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Extending the Duration of Inter-Washing Cycles of a Multi-Tube Reactor for Linear Alkylbenzenes Sulfonation

Irena O. Dolganova, Igor M. Dolganov, Anastasiya A. Zykova, Emiliya D. Ivanchina, Elena N. Ivashkina*

Department of Chemical Engineering and Chemical Cybernetics, Institute of Natural Resources, Tomsk Polytechnic University; Russia

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Abstract

In this work, we analyze the influence of the linear alkylbenzenes consumption of in a multitube film sulfonation reactor on the formation of viscous by-products, tetralins and sulfones, using the method of mathematical modeling. It was found that an increase in the consumption of raw materials from 3500 to 4500 kg/hour at a constant molar ratio of SO_3/LAB equal to 1.08 makes it possible to achieve a decrease in the contact time of linear alkylbenzene with a sulfonating agent from 30.1 to 25.4 seconds and an increase in the duration of inter-flushing cycles due to a decrease in the viscosity of the organic liquid film and the normalization of the hydrodynamic regime of the flow of raw materials. It was also determined that the duration of inter-flushing cycles is influenced by the content of light aromatic hydrocarbons in the sulphonated raw material. An increase in the content of aromatic hydrocarbons leads to a decrease in the duration of the inter-flush cycles. This is due to the fact that light aromatic hydrocarbons are the source of the formation of viscous by-products - tetralins, which have a negative effect on the hydrodynamic regime of the liquid film flow. Calculations using a mathematical model showed that with an aromatic hydrocarbon content in the feed of 2 %wt. the duration of the inter-washing cycle at a standard flow rate of 3500 kg/hour is 15 days, and at 6 % wt. - 10 days. At the same time, an increase in consumption up to 4500 kg/hour makes it possible to achieve a cycle time at 2% wt. up to 17 days, and at 6% wt. up to 16 days.

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

1. Introduction

Currently, synthetic detergents (SD) are used not only in industry, but also in household. The annual growth in the consumption of SD leads to an increased interest in methods for the production of their main components, including the technology for the production of linear alkylbenzenesulfonic acids (ABSA) obtained in the process of sulfonation of linear alkylbenzenes, with further alkalinization of ABSA with sodium hydroxide, sodium salts of ABSA are obtained, which are the main component of numerous products used in household chemicals, in personal care products, as well as in industry [1-2].

Linear alkylbenzene sulfonate is the major anionic nonsoap surfactant used in laundry products. It is made by sulfonation of linear alkylbenzenes (LAB). LAS is presently made predominantly by sulfonation with sulfur trioxide, although in the past oleum and sulfuric acid were widely used and are still not completely obsolete in this role [3-10].

Although the manufacture of LAS has been practised for many decades, new insights into the sulfonation chemistry and more stringent quality requirements continue to evolve [11].

The sulfonation process is mainly carried out in film reactors. The sulfonation of linear alkylbenzene (LAB) in a multi-tube film reactor with sulfuric anhydride is accompanied by a high heat release; for this purpose, heat is removed by supplying water to the annular space. Also, the process is complicated by the formation of viscous side components that impede the uniform flow of the liquid film. Violation of the hydrodynamic regime leads to complete clogging of the reactor tubes and stopping the technological process, washing the reactor tubes with water, which allows removing by-products from the reaction space.

In previously published works [12-16], the influence of the design of the reactor and the consumption of reactants on the duration of the inter-flushing cycles was investigated.

In this work, the influence of the reagents consumption on the duration of the inter-washing cycles has been investigated. The problem is solved due to the fact that the method for controlling the duration of inter-washing cycles is to reduce the viscosity of the organic liquid film by increasing the consumption of sulfonated raw materials.

2. Sulfonation process mathematical model

An increase in the duration of the inter-washing cycle is regulated by a change in the hydrodynamic mode with accumulation of a large amount of a highly viscous component. When the concentration of the highly viscous component reaches 0.01 mol /l, the LAB consumption in the sulfonation reactor is increased. As a result, the contact time of the reagents decreases, the excess of highly viscous component is washed out from the reactor, and the thickness of the LAB film decreases.

According to the scheme of hydrocarbon transformations in the sulfonation process (Fig. 1), a highly viscous component formed in reactor is represented by tetralins and sulfones.

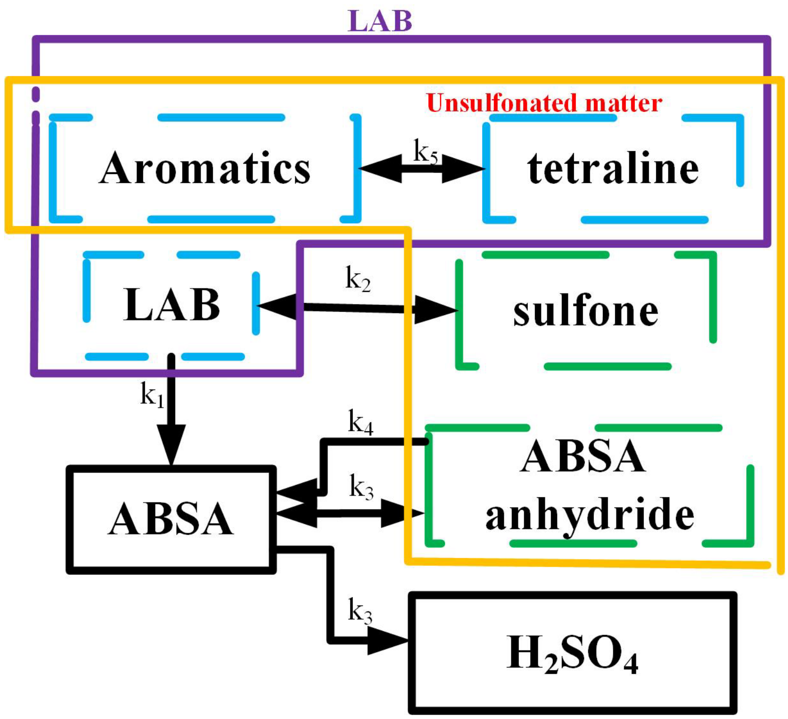

Figure 1. Reaction network of the sulfonation process

The process indicators are calculated by calculating a system of differential equations using a computer simulation system.

The change in the concentration of the highly viscous component is calculated using a mathematical model according to the equation:

$$G\frac{\partial C_{unsulf}}{\partial Z} + G\frac{\partial C_{unsulf}}{\partial V} = k_2 a_2 C_{LAB} C_{ABSA} - k_{-2} a_{-2} C_{unsulf} C_{H2O} + k_7 a_7 C_{LABuns} C_{SO3} \quad (1)$$

where G – feedstock flowrate (kg·h^{-1}); Z – total volume of processed raw materials (m^3); C_i - concentration of the *i*-th component (mol·m^{-3}); k_j – reaction rate constant of the j-th reaction; a_j – activity of the reaction medium for *j*-th reaction, rel. units.

The thickness of the flowing LAB film, which changes during the formation of a highly viscous component, is determined by the formula:

$$\delta = \sqrt[3]{\frac{2{,}4\Gamma \nu_l}{g}} \quad (2)$$

where δ – thickness of the liquid film, m; Γ – irrigation density, m^2/h; ν_l – fluid kinematic viscosity coefficient, m^2/h; g – acceleration of gravity, m/s^2.

An increase in the thickness of the sulfonated liquid film leads to an increase in the contact time determined by the formula:

$$\tau = \frac{V_{reactor}}{V_l} = \frac{(\frac{\pi d^2}{4} - \frac{\pi(d-2\delta)^2}{4}) \cdot n \cdot L}{V_l} \quad (3)$$

where τ – contact time, s; $V_{reactor}$ – reaction zone volume, m^3; V_l – LAB volumetric flow rate, m^3/h; d – reactor tube inner diameter, m; δ – liquid film thickness, m; n – number of tubes; L – reactor tube length, m.

At the moment, the average LAB consumption at the reactor inlet on one line is 3500 kg / h. At the same time, the design limits for the sulfonation reactor are 4500 kg / h. At a given flow rate, the contact time τ = 25 seconds.

An increase in the LAB consumption at the reactor inlet at a highly viscosity of the organic liquid film leads to a decrease in the contact time, as a result of which a decrease in the film viscosity and normalization of the hydrodynamic flow regime occurs. Table 1 shows the values of the contact time and the thickness of the LAB film at various values of the LAB flow rate into the sulfonation reactor.

Table 1. Values of the contact time and the thickness of the LAB film depending on the feedstock flowrate

LAB flowrate, kg/hour	3500	3700	3900	4100	4300	4500
τ, sec	30.1	29.0	28.0	27.1	26.2	25.4
Mixture viscosity at the end of inter-washing cycle, cSt	544.67	544.32	544.82	544.5	544.95	544.64
Inter-washing cycle duration, days	10	10	11	11	12	12

In addition to the consumption of LAB in the sulfonation reactor, the viscosity of the mixture, the quality of the obtained ABSA and the concentration of the viscous component are also influenced by the content of light aromatic compounds in the sulfonated raw material, since they are the source of the formation of tetralins. An increase in the content of light aromatics in the raw material leads to an increase in the concentration of the high-viscosity component. At the same time, an increase in the consumption of sulfonated raw materials makes it possible to reduce the concentration of the highly viscous component (Fig. 2) and the viscosity of the mixture (Fig. 3).

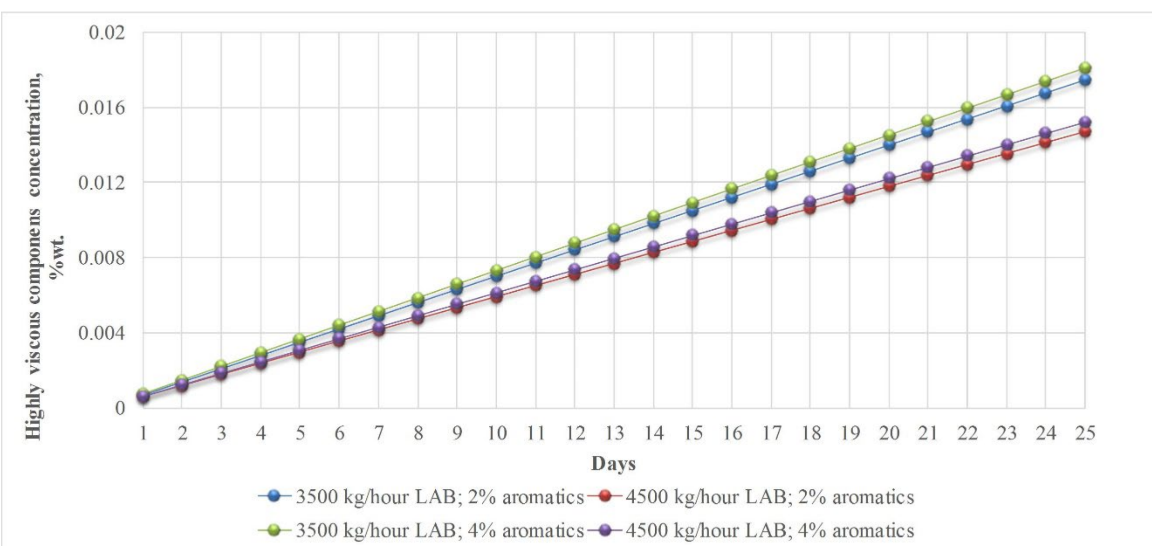

Figure 2. Dynamics of highly viscous component accumulation at different flowrates and content of aromatic hydrocarbons in the feedstock

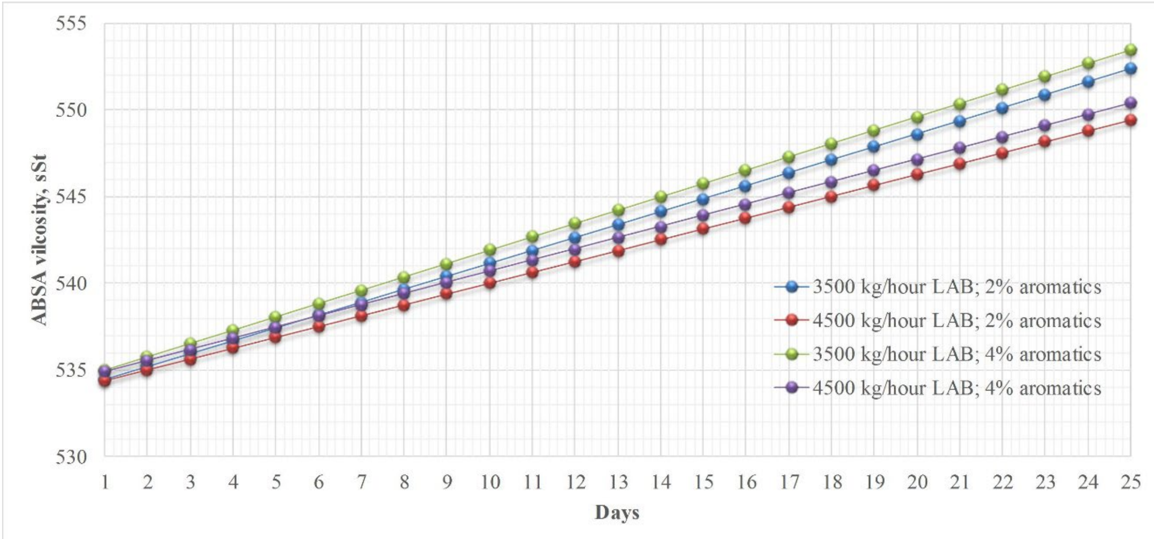

Figure 3. Dynamics of the viscosity increase at different flowrates and content of aromatic hydrocarbons in the feedstock

Table 2 shows the results of calculations on the model when using as a raw material LAB C_{10}-C_{14} with a light aromatics content of 2, 4, 6 and 10% wt. The initial consumption in the sulfonation reactor is 3500 kg/h, the SO_3/LAB ratio is 1.08. When calculating on the model, it is assumed that the critical concentration of the highly viscosity component is 0.01 mol/L; the viscosity of the medium is approximately 544.87 cSt. When these values are reached, the reactor is flushed with water. With an increase in the LAB flow rate into the reactor to 4500 kg/h, the contact time of the reagents decreases from 30.1 to 25.4 seconds, the increase in the viscosity of the mixture slows down, thus an increase in the duration of inter-flushing cycles is achieved.

Table 2. Results of model calculation

Aromatic content in raw materials,% wt.	Inter-washing cycle duration at feedstock flowrate of 3500 kg/hour	Inter-washing cycle duration at feedstock flowrate of 4500 kg/hour
2	15	17
4	14	16
6	10	12
10	2	3

3. Conclusion

Thus, the result of this work is an increase in the duration of the inter-washing cycles of the sulfonation reactor by adjusting the viscosity of the organic liquid film with an increase in the LAB flow rate into the reactor from 3500 to 4500 kg/hour.

An increase in the consumption of raw materials makes it possible to achieve an increase in the duration of inter-washing cycles, regardless of the composition of the raw materials. However, an increase in the content of aromatic compounds in raw materials leads to a decrease in the duration of inter-washing cycles. This is due to the fact that light aromatic compounds are the source of the formation of tetralines.

Calculations based on the developed mathematical model showed that an increase in the consumption of raw materials supplied to the reactor by 1000 kg/hour at a constant SO_3/LAB molar ratio makes it possible to increase the duration of the inter-flushing cycle by an average of 2 days.

Acknowledgements

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To whom correspondence should be addressed: Dr. Irena O. Dolganova, Department of Chemical Engineering and Chemical Cybernetics, Institute of Natural Resources, Tomsk Polytechnic University; 30, Lenina Av., Tomsk, 634050, Russia; e-mail: dolganovaio@tpu.ru