# Petroleum and Coal

## IMPROVING THE EFFICIENCY OF MULTISTAGE PRODUCTION OF ALKYLBENZENE SULFONIC ACID

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**Abstract**

The object of the research is multi-stage integrated production of linear alkylbenzenes and linear alkylbenzene sulfonic acid. The established thermodynamic and kinetic laws of the transformations of $C_9$–$C_{14}$ hydrocarbons and the activity of catalysts used in the synthesis of linear alkylbenzenes provided the creation of mathematical models suitable for optimizing the main stages of the synthesis. the assessment of the full range of nonstationarity factors caused by the deactivation of catalysts was made on the basis of a computational and industrial experiment simulation. the model calculations allowed improving the efficiency of multistage production of alkylbenzene sulfonic acid and to increase the desired product yield from 170 –172 to 174–176 tones/day.

*Keywords*: *Mathematical modeling; Dehydrogenation; Alkylation; Sulphonation; Catalyst activity.*

## 1. Introduction

The technology of multi-stage integrated production at oil refinery should ensure the maintenance of high yield of target products with required quality and minimum waste (sub-standard lots of products with a high content of by-products).

The creation of such a technology is possible only if the efficiency of each of the associated processes and devices at all stages is increased, considering their interconnection by the method of mathematical modeling. With large volumes of commodity production, economic indicators can reach a significant value.

Long-term studies of the Tomsk Polytechnic University [1–3] of the processes of production of alkylbenzene sulfonic acid (ASA) and linear alkylbenzene sulfonates determined the creation of an integrated mathematical model of the ASA technology describing the processes proceeding as at separate stages of hydrogenation, alkylation, sulfonation, and the relationship between the structural units of the entire chemical-technological system.

The application of the developed model at one of the Russian refineries ensured the fulfillment of forecast and optimization calculations and made it possible to establish the mutual influence of the processes and phenomena occurring in the LAB-ASA technology apparatuses.

A method has been developed for controlling the catalyst activity of the alkanes dehydrogenation process, which consists in controlling the catalyst activity by increasing the water supply to the dehydrogenation reactor to reduce the intensity of coke formation [4-5].

Conducted numerical and pilot-scale studies in industrial conditions allowed developing a new method to control the catalyst activity of the dehydrogenation process, increasing the yield of the target product and preserving the service life of the catalyst.

The development of work in this direction should consider studies of the HF-catalyst in the benzene with higher olefins alkylation process. Their main task is to theoretically substantiate the existence of optimal operating conditions for the HF catalyst and to develop recommen-

dations for maintaining the optimal consumption of HF-acid supplied for regeneration to ensure stable operation of the chemical-technological system for LAB production using a toxic catalyst.

The introduction of the developed model to predict the dynamics of the formation of high-molecular organofluorine aromatic hydrocarbons in the alkylation process o made it possible to increase the duration of stable operation of the column from one to three months to one year. At the same time, increasing the production efficiency of ASA production depends on the final stage of LAB sulfonation in a decisive way [6-9].

## 2. Experimental

When modeling multicomponent hydrocarbon synthesis processes, a large amount of experimental research is required. To reduce them when comparing various chemical synthesis schemes, the laws of chemical thermodynamics are widely used.

For the thermodynamic calculation of the dehydrogenation process of higher C9–C14 paraffins, the method of quantum chemical modeling was used. For reactions of all types, the Gibbs energies $\Delta Gr$, the enthalpies of the reactions $\Delta Hr$ and the entropy $\Delta S$ were calculated at an average process temperature of 753 K and a pressure of 0.2 MPa.

Thermodynamic analysis of reactions proceeding in the alkylation process was carried out at an average process temperature of 328 K and a pressure of 0.5 MPa.

The established thermodynamic laws formed the basis of a formalized scheme for the conversion of hydrocarbons, which takes into account the reactions of the alkylation process, which is presented in Fig. 1.
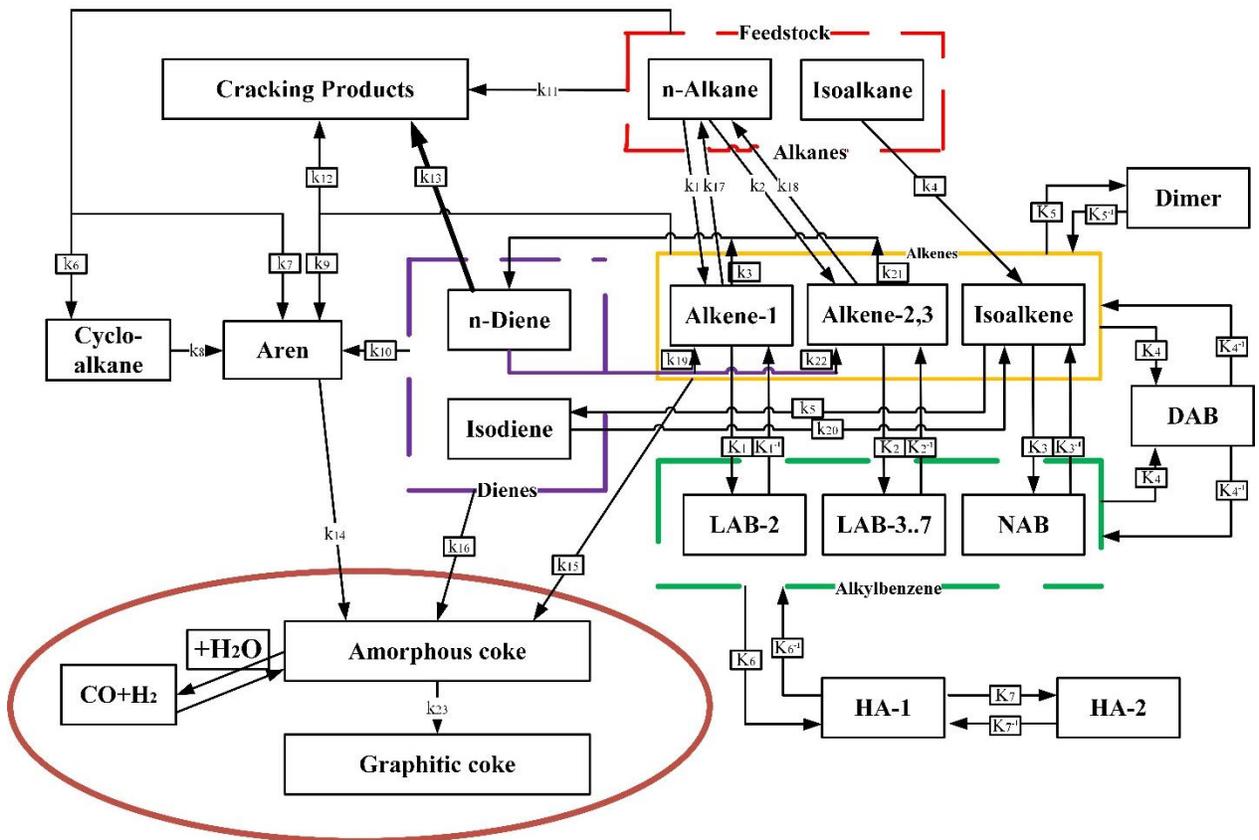


Fig. 1. Generalized reaction network of dehydrogenation and alkylation processes

Here LAB-2 - 2-phenylalkane; LAB-3 ... 7 - linear alkyl benzenes with a substituent in advising position; DAB - dialkylbenzenes; NAB - nonlinear alkylbenzenes; HAR-1, HAR-2 - "heavy" alkylaromatic compounds that have the following structure (Fig. 2):
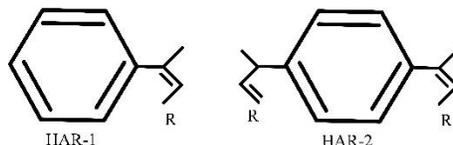


Fig. 2. Structure of HAR molecules

When developing a mathematical model, the components were combined into groups: the group of olefins includes the components α, β, γ-olefins, and isoolefins; the LAB group includes the LAB-2, LAB-3..7, NAB components; the HAR group includes the HAR-1 and HAR-2 components.

As can be seen from the reaction network, linear alkyl benzenes are intermediate substances in the formation of high molecular weight aromatic and alkylaromatic compounds. In this case, both the target and side reactions are catalyzed by HF-acid.

On the basis of the proposed reaction network, mathematical models were developed for the main stages of the synthesis of LAB, represented by a system of equations of material and heat balance. Thus, the model of the dehydrogenation process is made up of the assumption that the model of the ideal displacement reactor is applicable as a hydrodynamic model of the reactor.

Along with material and heat balances of the dehydrogenation reactor, the developed mathematical model includes a description of the Pt catalyst deactivation by coxogenic compounds (CGC). The coke concentration on the catalyst is calculated based on a formalized reaction network, as the product of coke-formation reactions from aromatic and diene hydrocarbons.

Considering the change in catalyst activity during coke accumulation provided its predictive ability with respect to the service life of the catalyst when changing the composition and consumption of raw materials, the process temperature, the circulation ratio of the hydrogen-containing gas.

The mathematical model of the alkylation reactor (1) contains the parameter for changing the activity of the HF catalyst, which is determined by the content of HAR-1 and HAR-2 and depends on the consumption of acid for regeneration.

$$\begin{cases} \dfrac{dC_i}{d\tau} = k_j \cdot a \cdot C_i \\[2mm] \rho\, C_P\, \dfrac{dT}{d\tau} = \sum_{j=1}^{N}(-\Delta H_j)W_j \end{cases} \quad (1)$$

where: Initial conditions: t=t0 Ci=Ci0; T=T0.

$\tau$ – contact time, s; $C_i$ – concentration of the i-th component (benzene, olefins, diolefins, LAB, heavy alkylate, HAR, dimers), mole/l; $k_j$ – the rate constant of the $j$-th reaction, l/(mol·s); $\Delta H_j$ – heat of chemical reaction, J/mole; $W_j$ – the rate of the $j$-th chemical reaction, mol/(m³·s); $C_p$– mass heat capacity of the reaction mixture, J/(kg·K); $\rho$ – density of the reaction mixture, kg/m³; $T$ – temperature, K; $a$ – catalyst activity (relative units).

## 3. Results and discussion

### 3.1. Increasing the selectivity of the dehydrogenation process by reducing coke formation in oxidation and hydrogenation reactions

A literature review has shown that techniques such as diluting raw materials with hydrogen or supplying water to the reactor can increase the selectivity of industrial synthesis of LAB at the dehydrogenation stage. At the same time, excessive moisture leads to an increase in

cracking reactions, with a lack of water, coke formation reactions are intensified, which also results in a lack of hydrogen in the system. At the same time, an increase in the rate of circulation of hydrogen-containing gas leads to a decrease in the yield of the target products - alkenes. Therefore, it is important to choose the optimal conditions for the industrial process, ensuring a long term stable operation of the catalyst with the desired yield of the target product and the minimum concentration of secondary components.

The next stage of research was to consider the possibility of the reaction of the oxidation of amorphous coke with water.

The numerical and experimental-industrial studies at the oil refining enterprise allowed us to perform thermodynamic analysis of the coke formation process and using a mathematical model of the dehydrogenation process to develop an optimal flow calculation method water. This technique is based on the need to maintain the conversion of an amorphous coke-forming structure with water over the entire temperature range of the process being constant.

But in the case of operation of the dehydrogenation catalyst under conditions of a lower hydrogen/hydrocarbon molar ratio, it is necessary to adjust the schedule of water flow to the reactor due to the increased intensity of coke formation reactions. To assess the performance of the dehydrogenation process when operating the unit at a lower hydrogen/hydrocarbons molar ratio, an industrial experiment was conducted at the plant for the production of alkenes-precursors.

Fig. 3 shows the temperature of the dehydrogenation process before and during the industrial experiment, as well as in the raw material cycle of the platinum-containing dehydrogenation catalyst of the same brand and batch in 2013–2014.
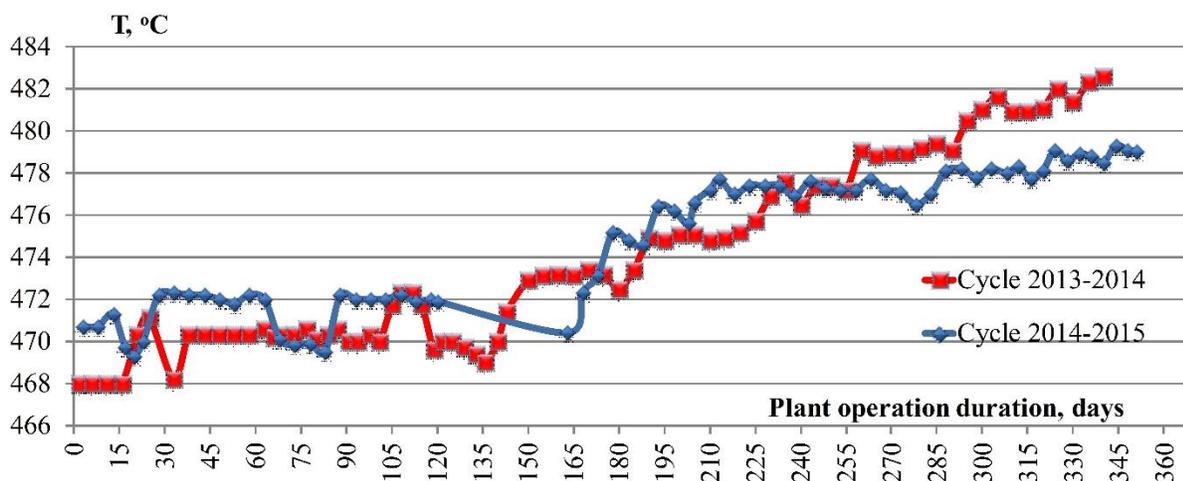


Fig. 3. Temperature mode of operation of the dehydrogenation reactor in two raw cycles of the catalyst

As can be seen, since the start-up of the reactor after the installation was repaired, the process temperature was increased to 475 °C, and over the next 4.5 months, it was increased by 3°C to 478°C, while not changing significantly during the experiment.

In the raw material cycle of the catalyst in 2013–2014, the temperature of the process on average was 1.5–2.5ºC higher than in the 2014–2015 cycle in the period of the industrial experiment.

The decrease in the hydrogen/feedstock molar ratio from 7/1 to 6/1 made it possible to increase the yield of alkenes due to a shift in the equilibrium of the target dehydrogenation reaction towards the formation of products to 8.8–9.4 wt % instead of 7.8–9.1 wt. % at a molar ratio of hydrogen / raw materials, equal to 7/1.

Thus, the experiment allowed us to establish the positive effect of reducing the hydrogen / feedstock molar ratio. At the same time, quantitative patterns of changes in water consumption were established using a mathematical model in the face of changes in the hydrocarbon composition of the processed raw materials.

### 3.2. Increasing the selectivity of the alkylation process by reducing the HF consumption

Alkanes are a source of education and such by-products as dienes, entering into chemical interaction with LAB at the stage of alkylation with the formation of heavy aromatic compounds - HAR. This reaction is catalyzed by HF, and the activity of the HF catalyst is defined as the ratio of the amount of acid, not deactivated by HAR, to its total amount.

Thus, HF activity depends on the current HAR concentration in the alkylation reactor, that is, on the concentration of dienes formed at the dehydrogenation stage and the amount of HAR discharged to the regenerator in the acid flow.

The results of the predictive calculations of the parameters of the joint operation of the alkylation reactor and the acid regenerator, depending on the number of dienes in the feed-stock, is presented in Table 1.

Table 1. Predicting the optimal consumption of HF-acid, depending on the consumption of dienes in the alkylation reactor

| Consumption of dienes in the alkylation, kg/hour | Amount of TAP accumulating in the alkylation reactor, kg/hour | Optimum HF flow rate to regeneration column, $m^3$/hour | ΔLAB, tones/day |
|---|---|---|---|
| 56.25 | 20.27 | 3.64 | 2.10 |
| 58.78 | 21.18 | 3.80 | 2.1 |
| 61.31 | 22.10 | 3.97 | 2.3 |
| 63.83 | 23.00 | 4.13 | 2.0 |
| 66.36 | 23.91 | 4.29 | 2.2 |
| 68.89 | 24.82 | 4.46 | 2.5 |
| 71.42 | 25.74 | 4.62 | 1.9 |
| 73.94 | 26.64 | 4.78 | 2.2 |

It follows from the above data that in order to maintain maximum LAB production, it is required to increase HF flow rate regeneration column from 3.64 to 4.78 $m^3$/hour as the diene consumption in the alkylation reactor increases from 56.25 kg/hour to kg/hour. At the same time, the amount of HAR formed in the alkylation reactor increases from 20.73 to 26.64 kg/hour. The positive effect of maintaining the consumption of HF-acid at an optimal level is to increase the average daily production of the target product by an average of 2.0-2.5 tones/day.

### 4. Conclusion

The recommended hydrogen/feedstock molar ratio of 6/1, which increases the selectivity of the dehydrogenation stage in the synthesis of LAB, requires adjusting the flow rate of water supplied to the dehydrogenation reactor to 13–14 L/hour instead of 9–10 L/hour by the end of the feed cycle.

The introduction of recommendations for changing the consumption of HF-acid in the regenerator, ensuring the maintenance of catalyst activity at an optimal level, has increased the yield of LAB rom 170 –172 to 174–176 tones/day.

### References

[1]   Roberts D. Optimisation of the Linear Alkyl Benzene Sulfonation Process for Surfactant Manufacture. Organic Process Research & Development, 2003; 7: 172−184.
[2]   Dolganova IO, Dolganov IM, Ivanchina ED, Ivashkina EN. Alkylaromatics in Detergents Manufacture: Modeling and Optimizing Linear Alkylbenzene Sulfonation. Journal of Surfactants and Detergents, 2018; 21(1): 175-184.
[3]   Kafarov V. Mathematical modeling of the basic chemical production processes: a tutorial. Kafarov V.V., Glebov M.B. - M.: High School, 1991. - 399 p. (in Russian)

[4] Kravtsov AV, Fetisov VA, Frantsina EV. Technology and modeling of reactive processing of higher paraffins to linear alkylbenzenes: a tutorial. - Tomsk: Publishing house of Tomsk Polytechnic University, 2010. - 297 p. (in Russian)

[5] Frantsina E, Ivashkina E, Ivanchina E, Romanovskiy R. Decreasing the hydrogen-rich gas circulation ratio and service life extension of the C9–C14 alkanes dehydrogenation catalyst. Chemical Engineering Journal, 2015; 282: 224–232.

[6] Corma A, Martínez-Soria V, Schnoeveld E. Alkylation of Benzene with Short-Chain Olefins over MCM-22 Zeolite: Catalytic Behaviour and Kinetic Mechanism. J Catal., 2000; 192(1):163–73.

[7] Odedairo T, Al-Khattaf S. Comparative study of zeolite catalyzed alkylation of benzene with alcohols of different chain length: H-ZSM-5 versus mordenite. Catal Today, 2013; 204:73–84.

[8] Zaid TA, Benmaza K, Chitour CE. Sulfonation of linear alkylbenzene (LAB) in a corrugated wall falling film reactor. Chem Eng J., 2000; 76(2):99-102.

[9] Molever K. Monitoring the linear alkylbenzene sulfonation process using high-temperature gas chromatography. J Surfactants Deterg., 2005; 8(2):199-202.

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