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Optimal Design of the Film Sulfonation Reactor in Linear AlkylBenzene Sulfonic Acid Manufacturing Technology

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Abstract

Alkylbenzene sulfonic acid (ASA) is a valuable petrochemical product that is obtained using a variety of technologies. The purpose of this article is to compare the designs of the film sulfonation reactors and choose the most optimal one. The calculations were made using non-stationary mathematical models. For calculations, data were taken from operating LAB sulfonation plants.

Keywords*: Sulfonation; Alkylbenzene sulfonic acid; Single-tube film reactor; Multi-tube film reactor; Mathematical modeling.*

1. Introduction

Alkylbenzenesulfonic acid (ASA) is a chemical compound widely used as the main component of biodegradable detergents. ASA is a valuable petrochemical product obtained through the multi-stage process, the final stage of which is the sulfonation of linear alkylbenzenes (LAB). There are various sulfonation technologies: it is carried out in mixing reactors, rotated packed bed reactors, film reactors, and others [2-4].

Currently, sulfonation technology in thin films has become more widespread. The reactors developed for this technology come in different designs: consisting of two concentric tubes or a single-tube reactor, and a multi-tube reactor. The objective of the study was to compare reactor designs and choose the most optimal design.

The complexity and multi-stage process of obtaining ASA cause interest in its optimization and forecasting. However, the specificity of the process makes it impossible to use the existing universal modeling systems for these purposes [5].

2. Methodology [7]

The sulfonation reactor model can be described as follows:

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

(1)

$$G\frac{\partial T}{\partial Z} + G\frac{\partial T}{\partial V} = \frac{1}{C_p}\sum_j W_j \cdot (-\Delta H_j) \cdot a_j$$

where: a_j – activity, 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}); Cv.c. – concentration of highly viscous components (mol·m^{-3}); G – flow rate (kg h-1); T – temperature (K); T_0 – initial temperature (K); Wj – reaction rate (mol m^{-3} hour-1); Z – the total volume of the recycled raw materials (m^3); –ΔHj – heat of the j-th reaction (J mol^{-1}); δ – a change in the j-th reaction rate due to viscous component or coke accumulation.

2.1. Highly viscous component accumulation

The highly viscous component is formed during side reactions, and in addition, it depends on the composition of the feed at the alkylation stage. The more aromatic compounds contain in feed, the higher is the probability of tetralines formation. The accumulation of a highly viscous component is also facilitated by the nonuniformal flow of the organic film, the increase in its thickness, and the increase in temperature of the process [8]. So, in the arising areas of film thickening, not all linear alkylbenzene is able to turn into sulfonic acid; in other words, an area of undersulfurization is formed in this place [9]. In areas where the film is thinned, the ratio of LAB and sulfur oxide increases towards a sulfonating agent. Thus, more than one trioxide molecule can be attached to one linear alkylbenzene molecule. Various side components can form here, in particular, sulfones, which have a higher viscosity, and, accordingly, further exacerbate the unevenness of the process. Together, the areas of over-sulfonation, as well as undersulfonation, contribute to the active formation and accumulation of a highly viscous component. Upon reaching a critical concentration of a highly viscous component in the reaction mixture, it is necessary to flush the reactor in order to avoid obtaining an off-spec product batch. The critical concentration of the highly viscous component in the product stream is 0.034% by mass, which was determined based on the regulatory viscosity of the key product.

3. Experimental

The LAB single-tube sulfonation reactor consists of two concentric tubes; organic raw materials flow down the inner surface of the inner tube, forming a thin film and interacting with the gas supplied co-directionally into the tube space. The refrigerant is fed into the space between tubes.

The LAB multi-tube sulfonation reactor is consists of vertical reaction tubes located as in a shell-and-tube heat exchanger, with an internal diameter of 25 mm and a length of 6 meters. A stream of a mixture of gaseous sulfur trioxide and the air is passed through a vertical pipe, where organic liquid feed flows simultaneously along the wall. When liquid and gas flow through the pipe, sulfur trioxide is absorbed by the liquid and reacts to form a sulfonated product.

The development of a computer modeling system for the LAB sulfonation process allows us to predict the effect of various technological parameters and the composition of raw materials on the volume and quality of the products obtained [6].

4. Results and discussion

During the research, the effect of some technological parameters on the film reactors of a single-tube and multi-tube design was studied.

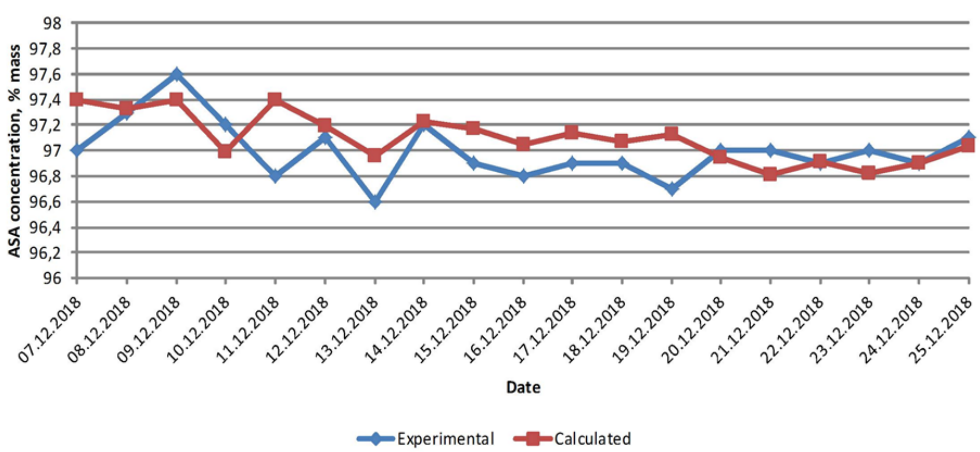

Figure 1. Dynamic of ASA concentration during the period between reactor washings in a multi-tubular reactor

The design parameters were evaluated, as well as the duration of the periods between reactor washings, the dynamics of the accumulation of the highly viscous component formed by sulfones and tetralines-the products of side reactions at the sulfonation stage, as well as the production of linear alkyl benzene. Along with this, the influence of the temperature at the inlet to the reactor on the yield of the key product was evaluated. In addition, the amount of sulfur supplied to the furnace to produce a sulfonating air-gas mixture was varied. The calculations were carried out on mathematical models, the adequacy of which was proved by a small discrepancy between the experimental and calculated data. For calculations, we used data from existing sulfonation plants during their operation at the plant.

Figure 1 shows the experimental and calculated dependence of the formation of ASA during the period between reactor washings. The small difference between the results of calculations and experimental values allows us to speak about the adequacy of the model.

4.1. Design and technological parameters

Table 1 shows a comparison of single-tube and multi-tube reactors by such parameters as the reaction surface, film thickness, and others.

Table 1. Comparison of single-tube and multi-tube reactors

Parameter	Single-tube reactor	Multi-tube reactor
Number of tubes	1	120
Tube length, m	3,0	6,0
Tube diameter, mm	133,0	25,0
Reaction surface area, m^2	12,5	56,5
Film thickness, mm	0,68	0,56
LAB flow rate, kg/h	2600	3500
Sulfur flow rate, kg/h	346	485
Average duration of period between reactor washings, days	14	20
Residence time, sec	10	27

As can be seen from the table, the amount of processed raw materials in a multi-tube sulfonation reactor is more than in a single-tube sulfonation reactor; however, the molar ratio of sulfur consumption and LAB is the same for both reactors.

You can also notice that the film thickness in a multi-tube reactor is less than in a single-tube one. In this regard, we can assume that the diffusion of sulfur trioxide into the organic phase is simpler, and accordingly, less favorable conditions are created for the occurrence of side reactions, which has a positive effect on the duration of the periods between reactor washings. So, the average length of the periods between reactor washings positively changed from a single-tube reactor to a multi-tube one.

4.2. Sulfur flow rate

To study the effect on the sulfonation process, the amount of sulfur supplied to the furnace was varied. For a single-tube reactor, the sulfur flow rate varied from 300 to 440 kg/h for a multi-tube reactor – from 450 to 590 kg/h. This is due to the fact that the flow rate of the supplied substances to the reactor of different designs varies. Calculation results are depicted in Figures 2-5.

Looking at the figures, it can be noted that for a single tube sulfonation reactor, the optimal sulfur flow rate is a concentration of about 380 kg/h. With an increase in sulfur consumption, the concentration of sulfuric acid also increases. This is an undesirable consequence since an increase in the concentration of sulfuric acid leads to a deterioration in the color of the product - the main indicator of quality.

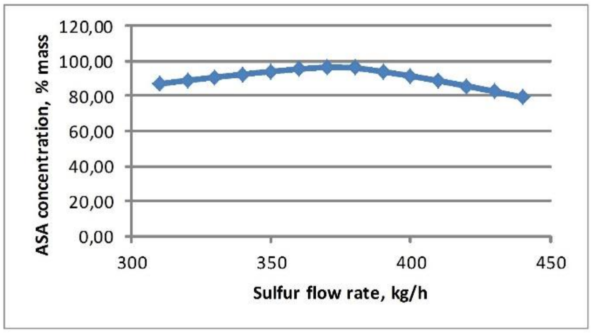

Figure 2. Dynamic of ASA concentration during the period between reactor washings in single-tube reactor at a various sulfur flow rate

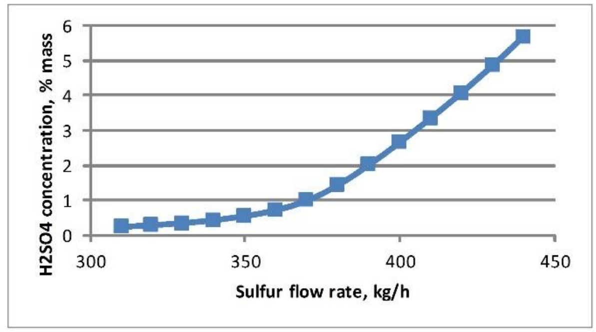

Figure 3. Dynamic of H_2SO_4 concentration during the period between reactor washings in single-tube reactor at a various sulfur flow rate

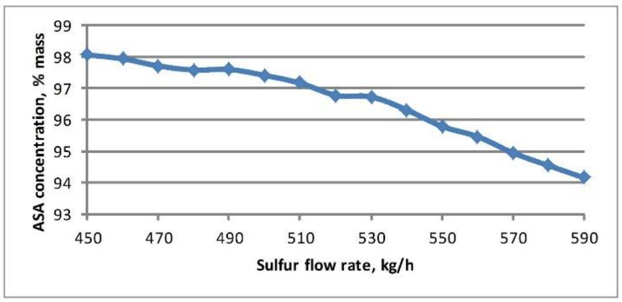

Figure 4. Dynamic of ASA concentration during the period between reactor washings in a multi-tube reactor at a various sulfur flow rate

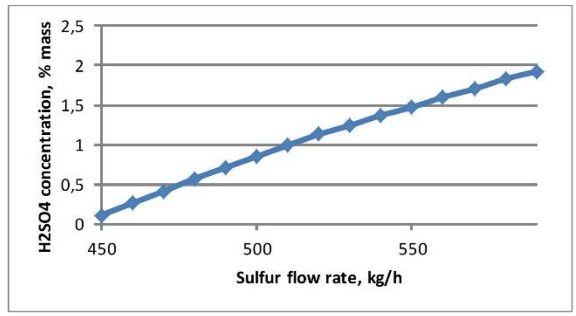

Figure 5. Dynamic of H_2SO_4 concentration during the period between reactor washings in a multi-tube reactor at a various sulfur flow rate

For a multi-tube reactor, it is more difficult to isolate the optimal value of sulfur consumption; however, it can be noted that the ASA yield is higher, the less sulfur is supplied for sulfonation.

4.3. Temperature affection

To study the effect of temperature on the sulfonation process, the temperature of the reaction medium in single-tube and multi-tube reactors was varied in the range from 30 to 52°C. The dependences obtained during the calculations are presented in Figures 6 and 7.

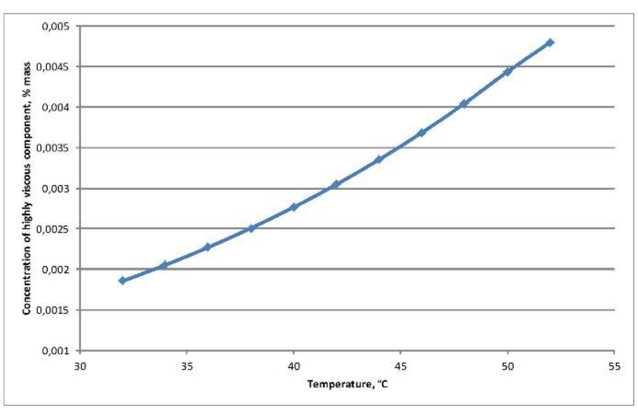

Figure 6. Dynamic highly viscous component accumulation during the period between reactor washings in single-tube reactor at various temperatures

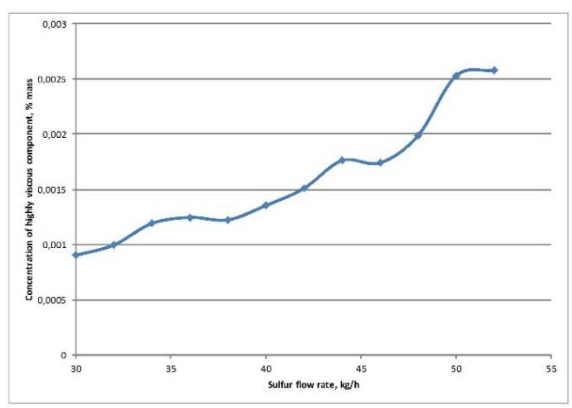

Figure 7. Dynamic highly viscous component accumulation during the period between reactor washings in the multi-tube reactor at various temperatures

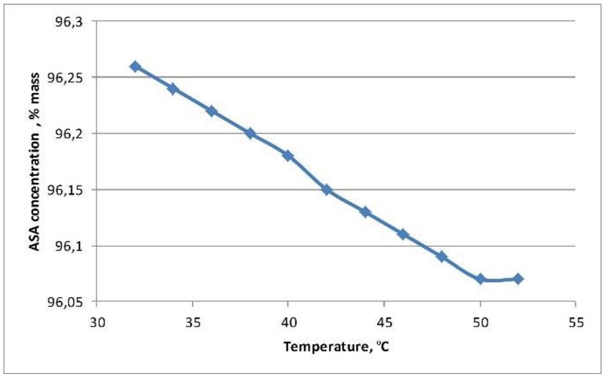

Figure 8. Dynamic of ASA concentration during the period between reactor washings in single-tube reactor at various temperature

From Figures 8 and 9, it is noticeable that in both a single-tube and multi-tube reactor, an increase in the temperature of the reaction medium negatively affects the accumulation of a highly viscous component

An increase in the temperature in the reactor, in addition to the accumulation of a highly viscous component, negatively affects the formation of linear alkylbenzenesulfonic acid (ASA) in both single-tube and multi-tube reactors.

Accordingly, it is necessary to maintain the temperature in the sulfonation reactors at the level of 35-40ºC for carrying out the process in the most optimal way.

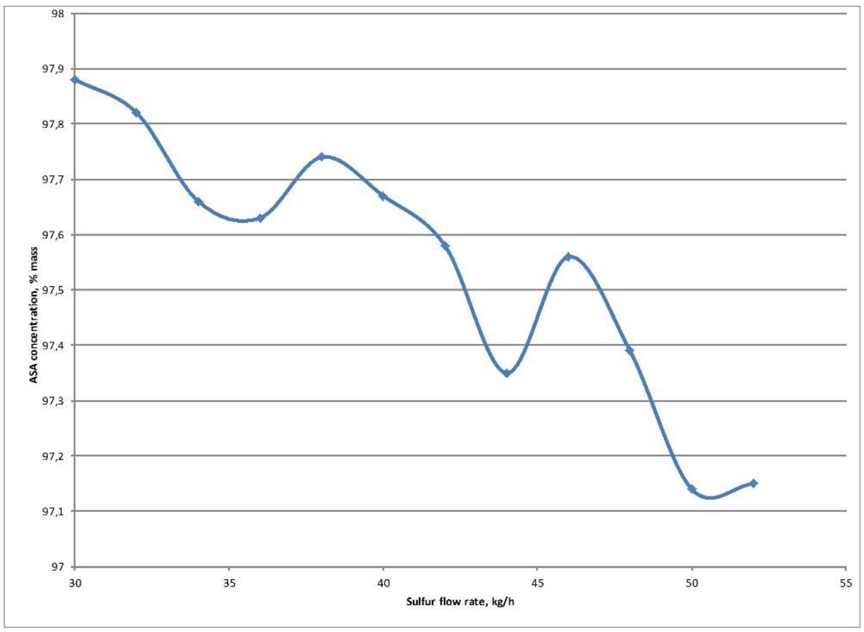

Figure 9. Dynamic of ASA concentration during the period between reactor washings in a multi-tube reactor at various temperature

5. Conclusions

The article compares the main characteristics of a single-tube and multi-tube sulfonation reactors by such parameters as the reaction surface area, the film thickness of the organic phase, the duration of the periods between reactor washings, and others.

In calculations on mathematical models, the effect of sulfur consumption upon receipt of sulfur oxide (VI), as well as the temperature of the process on the concentration of ASA and sulfuric acid in the product stream was estimated.

The duration of the period between reactor washings was determined for single-tube and multi-tube reactors. A multi-tube reactor showed better results than a single-tube one as the ASA concentration is higher; accumulation of highly viscous components is slower; therefore, it is possible to carry out the process longer and in a more resource-efficient way.

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