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Mathematical Model of Alkylbenzenes Sulfonation Process Considering the Coloring Products Formation

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Abstract

This work is devoted to the development of a mathematical model of the process of alkylbenzene sulfonation with sulfuric anhydride in a multi-tube film reactor considering the deactivation of the reaction medium and the formation of coloring products that worsen the quality of alkylbenzene sulfonic acid and reduce its shelf life. It was decided to accept tetralins and polysulfonic acids as such coloring components, which can be formed during the resulfonation of alkylbenzenes in the upper layers of the organic liquid film. We developed a reaction network in the sulfonation process, taking these reactions into account, and modified the existing mathematical model of the sulfonation reactor with corresponding equations.

Keywords: *Sulfonation; Linear alkylbenzene; Alkylbenzenesulfonic acid; Coloring products; Mathematical modeling.*

1. Introduction

Synthetic detergents and surfactants based on alkylbenzenesulfonic acids (ABSA) are of great importance in meeting the needs of people, and are also used in various industries [1–3]. In the conditions of increasing market competition and strengthening measures aimed at environmental protection, as well as the need to reduce dependence on foreign technologies, it is extremely important to ensure maximum efficiency of production of environmentally friendly and highly effective surfactants. One of the domestic enterprises has implemented a full cycle of production of ABSA from higher paraffins, including successive stages of dehydrogenation of alkanes of the C_{10}-C_{14} fraction on a Pt catalyst, hydrogenation of by-products - alkenes, alkylation of benzene with olefins in the presence of HF and sulfonation of the resulting linear alkylbenzenes with sulfuric anhydride in a film-type apparatus under conditions of a highly viscous reaction medium [4-5].

Due to the inevitable formation of highly viscous and color-forming components in the sulfonation reactor, the efficiency of the multi-stage production of ABSA is determined by the efficiency of the stages and inevitably decreases during the catalyst cycle (for the catalytic stages of dehydrogenation and alkylation) and during the inter-wash cycle (for the non-catalytic stage of sulfonation) [6-7]. It is important to prevent the share of the target product in the product stream from decreasing below 96% by weight and from increasing the viscosity above 175 cSt. Due to the impossibility of solving such problems by means of an industrial experiment, it is advisable to develop a non-stationary mathematical model of the sulfonation process of linear alkyl benzenes, taking into account the reactions of formation of highly viscous and color-forming components in order to predict and improve the efficiency of a multi-tube film reactor in the technology of synthesis of surfactants based on ABSA. A distinctive feature of the study will be a combination of computational, laboratory and industrial experiments: using the laboratory setup available to the research team, the sulfonation process of alkylbenzene samples obtained from an industrial alkylbenzene sulfonic acid production plant

will be carried out; the established patterns of changes in the quality indicators of ABSA depending on the process parameters will form the basis of a non-stationary mathematical model that takes into account changes in the activity of the reaction medium of the sulfonation process during the formation of deactivating high-viscosity components and has predictive activity in relation to quantitative and qualitative indicators of the sulfonation process. The kinetic parameters of the mathematical model will be adjusted by processing experimental data from a real industrial plant over a wide time period. The results of the predictive and optimization calculations [8–10] will be tested on an existing industrial plant for the sulfonation of alkylbenzenes with sulfuric anhydride.

The sulfonation reactor operating at one of the refineries is a highly efficient device designed to optimize this process [11-12]. It has a vertical design consisting of reactor tubes placed inside a shell-and-tube heat exchanger. The reactor tubes have a throughput of 40 kg/h and an internal diameter of 25.4 mm. These parameters contribute to a high level of productivity and allow significant volumes of raw material processing. The length of the tubes is 6 meters, which provides sufficient time for reactions to occur and contributes to maximum product extraction. In the upper part of the reactor, there are distribution devices. The average SO_3 content in the gas mixture entering the reactor is 5% by volume [11].

During the sulfonation of alkylbenzenes the ABSA is formed. The temperature of the water cooling the reactor "jacket" should not exceed 36 °C. However, if the cylinder surface is cooled excessively, the viscosity of the reaction mass increases, and a product may be obtained that does not meet quality requirements.

The final cooling of the newly formed sulfonic acid in the reactor is carried out by mixing with the recirculated sulfonic acid cooled in the heat exchanger, which is returned to the bottom of the reactor (collecting chamber). The temperature of ABS and the waste gas at the outlet of the sulfonation reactor should not exceed 42°C. At a higher temperature, carbonized particles are formed and the color index of the product deteriorates (a darker acid is formed).

In the production of ABSA, an important aspect determining the quality of the final product is the ratio of sulfuric anhydride SO_3 and the active matter. Studies show that in order to achieve a high-quality product, it is necessary that the amount of SO_3 be in a slight excess relative to alkylbenzenes. This ratio provides sufficient reactivity for complete sulfonation of alkylbenzenes. If SO_3 is present in insufficient quantities, an increase in the proportion of non-sulfonated residue in the sulfonic acid is observed. Under conditions of excess sulfuric anhydride, the content of H_2SO_4 in ABSA increases, which causes a darker color of the product.

2. Mathematical model of sulfonation process

The thermodynamic characteristics of reactions occurring in the sulfonation reactor were calculated during the sulfonation process using the Gaussian software package. The reaction network of hydrocarbons in sulfonation process is presented in Fig. 1.

Unlike the previously existing one, this transformation scheme takes into account the reactions of formation of disulfonic acids as the main color-forming components.

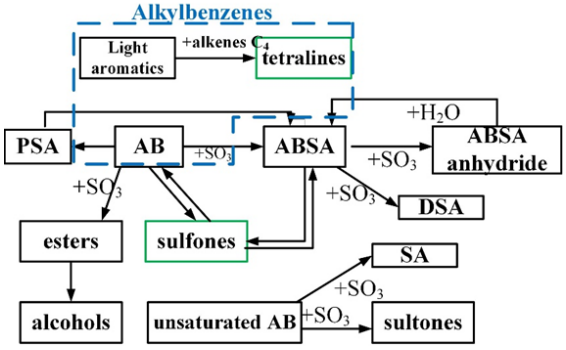

Figure 1. Reaction network of hydrocarbons in alkylbenzenes sulfonation process. AB – alkylbenzenes, PSA – pyrosulfonic acid, DSA – disulfonic acids (coloring components), SA – the product of unsaturated AB sulfonation into the side chain.

Based on the presented scheme of component transformations shown in Fig. 1, a mathematical model was developed that describes the process of alkylbenzenes sulfonation with sulfuric anhydride in a film reactor. This model is based on the assumption of an ideal displacement mode, which implies a uniform distribution of reagents in the reaction medium. The model considers changes in the composition of the reaction mixture, but also such parameters as temperature, pressure and reagent concentrations. To determine the kinetic parameters of the reactions, pilot-scale experimental data from the AB sulfonation unit were used. In general, the mathematical model of the benzene sulfonation reactor with olefins should consider convective transfer, molecular diffusion in the longitudinal and radial directions, temperature changes in the reactor due to cooling, and chemical transformation. Then the equations of material and heat balance in non-stationary form will have the following form.

$$\begin{cases} \frac{\partial C_i^l}{\partial t} = -u\frac{\partial C_i^l}{\partial l} + D_l\frac{\partial^2 C_i^l}{\partial l^2} + D_r\left(\frac{\partial^2 C_i^l}{\partial r^2} + \frac{1}{r}\frac{\partial C_i^l}{\partial r}\right) + \sum_{j=1}^{N} W_{ij} \\ \frac{\partial C_{SO_3}^g}{\partial t} = -u\frac{\partial C_{SO_3}^g}{\partial l} - \frac{\beta F \Delta C_{SO_3}}{V_r} \\ \rho^{mix} C_p^{mix}\frac{\partial T}{\partial t} = -u\rho^{mix} C_p^{\text{см}}\frac{\partial T}{\partial l} + \lambda_l\frac{\partial^2 T}{\partial l^2} + \lambda_r\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \sum_{j=1}^{N}(-\Delta H_j)W_j \end{cases} \quad (1)$$

Initial conditions: $t=t_0$ $C_i^l=C_{i0}^l$; $C_{SO_3}^g=C_{SO_{3(0)}}^g$; $T=T_0$

Boundary conditions: $l=0$ $C_i^l=C_{i0}^l$; $C_{SO_3}^g=C_{SO_{3(0)}}^g$; $T=T_0$

at $l=L$: $\frac{\partial C_i^l}{\partial l}=0$; $\frac{\partial C_{SO_3}^g}{\partial l}=0$; $\frac{\partial T}{\partial l}=0$;

at $r=(R-\delta)$: $T=T_0$, taking into account mass transfer across the phase boundary:

$$D_r\left(\frac{\partial^2 C_i^l}{\partial r^2}+\frac{1}{r}\frac{\partial C_i^l}{\partial r}\right)=\frac{\beta F \Delta C_i}{V_l}$$

If $(R-\delta) < r < R$ or $(R-\delta) > r$:

$$D_r\left(\frac{\partial^2 C_i^l}{\partial r^2}+\frac{1}{r}\frac{\partial C_i^l}{\partial r}\right)=0$$

$$\lambda_r\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)=0$$

at $r=R$: $\frac{\partial C_i^l}{\partial r}=0$; taking into account heat transfer through the wall:

$$\lambda_r\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)=\frac{K_T F_T \Delta T}{V_l}$$

where C_i – concentration of the i-th component, mole/m^3; C_i^l – concentration of the i-th component in liquid phase, mole/m^3; C_p^{mix} – mass heat capacity of the reaction mixture, J/(kg·K); $C_{SO3}{}^g$ – concentration of SO_3 in gas phase, mole/m^3; R – reactor radius, m; r – coordinate along the radius of the device, m; W_{ij} – rate of change in the concentration of the i-th component in the j-th chemical reaction, mole/(m^3·sec); ΔC_i – difference in component concentrations, mole/m^3; $(-\Delta H_j)$ – heat of j-th chemical reaction, J/mole; β – mass transfer coefficient, m/s; $\lambda_l(\lambda_r)$ – thermal conductivity coefficient in longitudinal and radial direction, W/(m·K); T – temperature, K; K_T – heat transfer coefficient, W/(m^2·K); F – interface area, m^2; u – linear flow velocity, m/s.

3. Results and discussion

When solving the inverse kinetic problem by the random search method with parabolic descent in the chosen direction of constant search. The accuracy of the description of experimental data is within the limits of quantitative analysis error.

The experimental and calculated using the mathematical model performance indicators of the sulfonation reactor are comparable (Table 1).

Table 1. Verification of the adequacy of the mathematical model of the alkylbenzene sulfonation process.

Output temperature, K			Ratio of unsulfonated matter in the product stream, %wt.			ABSA ratio in the product flow, %wt.		
Calc.	Exp.	Δ, %	Calc.	Exp.	Δ, %	Calc.	Exp.	Δ, %
41.0	40.6	0.9	1.9	1.7	14.1	96.8	96.4	0.4
40.9	40.8	0.1	1.9	1.7	13.5	96.9	96.4	0.5
40.9	41.1	0.5	2.2	1.9	13.2	96.5	96.8	0.3
41.0	40.7	0.8	1.9	1.7	12.9	96.9	97.0	0.1
41.1	40.5	1.5	1.9	1.7	12.9	96.9	96.9	0.0
40.9	40.6	0.6	2.0	1.8	12.2	96.8	96.3	0.5
41.1	40.7	0.9	1.8	1.6	11.3	97.0	96.3	0.7
41.0	40.9	0.1	1.9	1.7	10.0	97.0	97.0	0.1
41.1	40.7	1.2	1.9	1.7	10.0	97.0	96.9	0.1
40.9	40.7	0.4	2.1	1.9	10.0	96.6	96.6	0.0
41.0	40.5	1.2	1.8	1.6	10.0	97.0	96.9	0.1
40.9	41.1	0.5	1.8	1.6	9.4	97.1	96.6	0.5
41.2	41.1	0.3	2.1	1.9	9.0	96.7	96.8	0.1
40.9	40.2	1.6	2.1	1.9	9.0	96.6	96.7	0.1
40.9	40.6	0.7	1.7	1.6	8.8	97.0	96.8	0.2
41.0	40.8	0.4	1.7	1.6	8.8	97.1	96.8	0.3
40.9	40.9	0.1	1.7	1.6	8.8	97.1	96.7	0.4
41.6	41.0	1.6	2.0	1.8	8.3	96.7	96.5	0.2
41.0	40.6	0.9	1.8	1.7	8.2	97.0	96.7	0.3
41.1	41.0	0.3	1.8	1.7	8.2	97.0	96.9	0.1

Fisher and Student's criteria were also used to assess the adequacy of the mathematical model. Having calculated the variances for the variables X_{ABSA}^{calc} и X_{ABSA}^{exp} (calculated and experimental ratios of ABSA in the product flow), we obtain 0.053 and 0.020.

Then, using the formula for calculating Fisher's F-criterion, we find:

$$F = \frac{0{,}053}{0{,}02} = 2.66 \quad (2)$$

According to the Fisher criterion distribution table [13-14] with degrees of freedom equal to 109 in both cases, we determine that with significance levels of 0.05 and 0.01, the Fisher criterion table was 1.6 and 1.87, respectively. Thus, the obtained value *F* =2.66 falls within the significance zone. The Fisher criterion values were calculated similarly for such parameters as the proportion of unsulfonated residue in the product stream and the temperature at the reactor outlet. The results are presented in Table 2.

Table 2. Values of the Fisher criterion for the parameters of the mathematical model of the alkylbenzene sulfonation process.

Parameter	Values of the Fisher criterion	Values of the Students criterion
ABSA ratio in the product flow, %wt.	2.66	0.93
Ratio of unsulfonated matter in the product stream, %wt.	2.27	0.32
Output temperature, K	3.63	0.43

Thus, for all the parameters under study, the Fisher criterion value exceeds the table value, which indicates an adequate description of the sulfonation process by the mathematical model. The critical value of the Student criterion for the required significance level is determined from the Student distribution table. At significance levels of 0.05 and 0.01, this value was 2.0 and 2.66, respectively [15-16].

The values of the Student criterion for the parameters of the mathematical model of the benzene alkylation process with olefins are given in Table 2.

Thus, for all the parameters under study, the Student's criterion value is less than the table value. The values calculated using the mathematical model are adequate to the experimental data with the specified reliability. The developed mathematical models of the alkylation and sulfonation processes are implemented in software in the Delphi programming language and are made in the form of modules of the computer modeling system of the ABSA production complex, which is a tool for optimizing and predicting the operation of the main stages of synthesis.

The developed modeling system allows performing

- a forecast calculation that allows determining the duration of the inter-wash cycle and product color at a given composition of the sulfonation feedstock;
- an optimization calculation that allows determining the schedule of optimal sulfur consumption for combustion at a given content of highly viscous and coloring precursors in the sulfonation feedstock.

4. Conclusions

In the production of ABSA, an important aspect determining the quality of the final product is the ratio of sulfur trioxide SO_3 and alkylbenzene. Studies show that in order to achieve a high-quality product, it is necessary for the amount of SO_3 to be in a slight excess relative to AB. This ratio provides sufficient reactivity for complete sulfonation of AB substances. If SO_3 is present in insufficient quantities, an increase in the proportion of unsulfonated residue in the sulfonic acid is observed. Under conditions of excess sulfur trioxide, the content of H_2SO_4 in ABSA increases, which causes a darker color of the product. The quality of the sulfonation product depends on the composition of alkylbenzene. If the component composition of alkylbenzene is more uniform (alkyl radicals C_{11}-C_{12} predominate), then its sulfonation will be more uniform. Fractions below C_{11} are sulfonated faster, and fractions above C_{12} are slower, since the length of the alkyl radical affects the rate of the sulfonation reaction. The quality of sulfonic acid (especially the color) is greatly influenced by the presence of olefin groups in the alkyl radical of alkylbenzene. The double bond is very reactive, so SO_3 first reacts with it. The number of olefin groups can be judged by the bromine index, which for AB should not exceed 15 (mg Br_2/100 g).

The further objectives of the study are to establish the patterns of color change of ABSA and to find ways to improve the color characteristics of products using the developed computer modeling system.

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