatic Hydrocarbons on the Activity of the HF Catalyst for Benzene Alkylation with C9–C14 Olefins. Petroleum Chemistry. 2014; 54(6): 445-451.

[13] Pisarev MO, Dolganov IM, Dolganova IO, Ivashkina EN. Modes of Gas And Gas Condensate Preparation Unit in Low temperature Separation Technology Modeling. Pet. Coal.2014; 56(2): 182-187.

[14] Dolganova IO, Dolganov IM, Ivashkina EN, Ivanchina ED. Development of computer modeling system as a tool for improvement of linear alkylbenzene production. Pet. Coal. 2011; 53(4): 244-250.

[15] Dolganova IO, Dolganov IM, Ivashkina EN, Ivanchina ED. Development of approach to simulation of oil refining processes on example of benzene alkylation with ethylene. Pet. Coal. 2012; 54 (2): 213-219.

[16] Shcherbakova YA, Dolganova IO, Belinskaya NS. Benzene Alkylation With Ethylene Process Mathematical Modeling. 7th International Forum on Strategic Technology (IFOST - 2012): Proceedings: in 2 vol.–Tomsk, September 18-21–2012. – Tomsk: TPU Press,–2012 - Vol. 1 - p. 50-53.

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