# Petroleum and Coal

## STUDYING THE INFLUENCE OF THE CONJUGATE TECHNOLOGICAL STAGES ON THE PERFORMANCE OF LINEAR BENZENES SYNTHESIS UNIT VIA THE MATHEMATICAL MODEL

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**Abstract**

Optimization of the operation of the chemical-technological system as a whole is possible only if the efficiency of each of the associated processes of all stages of production is increased, taking into account their interrelationship. These problems are successfully solved using the methods of mathematical modeling and computer modeling systems that take into account the volatility of the raw material composition, the change in catalyst activity and a large number of control parameters. This approach was used for benzene alkylation process and allowed us to reveal regularieties of alkylation reactor depending on the technologiscal conditions in the conjugate apparatuses. Thus, optomal HF-catalyst activity depends signifacantly both on the dehydrogenation feedstock composition and its flow rate.

***Keywords:*** *mathematical modeling; alkylation; catalyst activity; optimal technological mode.*

## 1. Introduction

The increasing demand for detergents with stable foaming and biodegradability necessitates the development of new ways to increase the efficiency and operational safety of potentially hazardous production of linear alkylbenzenes (LAB) with a predominance of 2-phenyl-alkanes that can be converted to surfactants by sulfonation.

A multistage technology for LAB production consists in the sequential dehydrogenation of n-paraffins to olefins, followed by alkylation of benzene in the presence of a hydrogen fluoride catalyst [1–5]. The resulting LAB is subjected to sulfonation - the addition of a sulfuric anhydride $SO_3$ molecule, resulting in the formation of alkylbenzene sulfonic acid (ASA) [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 the efficiency in different technological processes [11–14].

The change in the HF catalyst activity is mainly affected by the concentration of heavy alkylaromatics (HAR) in the alkylation reactor, as well as the acid consumption in the regenerator, since HAR is capable of dissolving in the acid and being removed in its stream from the reactor. The increase in the value of the catalyst activity is due to an increase in the flow rate of acid withdrawn to the regenerator column should lead to an increase in the production of all products [15–18]. On the other hand, the increase in the HAR concentration leads to a decrease in HF activity [19-20].

Thus, it is necessary to establish such a flow of HF for regeneration, which will ensure optimum catalyst activity and high production of the desired product of the required quality. The peculiarity of the LAB production process as any multistage process is that the operating modes of the conjugate stages are interrelated, therefore, it is possible to recommend the

optimal parameters of the alkylation process only taking into account the operation modes of the apparatuses at the previous stages of the technology [21–25].

The concentration of HAR formed in the alkylation reactor is determined by the content of diolefins in the feed [26]. Therefore, it is necessary consider the dependence of the optimal activity of the HF catalyst on the composition and rate of the feed flow, the type and activity of the dehydrogenation catalyst, the hydrogen/feed ratio in the dehydrogenation reactor [27].

## 2. Experimental

To describe the sulfonation reactor, the standard plug-flow reactor model was adopted to describe the reactor process. After that it was modified in the following way. Under unstable load conditions on the raw material we use the term "reduced time", or the total amount of recycled raw materials $Z=G \cdot t$. Then $\partial t = \frac{\partial Z}{G}$ and, subsequently,

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

$$G\frac{\partial T}{\partial Z} + G\frac{\partial T}{\partial V} = \frac{1}{C_p}\sum_j W_j \cdot \Delta H_j \cdot a_j \qquad . \qquad V=0, \ C_i=C_i^{in}, \ T=T^{in}.$$

The $Z$ parameter was calculated according to the values of the raw material flow rates. Replacing of $t$ by $Z$ reflects the process non-stationarity due to deactivating substances accumulation (coke for dehydrogenation, heavy aromatics for alkylation, high viscosity component for sulfonation) with the changing values of $G$. For dehydrogenation process, the $a_j$ value for desired reaction varies from 1 to 0.57 along with $Z$ increasing from 0 to 650000 m³. For alkylation process, the $a_j$ value for desired reaction varies from 0.7 to 0.4 along with $Z$ increasing from 0 to 750 m³.

## 3. Results and discussion

### 3.1. Dependence of the optimal parameters of the alkylation process on the composition of the dehydrogenation reactor feed stock

It is known that $C_{12}$-$C_{13}$ paraffinic hydrocarbons have a greater reactivity in dehydrogenation reactions than $C_{10}$-$C_{11}$ hydrocarbons. Isoparaffin hydrocarbons have a high reactivity in dehydrogenation and dehydrocyclization reactions. Due to the presence of heavy hydrocarbons in the feed stock, during the dehydrogenation on the platinum-containing catalyst, coke-based structures are formed. This leads to a drop in its activity. Thus, the recommended feedstock composition for a dehydrogenation reactor is a feedstock with a minimum content of isoparaffins and aromatic hydrocarbons, but with a sufficiently high content of $C_{12}$-$C_{13}$ paraffins having high reactivity with respect to target reactions.

To study the effect of the dehydrogenation feedstock composition on the optimal operating conditions of the alkylation reactor, the process indices for the feedstock compositions that differed as much as possible from the ratio of light and heavy hydrocarbons to the feedstock of the dehydrogenation reactor were computed (tab. 1).

Model calculation results are presented in tab. 2. As presented in tab. 2, the use of lighter feedstocks in the dehydrogenation process (with a higher ratio of $(C_{10} + C_{11})/(C_{12} + C_{13})$) results in a smaller amount of olefins being the raw material of the alkylation reactor, due to the low reactivity of the light paraffin components.

Fig. 1 shows the dependence of the LAB yield on the activity of the HF catalyst for various types of the dehydrogenation reactor feedstock.

Tab. 3 shows the optimal activity of HF and the ratio of acid to the reactor and for the types of raw materials characterized by different contents of light and heavy hydrocarbons: $(C_{10} + C_{11})/(C_{12} + C_{13})$.

Table 1. Compositions of the dehydrogenation feed stock samples

| Component | Content in the feedstock, wt. % | | |
|---|---|---|---|
| | 06.04.2013 | 02.04.2012 | 22.10.2012 |
| $C_9$ | 0.00 | 0.00 | 0.00 |
| $C_{10}$ | 11.58 | 14.22 | 12.70 |
| $C_{11}$ | 27.57 | 30.90 | 36.73 |
| $C_{12}$ | 34.23 | 30.72 | 28.97 |
| $C_{13}$ | 23.67 | 21.25 | 18.74 |
| $C_{14}$ | 0.18 | 0.38 | 0.95 |
| Circulating LAB | 0.18 | 1.03 | 1.87 |
| Isoparaffins | 2.59 | 1.50 | 2.73 |
| $(C_{10}+C_{11})/(C_{12}+C_{13})$, rel. units. | 0.676 | 0.861 | 1.033 |

Table 2. Dehydrogenation process calculation results

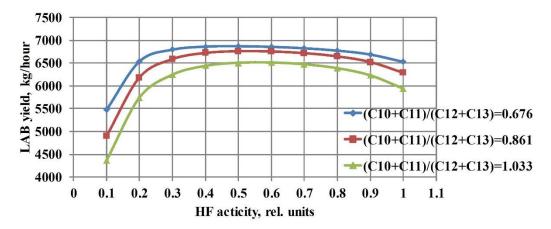| $(C_{10}+C_{11})/(C_{12}+C_{13})$ in the dehydrogenation feedstock, rel. units | $(C_{10}+C_{11})/(C_{12}+C_{13})$ olefines in the dehydrogenation products, rel. units | Olefines yield, kg/hour |
|---|---|---|
| 0.676 | 0.565 | 4843.25 |
| 0.861 | 0.476 | 4854.75 |
| 1.033 | 0.599 | 4775.25 |



Figure 1. Dependence of the LAB yield on the activity of the HF catalyst for various types of the dehydrogenation reactor feedstock

Table 3. Optimal alkylation process parameters depending on the dehydrogenation feedstock composition

| $(C_{10}+C_{11})/(C_{12}+C_{13})$ in dehydro-genation feed-stock, rel. units | Optimal HF catalyst activity, rel. units | HAr, kg/hour | Optimal HF flow rate to regene-ration, m³/hour | LAB, kg/hour | | ΔLAB, t/days |
|---|---|---|---|---|---|---|
| | | | | Optimal mode | Current mode | |
| 0.676 | 0.44 | 20 | 3.59 | 6610 | 6522 | 2.1 |
| 0.861 | 0.50 | 23 | 4.13 | 6693 | 6606 | 2.0 |
| 1.033 | 0.60 | 26 | 4.67 | 6592 | 6504 | 2.1 |

From the table 3 it follows that in order to ensure maximum LAB yield when feeding light feedstock to the reactor, it is required to maintain a higher HF activity and, consequently, a higher consumption of acid in the regenerator column. This is explained by the need to

compensate for the low reactivity of light hydrocarbons with a high activity of the HF catalyst. Thus, the smaller the ratio $(C_{10} + C_{11})/(C_{12} + C_{13})$, the less "tough" conditions are required for the dehydrogenation reaction in the first stage of production. This leads to a decrease in the content of diolefins in the feedstock of the alkylation process and, accordingly, to a decrease in the rate of HAR accumulation in the reactor.

Thus, from the point of view of LAB yield, it is advisable to use heavier raw materials in the paraffin dehydrogenation stage. All other things being equal, such raw materials make it possible to obtain the maximum LAB yield due to the high reactivity of hydrocarbons with a longer chain length. At the same time, each value of the feedstock of the dehydrogenation process corresponds to a certain value of the optimal activity of the HF catalyst, which makes it possible to increase the production of LAB in the alkylation stage. Thus, for example, for a feedstock with a composition $(C_{10} + C_{11})/(C_{12} + C_{13})$ of 0.676, the optimum activity of HF is 0.44 rel. units, and for raw materials with the composition $(C_{10} + C_{11})/(C_{12} + C_{13})$ of 1.033 the HF optimum activity is 0.6 rel. units.

### 3.2. Dependence of the alkylation process optimal parameters on the feedstock flow rate to dehydrogenation
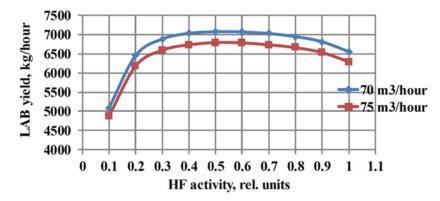
Despite the fact that in the olefin production plant the raw material consumption was maintained at a level of 75 m$^3$/hour for a long time, sometimes the load is reduced from 70 m$^3$/hour. The reduction in the load on the raw material affects the contact time of the reagents in the dehydrogenation process and, accordingly, at the output and composition of the product.

With the use of a computer simulation system, the parameters of the dehydrogenation of olefins and the hydrogenation of diolefins were calculated at various feedstock flow rates to the dehydrogenation reactor. The results of calculations are shown in tab. 4.

Table 4. Calculation results for dehydrogenation reactor

| Raw materials flow rate to dehydrogenation, m$^3$/hour | $(C_{10}+C_{11})/(C_{12}+C_{13})$ in the hydrogenation products, rel. units | Diolefins in the dehydrogenation product flow, wt. % | Olefins yield, kg/hour |
|---|---|---|---|
| 70 | 0.550 | 0.54 | 5096 |
| 75 | 0.549 | 0.52 | 4871 |

Calculations showed that when the feed flow rate to dehydrogenation reactor is 75 m$^3$/hour, less olefins are formed than at 70 m$^3$/hour (this is explained by the shorter contact time of the reactants), and the products of the dehydrogenation process are more heavy (this is due to the fact, that at a lower value of the contact time, more reactive olefins with a longer chain length can enter the dehydrogenation reaction). The low content of diolefins in the products of the dehydrogenation reactor at a higher consumption of raw materials is also due to a lower contact time.



Figure 2. Dependence of the LAB yield on the current HF catalyst activity at various feedrates to the dehydrogenation reactor
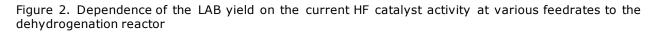
Fig. 2 shows the dependence of the LAB yield on the current HF catalyst activity at various feedrates to the dehydrogenation reactor for a feed composition characterized by a ratio of $(C_{10} + C_{11})/(C_{12} + C_{13}) = 0.861$.

Tab. 5 presents the optimal parameters of the alkylation process and the regenerator at various feedstock flow rates to dehydrogenation reactor.

Table 5 Optimal alkylation process parameters depending on the dehydrogenation feedstock flow rate

| Dehedrogenation feed flow rate, m³/hour | Diolefines in hydrogenation products | $((C_{10} + C_{11})/(C_{12} + C_{13})$ in hydrogenation reactor products | HAR, kg/hour | Optimal HF flow rate to regenerator m³/hour | HF activity, rel. units | LAB, kg/hour | | ΔLAB, t/day |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Optimal mode | Current mode | |
| 70 | 0.54 | 0.550 | 0.50 | 24.0 | 4.3 | 6963 | 6878 | 2.03 |
| 75 | 0.52 | 0.549 | 0.52 | 23.0 | 4.1 | 6668 | 6578 | 2.16 |

With an increase in the feed rate to the dehydrogenation reactor from 70 to 75 m³/hour, the olefin consumption is reduced from 5096 to 4871 kg/hour, the content of diolefins in the dehydrogenation reactor products is also reduced from 0.54 to 0.52 wt. %, which is associated with a decrease in time contact. When dehydrogenation and hydrogenation products enter the alkylation reactor, a decrease in the amount of HAR is observed, leading to a reduction in the recommended flow rate of HF to the regenerator from 4.3 to 4.1 m³/hour. Maintaining HF activity at the required level allows to increase the production of LAB by about 2 tons/day.

## 4. Conclusion

Thus, the theoretical and numerical studies carried out, as well as the analysis of available experimental data, allowed us to establish the following patterns of change in the optimal activity of the HF catalyst in the alkylation stage, depending on the operating conditions of the dehydrogenation reactor.
1. When using light feedstocks (with the ratio $(C_{10} + C_{11})/(C_{12} + C_{13}) = 1.033$), the dehydrogenation stage requires the maintenance of a higher activity of HF catalysts to provide the required LAB production (0.6 rel. units) and more high flow rate HF in the regenerator (4.67 m³/hour).
2. With an increase in the feed rate to the dehydrogenation reactor and also with an increase in the hydrogen / feed ratio, the optimum flow rate of HF to the HF regeneration column is reduced by reducing the content of diolefins in the dehydrogenation process products and therefore in the feedstock of the alkylation reactor.

## Acknowledgements

### List of symbols

$C_i$      concentration of the i-th component (mol m⁻³)
$C_p$      heat capacity of reaction mixture (J m⁻³ K⁻¹)
$G$      feed flow (m³ hour⁻¹)
$T$      temperature (K)
$T^{in}$      initial temperature (K)
$V$      reaction volume (m³)
$W_j$      reaction rate (mol m⁻³ hour⁻¹)
$Z$      the total volume of the recycled raw materials (m³)
$a_j$      a change in the j-th reaction rate due to viscous component or coke accumulation
$ΔH_j$      change in the enthalpy of the j-th reaction (J mol⁻¹)

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