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Mathematical Modeling of the Linear Alkylbenzene Sulfonation Process in A Multitube Film Reactor

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Abstract

In this paper, we analyze the influence of the content of aromatic hydrocarbon in the raw material flow on the concentration of the alkylbenzenesulfonic acid in the product mixture, the optimal sulfur consumption for combustion to obtain sulfonating gas, and the duration of the reactor operating period. It is shown that an increase in content in the raw material flow of aromatic hydrocarbon leads to a decrease of the alkylbenzenesulfonic acid in the product mixture, an increase the sulfur consumption, and a decrease in the duration of the reactor operating period.

Keywords: *Sulfonation; Linear alkylbenzene; Alkylbenzenesulfonic acid; Multi-tube film reactor; Tetralines; Sulfones; Mathematical modeling.*

1. Introduction

Alkylbenzenes are the most common organic raw material in the production of alkylbenzenesulfonic acids (ABSA) and consist of a benzene core with an alkyl chain attached to it. The length of the alkyl chain depends on the feedstock, and the point of attachment to the benzene ring is largely determined by the manufacturing process. The degree of branching of the alkyl chain makes it possible to distinguish between two classes of alkylbenzenes: "hard" and "soft". Compounds with a linear alkyl chain are formed because of the catalytic synthesis of benzene and a mixture of pure alkenes in presence of hydrogen fluoride (HF). Linear alkylbenzenes (LAB) have largely displaced branched alkylbenzenes due to their improved biodegradability. The ABSA with a side chain length of 10-13 carbon atoms, used as a raw material for the production of synthetic detergents, is obtained by sulfonating LAB, mainly in multi-tube film reactors.

During sulfonation in a multitube reactor, organic raw materials are uniformly fed into the tubes of the reactor and in the form of a film flows down the inner surface of each. Gas mixture with sulfonating gas content up to 5.5 vol. % evenly distributed over all reactor tubes. The reaction mixture is cooled with cooling water outside in a cooling jacket.

The sulfonation process is characterized by high heat release. At high temperatures, a large amount of by-products is formed, such as tetralines and sulfones [1], which deteriorate the quality of products. At the same time, the process temperature depends on the composition and consumption of the processed raw materials, which determines the design features of the equipment.

The formation and accumulation of viscous side compounds necessitates periodic washing of the reaction tubes with water. Currently, there are various approaches to mathematical modeling of film reactors [2-8], but none of them considers the sulfonation process unsteadiness. On the example of the process of obtaining ABSA at the LAB-LABS oil refinery, a mathematical model of the process of sulfonation of alkylbenzenes was developed [10-13]. The use of the developed mathematical model made it possible to solve an important problem of optimizing the operation of the existing installation.

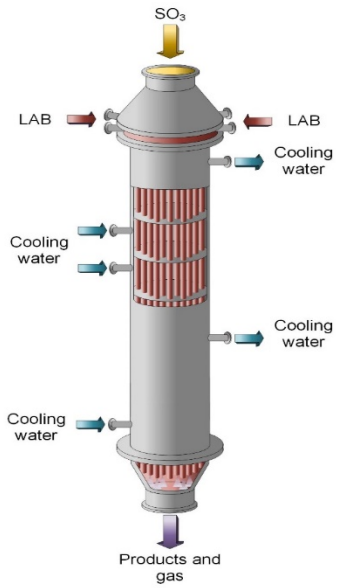

Figure 1. Sulfonation reactor construction

The mathematical model is a reliable tool for optimizing and predicting the operation of industrial reactors, allowing us to find new technical solutions to improve the efficiency of existing industries.

At the same time, mathematical modeling of chemical processes is based on experimental data. When it comes to developing a model of operating equipment, the first stage of research is always the analysis of a priori information about the process and available experimental data from an industrial plant.

The aim of this work is to increase the efficiency of the LAB sulfonation unit. The object of research is a multitube film reactor consisting of 120 tubes with a diameter of 25 mm and a length of 6 meters (Fig. 1) with a current LAB mass flow rate of 3500 kg/h, with a SO_3/LAB ratio of 1: 1.08 (the content of the sulfonating agent in the gas mixture is up to 5.5 vol.%). The contact time is τ = 27 sec.

2. Mathematical modeling

Based on the performed thermodynamic calculations, a formalized reaction network of transformations in the LAB sulfonation process and then the process mathematical model was developed. The mathematical model makes it possible to quantify the influence of such parameters as contact time, composition of the initial mixture, temperature and pressure in the system on the conversion rate of hydrocarbons. The calculation of the constants of chemical reactions was carried out by solving the inverse kinetic problem using experimental industrial experimental data. The sulfonation reactor model can be described as follows:

$$
\begin{cases}
G\frac{\partial C_{LAB}}{\partial Z}+G\frac{\partial C_{LAB}}{\partial V}=-k_1a_1C_{LAB}C_{SO_3}-k_5a_5C_{PSA}C_{LAB}-k_4a_4C_{LAB}C_{SO_3}^2- \\
-k_2a_2C_{ABSA}C_{LAB}+k_{-2}a_{-2}C_{unsulf.}C_{H_2O}; \\
G\frac{\partial C_{ABSA}}{\partial Z}+G\frac{\partial C_{ABSA}}{\partial V}=k_1a_1C_{LAB}C_{SO_3}+k_5a_5C_{LAB}C_{PSA}-k_3a_3C_{ABSA}C_{SO_3}^3+k_6a_6C_{ABSA\,unh.}C_{H_2O}- \\
-k_2a_2C_{LAB}C_{ABSA}+k_{-2}a_{-2}C_{unsulf}C_{H_2O}; \\
G\frac{\partial C_{PSA}}{\partial Z}+G\frac{\partial C_{PSA}}{\partial V}=k_4a_4C_{LAB}C_{SO_3}^2-k_5a_5C_{PSA}C_{LAB}; \\
G\frac{\partial C_{ABSA\,unh.}}{\partial Z}+G\frac{\partial C_{ABSA\,unh.}}{\partial V}=k_3a_3C_{ABSA}C_{SO_3}^3-k_6a_6C_{ABSA\,unh.}C_{H_2O}; \\
G\frac{\partial C_{unsulf}}{\partial Z}+G\frac{\partial C_{unsulf}}{\partial V}=k_2a_2C_{LAB}C_{ABSA}-k_{-2}a_{-2}C_{unsulf}C_{H_2O}+k_7a_7C_{LABuns}C_{SO_3} \\
G\frac{\partial C_{LABuns}}{\partial Z}+G\frac{\partial C_{LABuns}}{\partial V}=-k_7a_7C_{LABuns}C_{SO_3}; \\
G\frac{\partial C_{H_2SO_4}}{\partial Z}+G\frac{\partial C_{H_2SO_4}}{\partial V}=k_3a_3C_{ABSA}C_{SO_3}^3 \\
G\frac{\partial T}{\partial Z}+G\frac{\partial T}{\partial V}=\frac{1}{C_P}(Q_1k_1a_1C_{LAB}C_{SO_3}+Q_2k_2a_2C_{LAB}C_{ABSA}+Q_{-2}k_{-2}a_{-2}C_{unsulf}C_{H_2O}+ \\
Q_3k_3a_3C_{ABSA}C_{SO_3}^3+Q_4k_4a_4C_{LAB}C_{SO_3}^2+Q_5k_5a_5C_{PSA}C_{LAB}+Q_6k_6a_6C_{ABSA\,unh.}C_{H_2O}+ \\
+Q_7k_7a_7C_{LABuns.}C_{SO_3});
\end{cases}
\tag{1}
$$

$Z = 0,\ C_i = C_i^{in},\ T = T^{in}; V = 0,\ C_i = C_i^{in},\ T = T^{in}.$

Here the activity of the reaction mixture is determined as: $a_j = e^{-\alpha C_{v.c}}$.

If $Z = 0,\ C_{v.c} = 0,\ \alpha = 1,\ a_j = 1.$

Here: a_j – the activity of the reaction mixture in the j-th reaction, rel. units; C_i– concentration of the i-th component (mol/m^3); C_i^0 – initial concentration of the i-th component (mol/m^3); $C_{v.c}$ – concentration of the viscous component (mol/m^3); G – feedstock flowrate (kg/hour); T – temperature (K); ΔH_j – heat of the j-th rection (Дж/моль); α – parameter influencing the change in the rate of the j-th reaction due to the accumulation of a highly viscous component.

When creating a mathematical model, the following assumptions and assumptions were made:

- perfect displacement mode;
- no liquid droplets enter the gas or gas bubbles into the liquid film;
- fully developed film (effects of entry and exit into the reactor are not taken into account);
- the liquid film is symmetrical about the reactor axis;
- there are no radial gradients of temperature and concentration;
- deactivation of the reacting mixture occurs due to the formation of a viscous component, which inversely affects the reaction rate constants;
- the astronomical time of the process is replaced by the volume of processed raw materials during the time between reactor washings.

The film thickness in the model is taken into account when calculating the contact time for the current volumetric flow rate of the liquid:

$$\tau = \frac{(\frac{\pi d^2}{4} - \frac{\pi(d-2\delta)^2}{4}) \cdot n \cdot L}{V_r} \quad (2)$$

where V_r – reactor volume; m^3; L – reactor tube length; m; d – internal diameter of the reactor tube; m; n – number of tubes.

When calculating the concentration of ABSA in the product flow on the mathematical model, the error value does not exceed 1.5%, which does not exceed the error of the document, so the model can be considered adequate.

3. Experimental

An important quality indicator for sulfonated LAB is the content of aromatic compounds, for products of the sulfonation process - the mass fraction of ABS. The data on the qualitative chemical composition of LAB were obtained by GC-MS (gas chromatography-mass spectrometry), Trace DSQ equipment (Thermoelectron Corp., Xcalibur 1.4 software). The LAB composition was determined by IR spectroscopy using equipment Nicolet 5700 IR Fourier spectrometer. ABSK was investigated by IR spectroscopy and CHSN analysis. The compositions of unsulfonated residues were studied using IR spectroscopy and GC-MS.

The developed mathematical model of the LAB sulfonation process allows predicting the effect of technological parameters and the composition of raw materials on the volume and quality of the resulting product. The calculation was made on the basis of real data from the operating LAB sulfonation plant with sulfuric anhydride in a multitube reactor using the developed model for 4 periods between the reactor washings.

4. Results and discussion

4.1. Monitoring of the alkylbenzenes sulfonation unit operation using mathematical model

As a result of calculations on a mathematical model, the dynamics of changes in the concentrations of ABSA and H_2SO_4 were obtained during periods between the reactor washings (Fig. 2-9).

The standard deviation of the calculated values for period 27.12.2019 – 25.01.2020 is 0.3 for ABSA and 0.09 for H_2SO_4. The standard deviation of the calculated values for period 03.04.2020 – 20.04.2020 is 0.49 for ABSA and 0.15 for H_2SO_4. The standard deviation of the calculated values for period 24.04.2020 – 12.05.2020is 0.3 for ABSA and 0.13 for H_2SO_4. The standard deviation of the calculated values for period 13.03.2020 – 27.03.2020 is 0.38 for ABSA and 0.07 for H_2SO_4. As can be seen from Fig. 2-9**,** the standard deviation of the calculated data from the experimental data does not exceed 0.55 for ABSA and 0.15 for H_2SO_4.

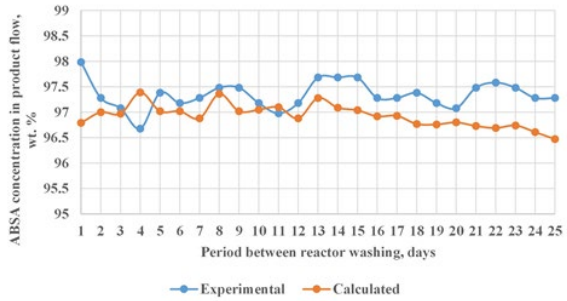

Figure 2. Experimental and calculated concentration of ABSA during the period 27.12.2019–25.01. 2020

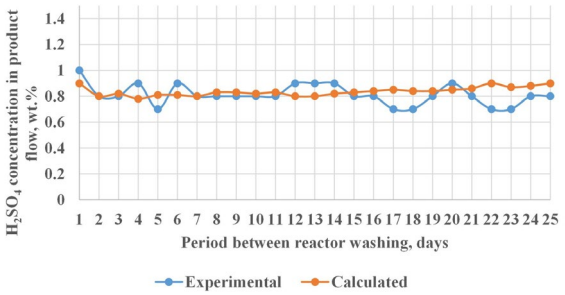

Figure 3. Experimental and calculated concentration of H_2SO_4 during the period 27.12.2019–25.01. 2020

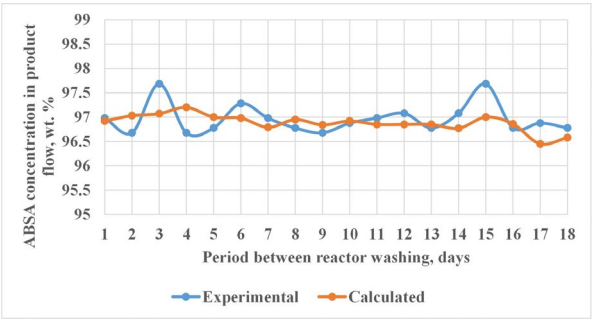

Figure 4. Experimental and calculated concentration of ABSA during the period 03.04.2020 – 20.04.2020

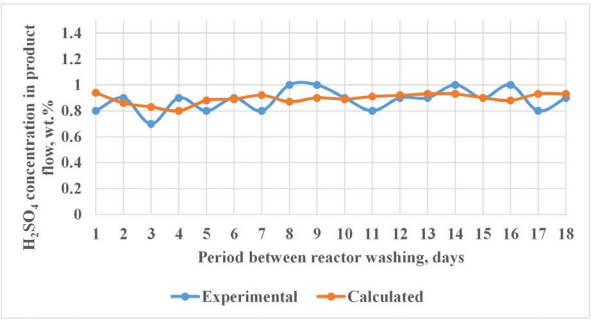

Figure 5. Experimental and calculated concentration of H_2SO_4 during the period 03.04.2020 – 20.04.2020

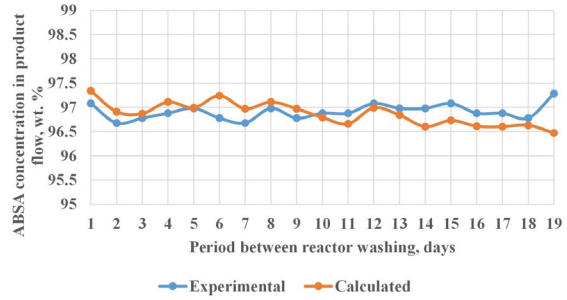

Figure 6. Experimental and calculated concentration of ABSA during the period 24.04.2020 – 12.05.2020

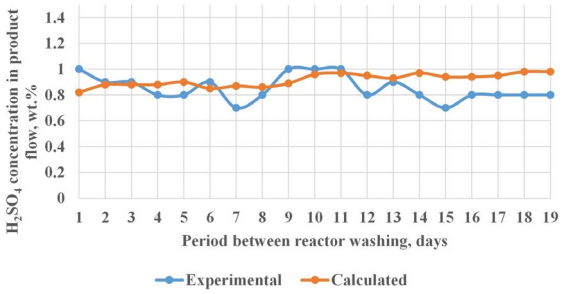

Figure 7. Experimental and calculated concentration of H_2SO_4 during the period 24.04.2020 – 12.05.2020

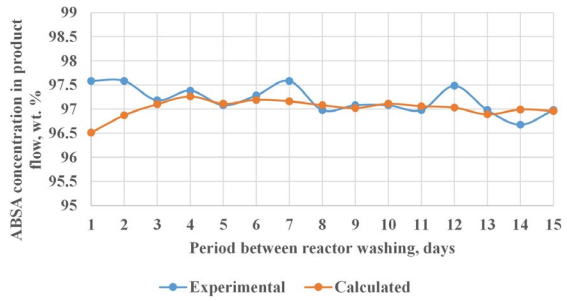

Figure 8. Experimental and calculated concentration of ABSA during the period 13.03.2020 – 27.03.2020

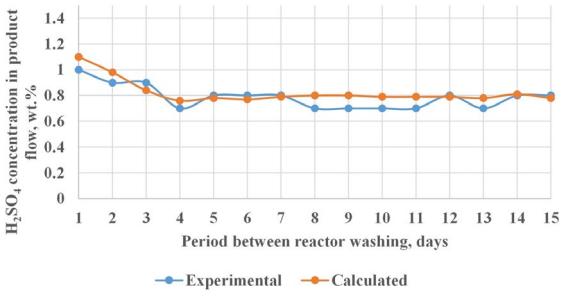

Figure 9. Experimental and calculated concentration of H_2SO_4 during the period 13.03.2020 – 27.03.2020

Table 1 shows the duration of the inter-flushing cycles, the calculated concentration of the viscous component on the last day of the unit operation cycle, the ratio of the content of phenyls with the length of the side chain $C_{10}+C_{11}/C_{12}+C_{13}$ in the feed and the average yield of ABSA in the product stream.

Table 1. Comparison of inter-flushing cycles

Period	Duration, days	Concentration of the highly viscous component, wt.%.	Phenyls ratio $C_{10}+C_{11}/C_{12}+C_{13}$	ABSA yield, wt.%
13.03.2020 - 27.03.2020	15	0.019	0.72	97.2
03.04.2020 - 20.04.2020	18	0.023	0.74	97.0
24.04.2020 - 12.05.2020	19	0.026	0.75	96.2
27.12.2019 - 25.01.2020	25	0.027	0.75	97.3

The concentration of the viscous component in the tubes of the reactor on the last day of the inter-washing cycle increases as the cycle time increases and the content of heavier components in the feed decreases (due to a decrease in the concentration of sulfonated feed molecules in the feed stream).

4.2. Study of the effect of the aromatic hydrocarbons content in the feedstock on the ABSA yield and the optimal consumption of combusted sulfur using a mathematical model

Using mathematical model, the optimal consumption of combusted sulfur and the ABSA yield were calculated for different concentrations of aromatic hydrocarbons in the feedstock (Fig. 10, 11). The calculations showed that an increase in the amount of aromatic compounds in the feedstock leads to a decrease in yield of the target product and to increase in the optimal consumption of combusted sulfur.

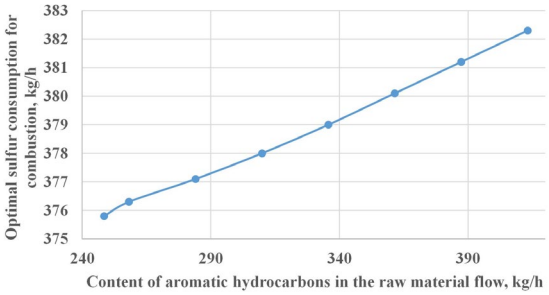

Figure 10. The ABSA yield depending on the content of aromatic hydrocarbons in the feedstock

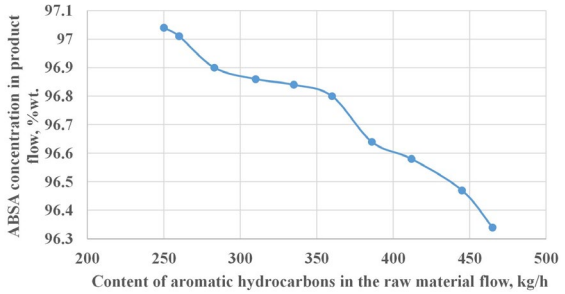

Figure 11. The optimal sulfur flowrate to combustion depending on the content of aromatic hydrocarbons in the feedstock

4.3. Calculating the duration of inter-washing period duration depending on the content of aromatic hydrocarbons in the feedstock

An important advantage of the mathematical model is that it allows you to calculate inter-flushing cycles depending on the concentration of aromatic compounds in the feed (Fig. 12).

A decrease in the content of aromatic compounds in the sulfonation feedstock leads to an increase in the duration of inter-washing cycles, since tetralines and sulfones, which are by-products of the process, are formed from aromatic compounds.

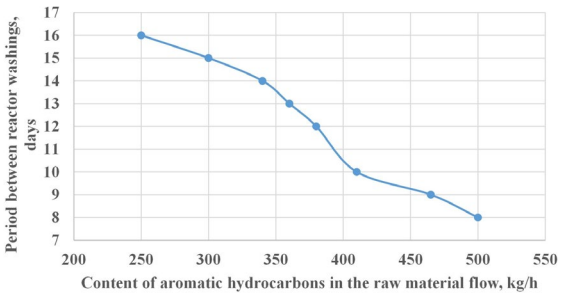

Figure 12. Inter-washing period duration depending on the concentration of aromatic hydrocarbons in the feedstock

5. Conclusions

It was found that the standard deviation does not exceed 0.55 for ASBA and 0.15 for sulfuric acid when carrying out calculations on the mathematical model of the LAB sulfonation process with sulfuric anhydride for 4 inter-washing cycles using data from the existing production.

The duration of the inter-washing cycles is influenced by the ratio of phenyls with the side chain length $(C_{10}+C_{11})/(C_{12}+C_{13})$ - with an increase in the molecular weight of the raw material, the duration of the inter-washing cycles increases.

The turbulent film flow of liquid increases the intensity of heat and mass transfer processes. Effective industrial implementation of heat and mass transfer processes in film-type reactors is largely constrained by the lack of mathematical models on a physicochemical basis, which make it possible to develop a scientifically grounded concept of their design and operation. The developed mathematical model on a physicochemical basis takes into account the unsteady reactants and accumulation of the viscous component in the reaction zone of the film sulfonation reactor.

According to calculations carried out using a mathematical model, it was found that the maximum concentration of ABSA is 97 wt.%. It can be obtained from raw materials with a concentration of aromatic substances entering the sulfonation reactor with LAB not exceeding 5.9 wt. %. According to the calculations, with an increase in the concentration of aromatic compounds in the raw material, it is necessary to increase the consumption of burned sulfur.

The duration of the sulphonation reactor inter-washing periods can be calculated in advance depending on the aromatics content in the feedstock. Calculations have shown that with a maximum aromatic hydrocarbon content of 498.76 kg/h, the cycle time is 8-9 days, and with a minimum aromatic hydrocarbon content of 238.63 kg/h, the cycle duration is about 15-16 days.

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