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Development of a Diffusion Mathematical Model for the Sulfonation of Linear Alkylbenzenes with Sulfuric Anhydride in A Multitube Film Reactor

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Abstract

The diffusion mathematical model of the linear alkylbenzenes sulfonation process with sulfuric anhydride in a multi-tube film reactor was developed. Using the developed mathematical model, the dynamics of changes in the target product - alkylbenzenesulfonic acid and by-product - sulfuric acid were obtained during two inter-flushing cycles. The dynamics of changes in the concentration of the high-viscosity component along the vertical and radial axes of the reactor tube is obtained. It is shown that the concentration of the highly viscosity component increases along the length of the reactor tube.

Keywords: *Sulfonation; Linear alkylbenzene; Alkylbenzenesulfonic acid; Multi-tube film reactor; Highly viscous component; Mathematical modeling.*

1. Introduction

Alkylbenzene sulfonic acid (ABSA) is an alkyl aromatic compound with a linear or branched side chain of varying length [1-7]. ABSA finds application in various fields due to its detergent, emulsifying and wetting properties, and ABSK salts are the main components in the production of surfactants used in household chemicals, personal hygiene products and in industry. Currently, the greatest demand is for ABSA with a linear side chain with a length of mainly 10-13 carbon atoms due to their good biodegradability.

ABSA is produced by sulfonation of linear alkylbenzenes (LAB) with various sulfonating agents in reactors of various designs. Currently, the most effective technology is the sulfonation of LAB with sulfuric anhydride in thin films [8-10].

The reactor for LAB sulfonation with sulfur trioxide considered in this work consists of 120 tubes with a diameter of 25 mm and a length of 6 m. When LAB sulfonation with sulfuric anhydride in a multitube film reactor, organic raw material flows uniformly along the inner perimeter of each tube. Air-gas mixture with a sulfonating agent content up to 5.5% vol. fed from the top of the reactor. The average mass flow rate of LAB is 3500 kg/h, with a SO_3/LAB ratio of 1: 1.08 mol/mol.

In practice, the technology for ABSA producing in a multitube reactor is complicated by the occurrence of side reactions with the formation of viscous products that clog the reactor tubes. Their negative effect mainly lies in the fact that the presence of deposits on the walls of the reactor tubes complicates the further diffusion of sulfur trioxide into the depth of the organic matter film. This, in turn, leads to the fact that the concentration of ABSA in the product stream decreases over time, since the sulfonation reaction of linear alkylbenzenes cannot proceed in the entire volume of the liquid phase. When a certain concentration of viscous components is reached, the reactor is flushed with water.

In industry, the main factor indicating the need to flush the reactor is the readings of the pressure sensor of the sulfur trioxide gas mixture entering the reactor. Thus, if a certain pressure value is exceeded, the LAB sulfonation unit completely stops and the reactor tubes are flushed with water.

An increase in the share of non-sulfonated compounds in ABSA (due to which the commercial properties of the product decrease, which is the reason for the release of substandard batches) is one of the pressing production problems that needs to be addressed. The results of multiple industrial experiments indicate that an increase in the sulfur consumption in the sulfonation reactor does not always lead to a decrease in the proportion of unsulfonated residue, but at the same time leads to an increase in the sulfuric acid content in the system. Experimental and numerical studies have shown that the reason lies in the formation of a highly viscous component, represented by tetralins and sulfones, which increase the viscosity of the mixture. In order to increase the efficiency of the operation of the sulfonation reactor, a single-tube reactor was replaced with a multi-tube one at the investigated industrial plant, which made it possible to increase the selectivity of the process to an average of 98%, but did not solve the problem of the formation of a high-viscosity component from aromatic compounds in the feedstock. With the accumulation of a high-viscosity component, the hydrodynamic flow regimes are violated, diffusion of SO_3 in the LAB film is hindered, over-sulfurization of LAB in the upper layers of the film can occur, while the lower layers can remain unreacted.

In this regard, another important aspect is the need to ensure optimal dosage of sulfur in the sulfonation reactor in order to ensure optimal acidity of the medium: with insufficient sulfur consumption in the product stream, a large amount of unreacted LAB is observed, with an excessive amount of sulfur, an increase in the acidity of the medium is observed, which intensifies the formation of highly viscous components. - sulfones, and also leads to an excess of the permissible concentration of H_2SO_4 in the composition of ABSA.

The aim of this study is to develop a non-stationary diffusion mathematical model [11-14] of the process of sulfonation of linear alkylbenzenes in order to predict and improve the efficiency of a multitube film reactor in the technology of surfactant synthesis based on sulfonic acids.

2. Development of a diffusion mathematical model of sulfonation process

In the process of developing a diffusion mathematical model of sulfonation, a ready-made program was used, which was a desktop application implemented in the Delphi language.

The architecture of the application is made according to the MVC design pattern, since it is advisable to store a large amount of data used in the process of program execution in a separate database. At the same time, for the convenience of the end user, it is necessary that the graphical representation is not affected in any way by changes in the data interaction model - that is, making changes to the application's API should not create inconvenience when interacting with its GUI.

Thus, the implementation of the diffusion model was a reengineering of the existing legacy code with refactoring before and after, as well as documentation during development in order to improve code maintenance.

The equation for the change in the concentrations of components in the diffusion model consists of several parts: the first, which describes the change in concentration along the length of the reactor, the second, takes into account its change in the radial direction, while the third is the sum of the reaction rates in which this component is involved - that is, it is the kinetic component equations.

Thus, the change in the concentration of the component along the tubes of the reactor will be described by the equation (1):

$$\left(\frac{\partial C}{\partial t}\right)_l = -u\frac{\partial C}{\partial l} \qquad (1)$$

where: u – linear velocity of the flowing liquid, m/sec; C – concentration of the component, mol/m^3; t – astronomical time, sec.

The minus sign in front of the value of the linear flow rate of the liquid film is due to the fact that its vector is directed in the opposite direction from the direction of the corresponding coordinate axis.

The change in concentration along the radial axis (along the film thickness) can be written using the diffusion coefficient *Dr* in the form of equation (2):

$$\left(\frac{\partial C}{\partial t}\right)_R = D_R\left(\frac{\partial^2 C}{\partial R^2}\right) + \frac{1}{R}\frac{\partial}{\partial R} \quad (2)$$

where D_r is the diffusion coefficient of gas into liquid; R is the radius of the reactor tube, m.

The kinetic model has already been described in previously published works [???]. We can say that for any component, the dynamics of changes in concentration will look like:

$$\left(\frac{\partial C}{\partial t}\right)_K = \sum_i W_i. \quad (3)$$

Thus, the resulting equation for the change in the concentrations of the components will have the following form:

$$\frac{\partial C}{\partial t} = \left(\frac{\partial C}{\partial t}\right)_l + \left(\frac{\partial C}{\partial t}\right)_R + \left(\frac{\partial C}{\partial t}\right)_K = -u\frac{\partial C}{\partial l} + D_R\left(\frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R}\right) + \sum_i W_i. \quad (4)$$

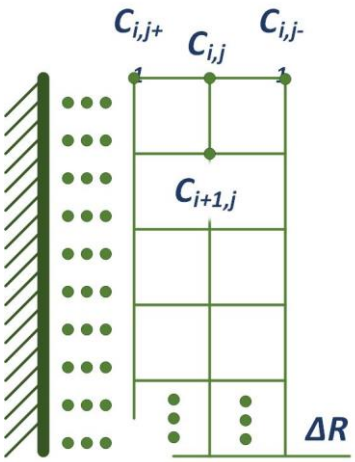

Figure 1. Breaking the liquid film into cells and assigning them indices

The main idea of the diffusion model is to break the liquid film into individual cells, as shown in Fig. 1.

The splitting of the liquid film into cells is as follows: along the vertical axis of the tube, the film is divided into layers - the length of the tube is divided by an infinitely small number, the height of the layer Δl. Similarly, this is carried out for the radial axes inside the tube: the value of the film thickness is divided by an infinitely small value - the value of the thickness of the film layer ΔR, in order to obtain an infinitely large value of the number of layers. Obviously, the accuracy of the calculations correlates with the frequency of the resulting grid in direct proportion.

In the application, layering is implemented as a function that takes the required film layer thickness as an argument, divides the film thickness by the function argument, and returns the resulting integer value of the number of layers. The same applies to the number of layers of film along the vertical axis. It should be noted that both of these quantities in one way or another depend on the contact time, a quantity characterizing the length of the tube. In the application, it is possible both to directly set the contact time value, and to set the parameters by which it will be calculated by the following expression:

$$\tau = \frac{\pi\delta DLN}{G} \quad (5)$$

where τ – the contact time, sec; δ – the film thickness, mm; D – the tube diameter, mm; L – the tube length, m; N –number of tubes; G – the volumetric flow rate, m^3/h.

To solve the resulting simplified differential equation, it must be transformed using the finite difference method to the following form:

$$\frac{u}{\Delta l}\left(C_{i+1,j} - C_{i,j}\right) = D_R\left(\frac{C_{i+1,j} - 2C_{i,j} + C_{i,j-1}}{\Delta R^2} + \frac{1}{R}\frac{C_{i+1,j} - C_{i,j}}{\Delta R}\right) \quad (6)$$

where $C_{i,j}$– component concentration in the cell; ΔR –thickness of the film layer, m; Δl – the height of the film layer. It is advisable to make the following substitutions for easier perception:

$$\begin{cases} a = \frac{U}{\Delta l} \\ b = \frac{D_R}{\Delta R^2} \\ c = \frac{D_R}{R\Delta R} \end{cases} \quad (7)$$

Expression for the concentration of a component in a cell with coordinates i and j:

$$C_{i,j} = \frac{(b+c)C_{i,j+1} - aC_{i+1,j} + bC_{i,j-1} + f\left(C_{i,j}\right)}{2b - a + c} \quad (8)$$

Thus, to calculate the concentration of components in any cell, it is necessary to know the concentrations of these components at a point in the same reservoir, in the next and previous layers, as well as in the same layer one layer below.

To calculate the first approximation in the diffusion model, for the first three layers along the entire length of the tube, the concentrations of the components calculated using the previously developed model of a plug-flow reactor are taken, while for other layers, the concentrations of the components are taken to be zero.

The next step in the work of the diffusion model of sulfonation is to calculate the kinetic reaction rates for each cell in a film of a liquid substance. The calculation is carried out according to the following expression:

$$W_{m_{i,j}} = \sum_{j=1}^{J} \sum_{i=1}^{I} \sum_{m=1}^{M} K_m \sum_{n=1}^{N} C_{n_{i,j}}{}^{a_{m,n}} \quad (9)$$

where $W_{m_{i,j}}$ – the reaction rate in a cell with coordinates *i, j*; J – number of film layers; I – number of film layers; M – number of reactions occurring in the sulfonation process;, N – number of components existing in the process - these include: initial, target and side; K_m – coefficient of the *m*-th reaction rate; $C_{n_{i,j}}$– concentration of the component *n* in the cell with coordinates *i, j*; $a_{m,n}$ – stoichiometric coefficient of the component *n* in the *m*-th reaction.

It should be noted that the reaction rate coefficients were determined earlier, based on work with a plug-flow reactor model. These values, as well as the values of the activation energies for the reactions occurring in the film of organic matter, are shown in Table 1.

Table 1. Rate constants of chemical reactions

№	Reaction	E_a, J/mol	k, s^{-1}
1	LAB+SO_3 → ABSA	38	$2.2 \cdot 10^7$
2	ABSA+LAB ↔ sulfone +H_2O	35	10^6
3	Sulfone+ H_2O → ABSA+ LAB	100	10^4
4	2 ABSA+ SO_3→ABSA anhydride + H_2SO_4	40	2000
5	LAB+2SO_3 → PSA	110	$9.9 \cdot 10^2$
6	PSA+ LAB →2ABSA	100	$1.04 \cdot 10^3$
7	ABSA anhydride + H_2O → 2ABSA	25	$2 \cdot 10^4$

The final concentrations of each component are calculated by adding its concentrations in each of the layers of the film in the last layer, after which this sum is divided by the number of layers to obtain an average value.

3. Results and discussion

To assess the adequacy of the calculations obtained using the developed diffusion model, a comparison was made between the experimental data obtained from the existing production facility and the calculated data obtained from the results of the program for two inter-flushing cycles (Fig 2).

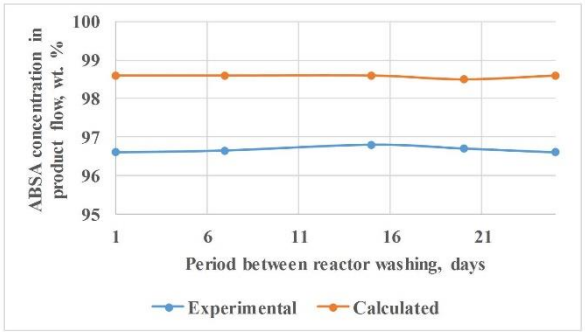

Figure 2. Comparison of the calculated and experimental ABSA yield in February 2020

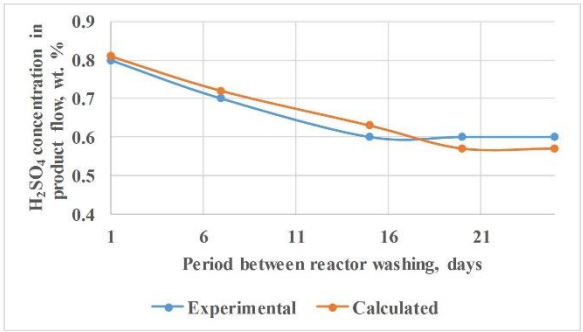

Figure 3. Comparison of the calculated and experimental sulfuric acid yield in February 2020

Drawing conclusions from the obtained values, we can conclude that the calculation according to this diffusion mathematical model is adequate from the point of view of the target component – alkylbenzene sulfonic acid, since the calculation error in this case does not go beyond 10%, which makes it possible to apply the model for further numerical studies.

Errors in calculating the concentration of sulfuric acid also have small values, the results of calculations for two inter-flushing cycles are shown in Fig. 3. Thus, the average value of the error in calculating the concentration of sulfuric acid is approximately 2.71%. Thus, we can conclude that the calculation of the yield of sulfuric acid is also adequate, since these error values do not exceed 10%.

3.1. Dynamics of the highly viscous component accumulation along the length of the reactor tube and the thickness of the organic matter film

As mentioned above, the simplification is accepted that the operating mode of the reactor is pseudo-stationary. In Fig. 4, it can be observed that the concentration of the highly viscous component changes depending on where in the virtual tube this parameter is considered. The concentration of the component on the first layers of the film increases the lower the layer of interest is located. It should be noted that the concentration of the highly viscous component, as well as of other components, decreases when it is observed along the radial axis.

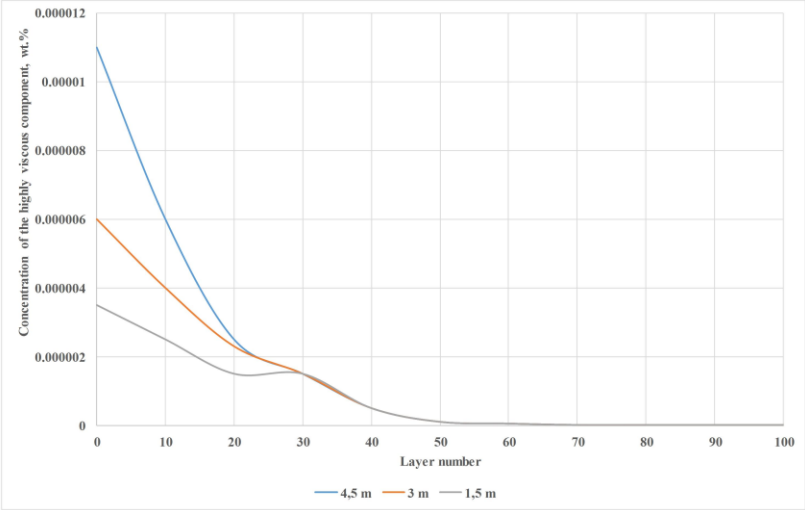

Figure 4. Dynamics of changes in the concentration of a highly viscous component along the vertical and radial axe

The presence of a highly viscous component in the reaction space can be explained by the fact that its formation is the result of chemical reactions of various side aromatic compounds at the previous technological stages of production.

4. Conclusions

In this research, a mathematical model of the LAB sulfonation process was developed with due consideration of the reaction medium deactivation by highly viscos components, diffusion and mass transfer, as well as the relationship with the mathematical models of the previous stages of production, sensitive to changes in the composition of raw materials, having a high predictive potential in relation to the yield and composition of products when changing technological conditions and composition of raw materials. The algorithm for solving a system of nonlinear non-stationary differential equations of material and heat balances of the sulfonation process was developed.

When carrying out calculations on the developed diffusion mathematical model of the process of sulfonation of linear alkylbenzenes with sulfuric anhydride in a multi-tube film reactor,

the dynamics of the target product yield, alkylbenzene sulfonic acid, and also the by-product, sulfuric acid, were obtained for two inter-washing cycles. These calculations were used to check the adequacy of the developed model - a comparison was made with the experimental values obtained from the existing production. In general, the obtained error values are in the region of 1.5-2.5%, which suggests that the model is adequate.

The dynamics of the accumulation of the high-viscosity component along the vertical and radial axes was demonstrated. The concentration of the highly viscous component increases along the length of the reactor tube.

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