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Estimation of Sulfocationites Application Expediency as Catalysts of Benzene Alkylation Process with Propylene

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Abstract

An alternative technology of benzene alkylation with propylene is proposed at OJSC Omsk rubber. The effectiveness of aluminum chloride catalyst replacement is evaluated on sulfocationites. A discrete supply of propane-propylene fraction to the alkylation reactor is proposed. The mathematical model of benzene alkylation process with propylene using the sulfocationites catalysts was developed. Mathematical model of the process was developed in the program environment AspenTech. The numerical values of the rate constants were determined. An adequate process model allow carrying out numerical experiments on the variation of the basic reagents relations reactions.

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1. Introduction

Development of the modern chemical industry cannot be considered ignoring effect on the environment and the consequences connected with it. The main task is to create new technological schemes or to improve the old ones when the new methods are used with minimizing harmful emissions into the environment; this promotes the increase the production ecological safety[3].

OJSC Omsky kautchuk is one of the petrochemical enterprises complexes influencing technogenically the

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ecological situation in Omsk. This enterprise implements the process of benzene alkylation with propylene while aluminum chloride is applied as a catalyst. The main problem of this process is a large number of ecologically dangerous drains containing condensed aromatic hydrocarbons and aluminum cations[4].

The purpose of the given paper is to select an alternative technology of the isopropylbenzene (IPB) or cumene production for the OJSC Omsky kautchuk.

The following tasks were formulated:

- to review the technologies of alkylbenzene manufacture;
- to calculate the basic parameters for alkylation process on the sulfocationites with mathematical model using.

The most widespread catalysts of the alkylation process are: $AlCl_3$, BF_3, solid kieselguhr phosphoric acid, zeolites. $AlCl_3$ and BF_3 cause the strongest corrosion of the equipment and formation of harmful drains. The process occurs with phosphoric acid, it demands high temperature. Therefore, such technologies are notable for low selectivity.

There is a set of various brands of the zeolites developed by scientific institutes worldwide. The main shortcomings of process on zeolites are:

- a short period of time between regenerations;
- a high regeneration temperature, and as a result much energy is needed.

But in turn they possess a number of indisputable advantages:

- high activity;
- a high selectivity to the desired product - cumene;
- a low selectivity of to by-products – n-propylbenzene, diisopropylbenzene, thriisopropylbenzene;
- the absence of the high aggressive medium, as a result of the corrosion of equipment, gas emissions, wastewater toxicity;
- availability;
- long service life of the catalyst.

Not each brand of zeolites is suitable for application in the industry. Despite the listed shortcomings the correct zeolites have to be chosen for special process[7-14].

In technologies of ethylbenzene (EB) and cumene production in the presence of $AlCl_3$, the processes of alkylation and disproportionation are combined in one reactor where these processes are forcedly carried out at high temperature as reactions of disproportionation demand temperature 30 - 40 ^oC higher than alkylation reactions do. It decreases process selectivity.

Researches of O.S. Pavlov[1,2] showed that sulfocationites application allows carrying out benzene alkylation at moderate temperatures: 70 - 80 ºC for IPB production.

Practically total conversion of propylene can be achieved in one pass when sulfocationites are used as catalysts, however the price and selectivity of IPB/DIPB (diisopropylbenzene) decrease. The ratio (selectivity) IPB/DIPB raises when molar ratio benzene: propylene increases, and alkene conversion reduces.

When sulfocationites are applied in the reaction mass for benzene alkylation with propene impurity of ethylbenzene, butylbenzene and heavy tars/ pitches (characteristic for process with $AlCl_3$) are absent.

High selectivity of alkylbenzene / ($\geq$20: 1) depends on dialkylbenzene disproportionation and allows carrying out alkylation at the optimum temperature.

Incomplete alkene conversion doesn't cause difficulties when using concentrated propylene as raw materials, however, in industry alkane-alkene fraction (for example, the propane-propylene fractions (PPF) of the catalytic cracking containing 70 - 80% of propylene) is more available and cheaper.

Such fractions may be used at incomplete conversion in one pass as simple concentration with propylene rectification is possible. Propylene contains PPF separated from the reaction mixture.

The distillate enriched with propylene is recycled in the reaction zone, and the excess of propane is removed. It provides conversion of propane up to 99% in total.

As for energy efficiency the alkylation on the sulfocationites is slightly more efficient than existing process with $AlCl_3$. The main advantages of the process is the absence of the following factors: high aggressive medium, the deep dewatering of raw materials and formation of harmful sewage.

Necessary molar ratio of components propylene : benzene is 7:1, it is achieved by separate feeding PPF into the reactor. It provides slower formation of sequential addition products DIPB and the polyalkylbenzene (PAB) leading to self-formation on the catalyst see Fig. 1.

Benzene + Propylene = IPB K_1
IPB + Propylene = DIPB K_2
DIPB + Propylene = PAB K_3
$K_1 >> K_2 >> K_3$

Fig. 1. Scheme of alkylbenzene transformations

Mathematical modeling of benzene alkylation with propylene was rarely used. Models of reactors of different types were generally created[7-8].

2. Mathematical modeling

The mathematical model of alkylation process assesses the efficiency of sulfocationites application in industrial technology of IPB production.

In the paper [1] the kinetic equation of the first order (1) is offered for the data description[2] in the mixture reactor of periodic action.

$$r = \frac{k \cdot \left[H^+\right]^n \cdot \alpha_A \cdot \alpha_B \cdot \beta_A \cdot \beta_B}{\left(\sum_j \alpha_i \cdot \beta_i\right)^2} \cdot \left(1 - \frac{\alpha_C}{K \cdot \alpha_A \cdot \alpha_B} \cdot \frac{\sum_j \alpha_j \cdot \beta_j}{\sum_j \alpha_j^p \cdot \beta_j}\right) \quad (1)$$

The data experimentally found by O. S. Pavlov were used when determining initial approximations to solve the reverse kinetic task.

The alkylation reactor was presented in cascades from the four devices with intermediate cooling of streams in the built-in tubular heat exchangers. PPF is fed discretely into each reactor that allows keeping a necessary molar ratio benzene : propylene (7:1).

Mathematical model of benzene alkylation process with propylene was developed with the specialized Unisim Design package which has broad base of physical and chemical constants of individual substances, a set of the thermodynamic state equations.

To create a model of the ideal mixing reactor, the equations of alkylation reactions were defined; the thermodynamic Peng-Robinson package was chosen; the reaction type (heterogeneous catalytic one) was selected; stoichiometric coefficients were placed.

Material and power streams were defined in the modeling medium.

The computer model of the IPB synthesis reactor from benzene and propylene is schematically presented in the following form see Fig. 2[15].

3. Results and discussions

Reverse kinetics problem was solved, kinetic constants values found with the data for input and output components concentration in the reactors (Table1).

Calculated values deviations of experimental concentration from the initial are presented in Table 2. The deviation of the main product IPB doesn't exceed 0.5% rel.

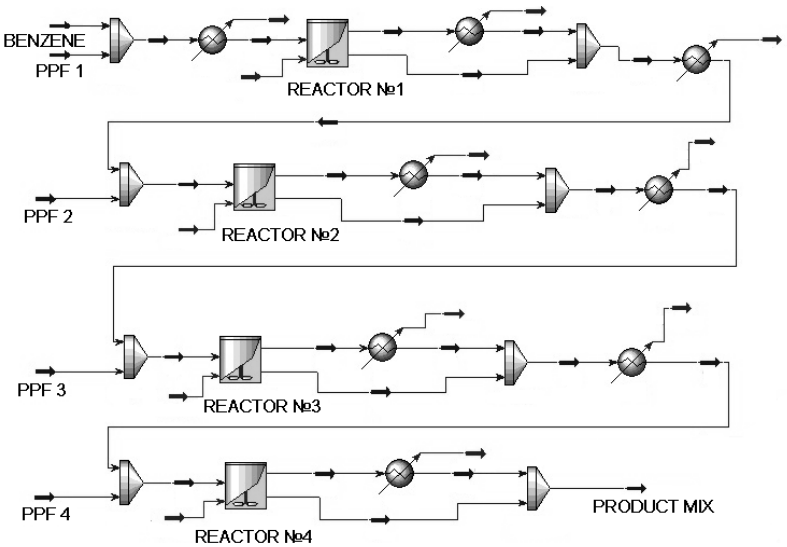

Fig. 2 . Mathematical model of alkylation reactor.

Table 1. Kinetic constants values for components

Reactor number	Kinetic constants values for components, h^{-1}		
	IPB	DIPB	PAB
1	0.007000	0.000140	-
2	0.002000	0.000140	0.0000007
3	0.003000	0.000500	0.0000008
4	0.001000	0.000700	0.0000015

Table 2. Model error in components' concentration

Component	Deviation from experimental concentration values, % rel.			
	1	2	3	4
IPB	0.26	0.14	0.08	0.38
DIPB	5.00	0.00	0.55	1.52
PAB	-	0.00	0.00	0.00

Application of the developed model makes possible to carry out numerical experiments in the ratios variation as for the main reagents and for PPF what defines process selectivity and therefore environmental friendliness of manufactured production.

4. Conclusions

It is possible to draw the following conclusions:

- the model of the reactor of receiving IPB is presented as a cascade of reactors in the environment of Unisim Desing intermediate heat exchanger is constructed with separate input of PPF;
- the model error (for the target product - IPB) doesn't exceed 0,5%;
- the model error (for DIPB) doesn't exceed 0,5%;
- the model error (for PUB) doesn't exceed 1 ppm.

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