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Mathematical Model of Benzene Alkylation in Linear Alkylbenzenes Manufacturing Technology

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Abstract

Alkylation of benzene with alkenes is one of the priority areas in the processes of the main organic and petrochemical synthesis due to the high demand for products derived from alkyl aromatic hydrocarbons. One of the most important technologies is the alkylation of benzene with C10-C14 alkenes with further sulfonation of linear alkylbenzenes obtained. In this work, we discuss the mechanism of the alkylation process, present the mathematical model and discuss the influence of main technological parameters on the process efficiency.

Keywords: *Mathematical modeling; Alkylation; Catalyst activity; Optimal technological mode.*

1. Introduction

Alkylbenzene sulfonates are typically used in the manufacture of synthetic detergents and surfactants. The main methods for the production of raw materials for detergents – linear alkylbenzenes (LAB), currently used in industry, are:

- chlorination of n-alkanes followed by alkylation of benzene with chloralkanes in the presence of $AlCl_3$;
- chlorination of n-alkanes followed by dehydrochlorination and alkylation of benzene with the obtained alkenes in the presence of $AlCl_3$;
- dehydrogenation of n-alkanes to n-alkenes followed by their alkylation of benzene in the presence of HF-catalyst;
- dehydrogenation of n-alkanes to alkenes with subsequent alkylation of benzene in the presence of heterogeneous catalysts [1–5].

About 80% of LAB produced in the world is obtained using the technology, where the C_{10}-C_{14} alkanes fraction is dehydrogenated and then subjected to hydrofluoric alkylation of benzene with dehydrogenizate, which contains olefins with internal double bonds. Another 11% of global LAB production is obtained using heterogeneous catalysts. The LAB fractions synthesized in this process contain a high content of 2-phenylalkanes, which ensure high solubility of sulfonated products in water [6–10].

The present study is devoted to the identification of optimal parameters for the alkylation process, depending on the performance of the equipment in the previous stages of production. The study was carried out using a specially developed mathematical model of the alkylation process, which sensitive to the composition of the feedstock and the change in the activity of the catalyst. This approach showed efficiency in different technological processes [11–14].

2. Experimental

The mechanism of acid-catalytic alkylation of benzene with olefins can be represented by the following scheme (Fig. 1).

At the first stage, carbocation is formed. Next, the carbocation obtained from olefin is attached to the benzene core with the formation of a sigma complex. Cleavage of the proton from the complex leads to the formation of reaction products. In addition to the main reaction,

side effects also occur. These include the formation of branched side chain phenylalkanes, disubstituted alkylbenzenes (heavy alkylate), and the formation of acid-soluble oils – heavy aromatics (HAR).

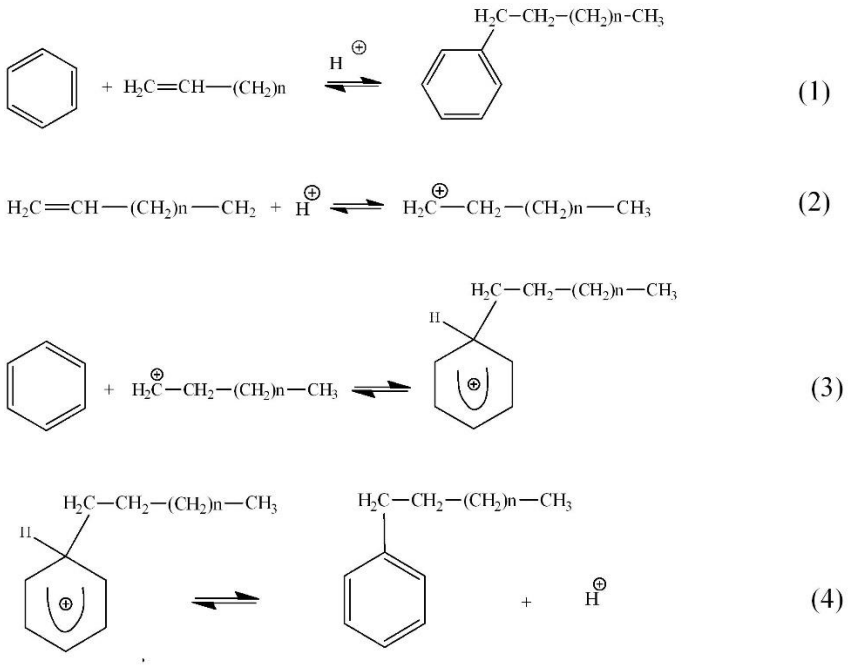

Figure 1. Mechanism of benzene alkylation with alkanes

The reaction network of the alkylation process is presented in Fig. 2.

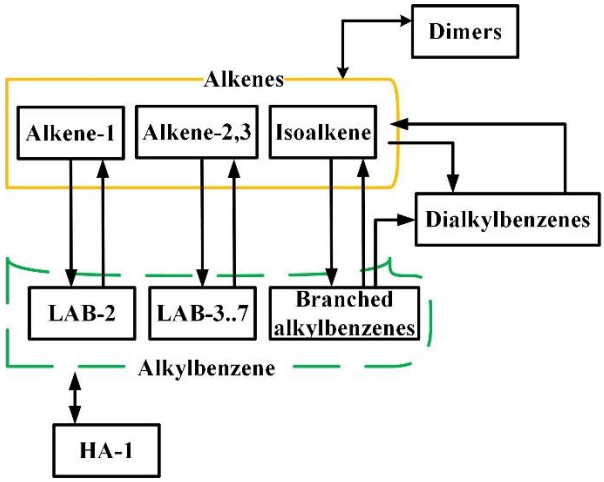

Figure 2. Reaction network of the alkylation process

The alkylation reactor model can be described as follows:

$$G\frac{\partial C_i}{\partial Z} + G\frac{\partial C_i}{\partial V} = \sum_j W_j \cdot a_j$$

$$G\frac{\partial T}{\partial Z} + G\frac{\partial T}{\partial V} = \frac{1}{C_p}\sum_j W_j \cdot (-\Delta H_j) \cdot a_j \qquad (1)$$

where a_j – activity, rel. units; Ci – concentration of the i-th component (mol m^{-3}); C_i^0 – initial concentration of the i-th component (mol m^{-3}); G – flow rate (kg h^{-1}); T – temperature (K); T_0 – initial temperature (K); Wj – reaction rate (mol m-3 hour-1); Z – the total volume of the recycled raw materials (m^3); $-\Delta Hj$ – heat of the j-th reaction (J mol^{-1}).

3. Results and discussion

With use of the alkylation process mathematical model, we studied the influence of control parameters on such indicators as the production of LAB and heavy alkylate, bromine numbers, optimal catalyst activity and optimal acid consumption for regeneration.

The main operating parameters of the alkylation process are the composition of the feedstock, the temperature, the flow rate of the feed stream and the catalyst stream. The composition of the raw materials was varied by the ratio of C_{10}-C_{11} olefins to C_{12}-C_{13} alkanes, and the content of aromatic compounds.

The change in the of the HF catalyst activity, as well as the consumption of acid in the regenerator column, depends mainly on the concentration of HAR in the alkylation reactor since these substances dissolve in the acid and are removed from the reactor in its stream.

It is necessary to maintain such a catalyst consumption for regeneration that will ensure optimal catalyst activity and high production of linear alkylbenzene of the required quality.

The concentration of HAR formed in the alkylation reactor is determined by the composition of the alkylation feedstock. Next, we consider the dependences of the optimal activity of the HF catalyst and its optimal consumption in the regenerator on the composition and consumption of raw materials.

Varying the ($C_{10\text{-}11}$/$C_{12\text{-}13}$) alkenes ratio in the composition of the feedstock was studied in the range of 0.8-1.2. As the studied parameters of the process, the production of LAB and heavy alkylate, the bromine number, the optimal activity of the catalyst, and the optimal consumption of catalysts for regeneration were selected. The results revealed that with an increase in t($C_{10\text{-}11}$/$C_{12\text{-}13}$) alkenes ratio from 0.8 to 1.2, a significant decrease in the LAB production is observed, of the order of 10%, the yield of heavy alkylate increases by 14.7% (Fig. 3, 4).

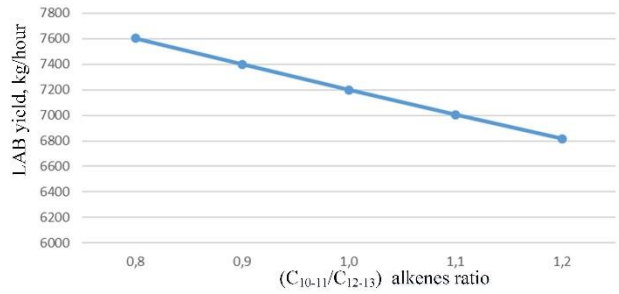

Figure 3. Yield of LAB depending on the ($C_{10\text{-}11}$/$C_{12\text{-}13}$) alkenes ratio

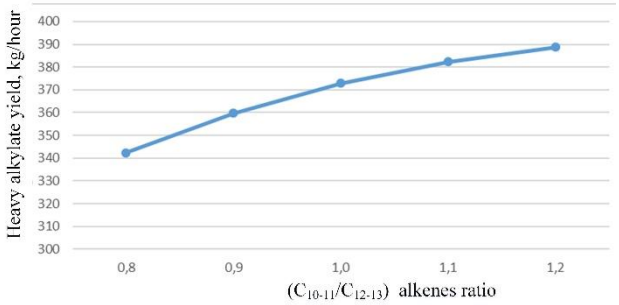

Figure 4. Yield of heavy alkylate depending on the ($C_{10\text{-}11}$/$C_{12\text{-}13}$) alkenes ratio

Further, the optimal catalyst activity and optimal catalyst consumption indicators were considered. For the optimal activity, we take the activity of the HF catalyst in which there is an equilibrium of reversible reactions of HAR formation from LAB. The optimal consumption of catalyst for regeneration, in turn, is such consumption of catalyst in the regenerator column, in which the optimum activity of the catalyst is maintained.

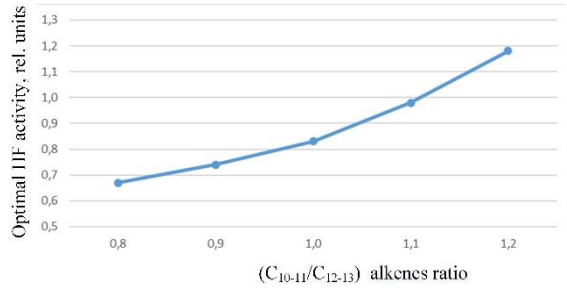

Fig. 5. Effect of feed composition on catalyst performance

The effect of the feedstock composition on the catalyst performance is presented in Fig. 5 and Table 1.

As can be seen from the dependence of the optimal activity of the catalyst and its flowrate for regeneration, the use of lighter feedstock entails both an increase in the value of the optimal catalyst activity and a regular increase in catalyst flow to regeneration.

The calculation was performed according to the data for January 1, 2019. The total consumption of alkenes was 4960.29 kg/hour, benzene - 10,078.84 kg/hour, dienes - 51.98 kg/hour.

Table 1. Alkylation process performance depending on the $(C_{10}+C_{11})/(C_{12}+C_{13})$ alkenes in the feedstock

$(C_{10}+C_{11})/(C_{12}+C_{13})$ alkenes	Optimal activity, rel. units	Optimal HF flowrate to regeneration, m^3/hour	HAR yield, kg/hour	LAB yield, kg/hour
0.8	0.67	4.25	342.33	7604.00
0.9	0.74	4.38	359.77	7400.26
1.0	0.83	4.50	372.83	7199.55
1.1	0.98	4.62	382.27	7004.58
1.2	1.18	4.72	388.76	6816.92

Table 1 allows us to conclude that the optimal catalyst activity and its optimal flowrate to the regenerator column depend on the composition of the feedstock. With the predominance of light olefins in the feed stream, it is necessary to maintain a higher activity of the catalyst and, as a result, a greater consumption of catalyst for regeneration.

Thus, in order to ensure the maximum flowrate of the target product with the predominance of light olefins in the feed stream, it is necessary to maintain a higher activity of the catalyst by using an increased consumption of HF in the regeneration stage. This need is due to the low reactivity of (C_{10+11}) olefins with respect to (C_{12+13}) alkenes.

In addition to benzene, olefins, and diolefins, heavy aromatic compounds, which were not completely recovered from the feed stream at the previous stages, enter the reactor to some extent. The study of the effect of aromatic content in the alkylation reactor showed that with an increase in the amount of these compounds, the value of HF optimal activity increases, and as a result, there is a need to maintain a higher catalyst consumption for the regeneration stage (Table 2).

Table 2. HF optimal activity and flowrate to regeneration depending on the aromatics content in the feedstock

Aromatics, wt%	Optimal HF activity, rel. units	Optimal HF flowrate to regeneration, m^3/hour
0.2	0.84	4.42
0.4	0.85	4.56
0.6	0.87	4.71
0.8	0.89	4.87
1	0.91	5.04
1.2	0.93	5.23
1.4	0.95	5.44
1.6	0.97	5.66
1.8	0.99	5.9

Thus, the use of raw materials with a high aromatic content implies an increase in the optimal activity of the catalyst by increasing the consumption of acid in the regenerator column. With an increase in aromatic content by 0.2%, the optimal consumption of HF for regeneration should be increased by 3.2 m^3/hour.

4. Conclusions

In this research, we considered the main industrial technologies for the alkylation of benzene with olefins, including the catalysts used in these processes. Thus, there is a distinct tendency towards the transition of benzene alkylation with higher alkenes from homogeneous catalysis to heterogeneous following the alkylation of benzene with light alkenes. However, for industries using homogeneous catalysis, process optimizations remain relevant.

As a result of the work performed, it was revealed that:

1. The main process control parameters for the process of benzene alkylation with C_{10}-C_{13} olefins are the ratio of benzene/alkenes, temperature, composition and flowrate of the feedstock, catalyst flowrate to regeneration.
2. The optimal catalyst activity and its optimal flowrate to the regenerator column depend on the composition of the feedstock. To ensure the maximum yield of the target product with the predominance of light olefins in the feed stream, it is necessary to maintain a higher activity of the catalyst by increasing the HF flowrate to regeneration. This need is due to the low reactivity of (C_{10}+C_{11}) alkenes in comparison with (C_{12}+C_{13}) alkenes.
3. The use of raw materials with a high aromatic content implies an increase in the optimal catalyst activity.

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