Petroleum and Coal

Article **Open Access**

PERFORMING THE CALCULATIONS ON LAB SULFONATION PARAMETERS USING THE MATHEMATICAL MODEL

Anastasiya A. Solopova, Maria A. Pasyukova, Ajur A. Bunaev, Irena O. Dolganova*

Engineering School of Natural Resources, Tomsk Polytechnic University, Russia

Received March 29, 2019; Accepted June 13, 2019

Abstract

The continuous growth of demand on synthetic detergents worldwide, which include such components as surfactants causes increasing of research and optimization interests towards the process of obtaining linear alkylbenzenes or the problem of linear alkylbenzenes sulfonation. The method of mathematical modelling used in this paper was chosen as the best concerning the optimization of the process. It allows monitoring the influence of main parameters without interfering in the process. As the result mathematical model of linear alkylbenzenes (LAB) sulfonation process was obtained. Adequacy of which is supported by the correspondence of calculated and experimental dependencies of the main parameters (such as yields of target and some side products, which are alkylbenzene sulfonic acid (ASA) and, for example, highly viscous component respectively). Also, information about the dependency of highly viscous component accumulation and ASA from temperature and film thickness in the reactor is obtained.

Keywords*: Sulfonation; Linear alkyl benzene; Alkylbenzene sulfonic acid; Highly viscous component; Multi-tubular film reactor; Mathematical modeling.*

1. Introduction

Linear alkylbenzene sulfonates (LAS) are among the most used component in the production of synthetic detergents and surfactants. LAS are alkyl aromatic chemical compounds which include saturated hydrocarbon side-chain of 10-13 carbon atoms and one or several sulfonic groups [1].

According to "BusinessStat," the demand for the detergents market in Russia in 2015 was 1.64 million tons. Until 2020, the market size will overpass 1.75 million tones so that the increase will be 6.7%. In 2017 the global market of liquid detergents was valued at $27,405 million, up to 2025 it is projected to reach $40,482 million, increasing by 5.2% from 2018 to 2025 according to "Allied Market Research" [2-3].

The continuous growth of world synthetic detergents production challenges the science with research and optimization of related production processes having an increase of economic efficiency as the main purpose.

The process of alkylbenzene sulfonic acid (ASA) production consists of following stages [1,4], introduced on Fig.1:

1. Unbranched (C_9–C_{14} mainly) alkanes dehydration: polyalkanes are the products in this stage;
2. Hydration of polyalkanes from the previous stage, in reverse, to monomers;
3. Benzene alkylation using liquid catalyst – hydrofluoric acid. In this stage linear alkylbenzenes are the products flowing further downstream while HF-catalyst treated in regenerator column;
4. Linear alkylbenzene sulfonation with sulfur trioxide in multitube film reactor. The final stage – alkylbenzene sulfonic acid is the main product of the whole process.

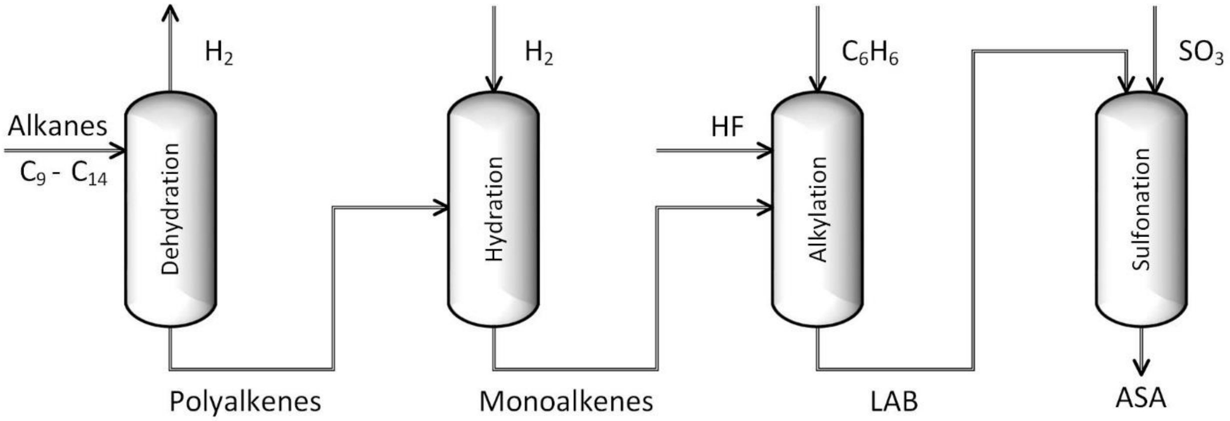

Figure 1. Stages of ASA production

2. Experimental

2.1. Study object

In this research, a multi-tubular film reactor for linear alkylbenzenes sulfonation installed in one of the real petrochemical productions was considered as the study object. The reactor itself is depicted in Fig. 2.

The sulfonation reaction takes place in the tube side consisting of 120 vertical tubes. Linear alkylbenzenes flow into the upper part of the reactor, where they are distributed uniformly by distribution device. Inside the tubes, linear alkylbenzenes run off in the form of thin film forced by gravitation and gaseous sulfur trioxide flow [5-7].

The optimal ratio of alkylbenzenes and gas is maintained inside each of the tubes. Thus, reaction gas includes 5-5.5% vol. of trioxide.

Heat reduction from the reaction volume is performed with cooling water circulation outside of tubes.

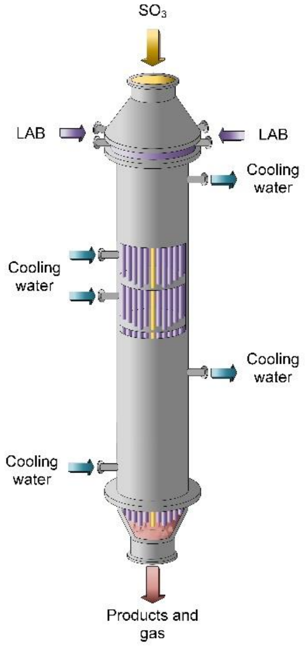

Figure 2. LAB sulfonation reactor

2.2. Sulfonation process chemistry

2.2.1. Gas mixture production

Sulfur anhydride obtaining occurs in stages:

1. Liquid sulfur burning in excess of treated air obtaining sulfur dioxide:

$$S + O_2 \rightarrow SO_2$$

2. Catalytic oxidation of the dioxide in excess of drain air with sulfur trioxide as the product:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

2.2.2. Sulfonation

The formation of sulfonic acid due to the interaction of linear alkyl benzene with a linear saturated hydrocarbon chain, consisting of 10 to 13 carbon atoms, with sulfuric anhydride:

$$R\text{-}C_6H_5 + SO_3 \rightarrow R - C_6H_4 - SO_3H$$

Possible side reactions with the formation of sulfonic anhydride or one of the types of sulfonic acid:

$$\mathbf{2\ R{-}C_6H_4{-}SO_3H + 3SO_3 \rightarrow R{-}C_6H_4{-}SO_2{-}O{-}SO_2{-}C_6H_4{-}R + H_2SO_4}$$

$$\mathbf{R{-}C_6H_5 + 2SO_3 \rightarrow R{-}C_6H_4{-}SO_2{-}O{-}SO_3H}$$

The concentration of sulfones, the part of unsulfonated matter, does not overpass 1 %wt. It does not depend from technological parameters unless SO_3/LAB ratio is more than 1.08 – in this case, a rapid increase of formation rate takes place.

Structure formula of sulfones is following:

$$\mathbf{R - C_6H_4 - SO_2 - C_6H_4 - R'}$$

Sulfonic acid may resolve, interact with remaining LAB or hydrolyze by water as well:

$$\mathbf{R{-}C_6H_4{-}SO_2{-}O{-}SO_3H + R{-}C_6H_5 \rightarrow 2\ R - C_6H_4 - SO_3H}$$

$$\mathbf{R - C_6H_4 - SO_2 - O - SO_2 - C_6H_4 - R + H_2O \rightarrow 2\ R - C_6H_4 - SO_3H}$$

2.2.3. Highly viscous component

Highly viscous component accumulation occurs during sulfonation. It is caused by aromatics contained in the stock. As those components accumulate, the uniform flow of the film in tubes of the reactor interrupts. Thus, trioxide diffusion into organic phase decreases, which leads to the low-quality product as an output – mass concentration of unsulfotated matter increases as well as the color index lowers [8-12].

When highly viscous component concentration in tube hits its critical point, the reactor is washed with water to eliminate products which interfere normal reaction course. Thus, monitoring of highly viscous component accumulation is essential to maintain the required quality of the product.

At present, the need for washing the reactor is determined by the pressure in it, which depends on the amount of highly viscous component. In practice, this method does not allow to achieve maximum efficiency of the process and is associated with the risk of formation of a substandard product.

2.2.4. Methodology

The model proposed involves energy and mass and balances. Finally, some additional assumptions were made for the mathematical model:

- No entrainments of liquid droplets into gas or of gas bubbles into the liquid film occur;
- Fully developed film (entrance and exit effects to the reactor are neglected);
- The liquid film is symmetric with respect to the reactor axis;
- There are no radial gradients, of neither temperature nor con-centration;
- The deactivation of reacting mixture stems from viscous component formation and affects the reaction rate constants inverse exponentially.
- The astronomic time is abandoned in favor of the volume of raw materials processed during the time between reactor washings.

In line with the assumptions above, the sulfonation reactor model can be described as follows:

$$G\frac{\partial C_i}{\partial Z} + G\frac{\partial C_i}{\partial V} = \sum_j W_j \cdot a_j \qquad (1)$$

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

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

where the activity of reaction mixture is defined as:

$$a_j = e^{\delta C_{v.c.}} \qquad \text{If } Z=0\ C_{v.c.}=0,\ \delta=1 \qquad (2)$$

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}); $C_{v.c.}$ – concentration of highly viscous components (mol·m^{-3}); G – flow rate (kg h^{-1}); T – temperature (K); T_0 – initial temperature (K); W_j – reaction rate (mol m^{-3} hour^{-1}); Z – the total volume of the recycled raw materials

(m^3); $-\Delta H_j$ – 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.

3. Results and discussions

During the modeling of the process of sulfonation in a multi-tubular film reactor, a dynamic model of the reactor was used under the assumption concerning the mode of plug flow. The chemical reactions rate constants were determined by solving the inverse kinetic problem on the basis of experimental data – Table 1.

Table 1. Base reactions of the sulfonation process

Reaction	Ea	k
LAB + SO_3 →ASA	$3{,}80\cdot10^4$	6,25
LAB + ASA →Unsulf. matter + H_2O	$3{,}50\cdot10^4$	$9{,}38\cdot10^{-2}$
2ABSK + SO_3 →ASA anhydride + H_2SO_4	$4{,}00\cdot10^4$	$4\cdot10^{-4}$
ASA anhydride + H2O →2ASA	$2{,}50\cdot10^4$	$9{,}89\cdot10^{-1}$
Unsulf. matter →VK	$4{,}00\cdot10^4$	$8{,}39\cdot10^{-5}$

3.1. Prediction of the period between reactor washings duration

Calculations concerning reactions taking place inside the sulfonation reactor were made using developed modelling system. As the result dynamics of the mass concentration of the key components such as ASA, unsulfonated matter, or sulfuric acid were obtained. Those results are presented for two periods between reactor washing: 16.02.2018 – 05.03.2018 and 15.09.2018 – 10.10.2018 on Fig. 3 and 4.

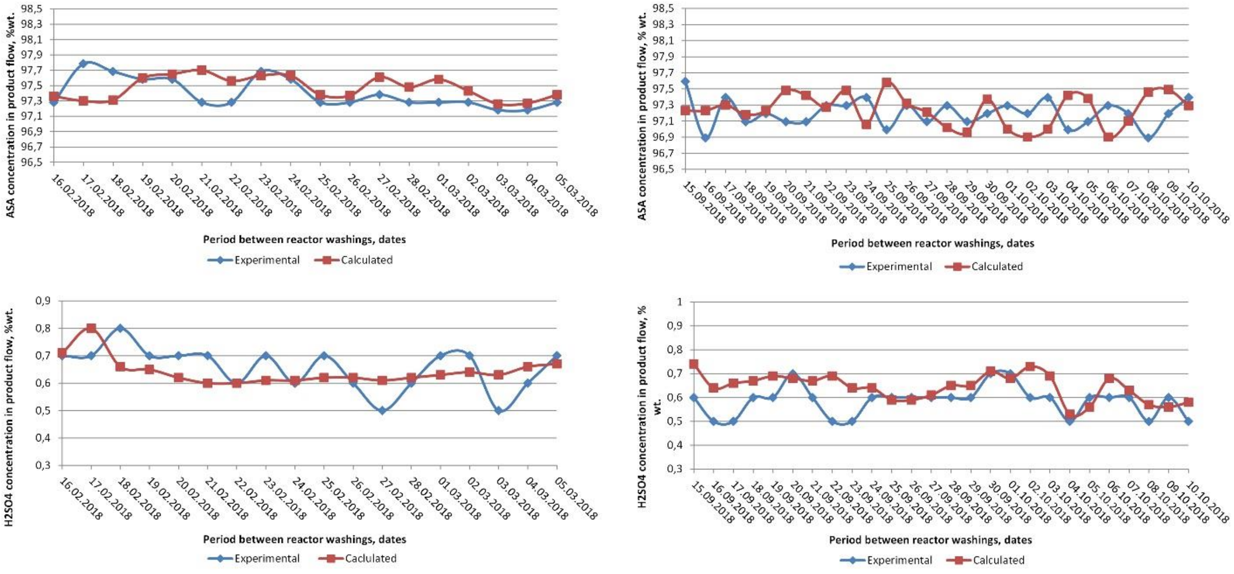

Figure 3. Dynamic of ASA and H_2SO_4 concentration during the period between reactor washing

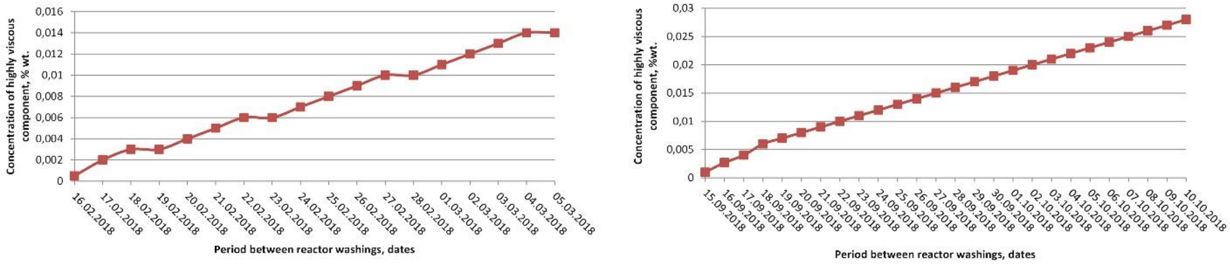

Figure 4. Dynamic of highly viscous component accumulation

Thus, the average deviation of the calculated data from the experimental data during the period between reactor washings was less than one percent, which suggests that the calculated dependencies correspond to the experimental data. This means that the model is adequate and may be used to study the main parameters of the process.

The usage of this computer simulation system allows making predictions about the duration of the period between reactor washings on the basis of the concentration of highly viscous components. The critical concentration was found by calculations based on the prescribed viscosity of the product and is 0.034 %wt.

Also, as a result of calculations, the dynamics of accumulation of a highly viscous component during the period between reactor washings were obtained. Fig. 4 show the results of calculations of the accumulation of a highly viscous component for two cycles.

Thus period between reactor washings from 16.02.2018 to 05.03.2018 ended up with highly viscous component concentration reaching 0.014 %wt., making the duration of the period itself 14 days long.

The duration of the second period made up 26 days; reactor washing was performed when highly viscous component concentration reached 0.028 %wt.

Then calculations were made until highly viscous component reach 0.034 %wt. With this, the duration of the first period extended on 22 days, while the second – 4.

3.2. Study of temperature influence in the reactor on the highly viscous component accumulation

The process of sulfonation can take place in the temperature range from 30 to 55°C. Thus, calculations were also made to study the effect of the temperature regime of the process on the concentration of the highly viscous component.

As can be seen in Fig. 5, the temperature of the sulfonation process affects the concentration of the highly viscous component. As the temperature in the reactor rises, the concentration of the highly viscous component formed over 1 day increases. Thus, at a temperature of 10 °C, 0.000321%wt. of a highly viscous component is formed per day, at 30°C - 0.000992 %wt., and at 50°C - 0.00263 %wt.

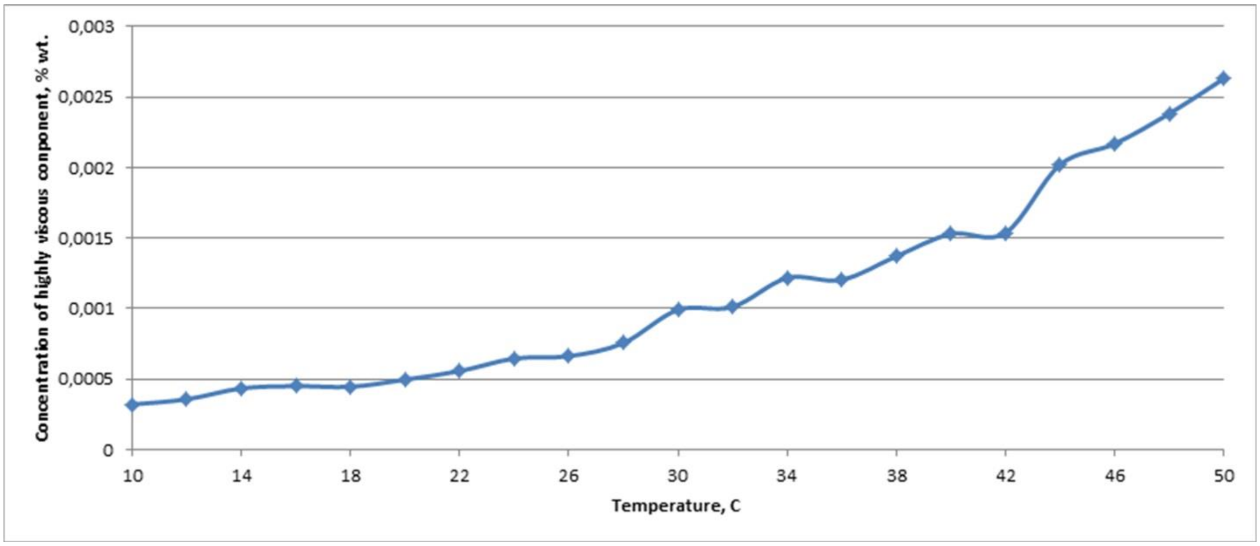

Figure 5. Concentration of highly viscous component on the first day of period between reactor washings at different temperature

Then calculations were carried out at different temperatures during two periods between reactor washings, the results of which are shown in Fig. 6.

At a temperature of 30°C, the concentration of the highly viscous component on the last day of the period was 0.024 %wt, at 40°C - 0.040 %wt., at 50°C - 0.065 %wt. Accordingly, with an increase in the temperature of the process, the rate of accumulation of the highly viscous component increases, the duration of the period between reactor washings is reduced.

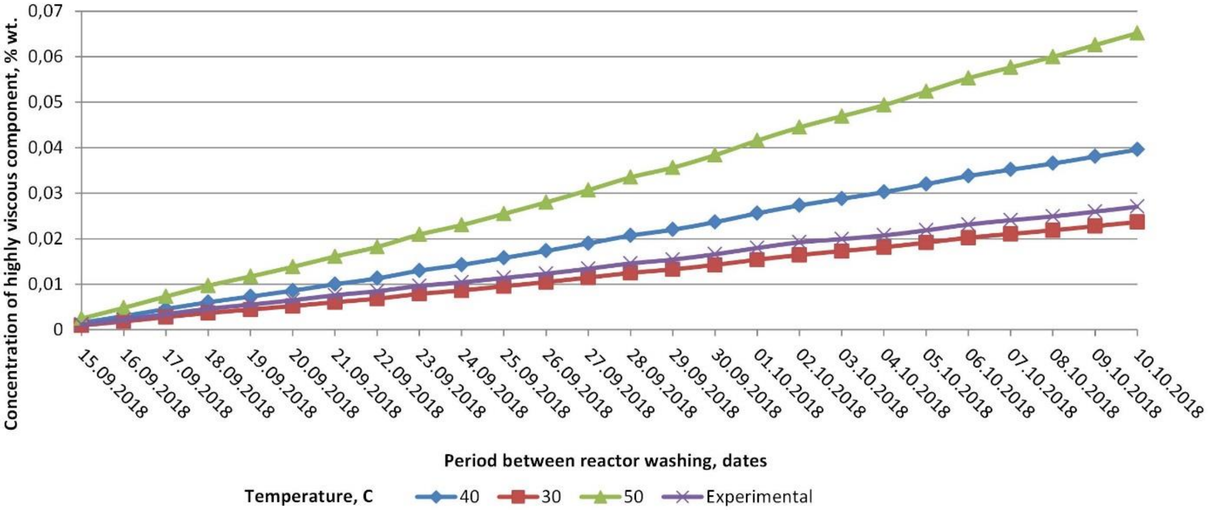

Figure 6. Dynamic of highly viscous component accumulation at different temperature.

3.3. Study of film thickness influence in the reactor on main parameters

A period between reactor washings with a duration of 20 days was chosen for analysis. Fig.7 shows the dynamics of accumulation of a highly viscous component when varying the film thickness in the reactor from 0.3 mm to 3 mm.

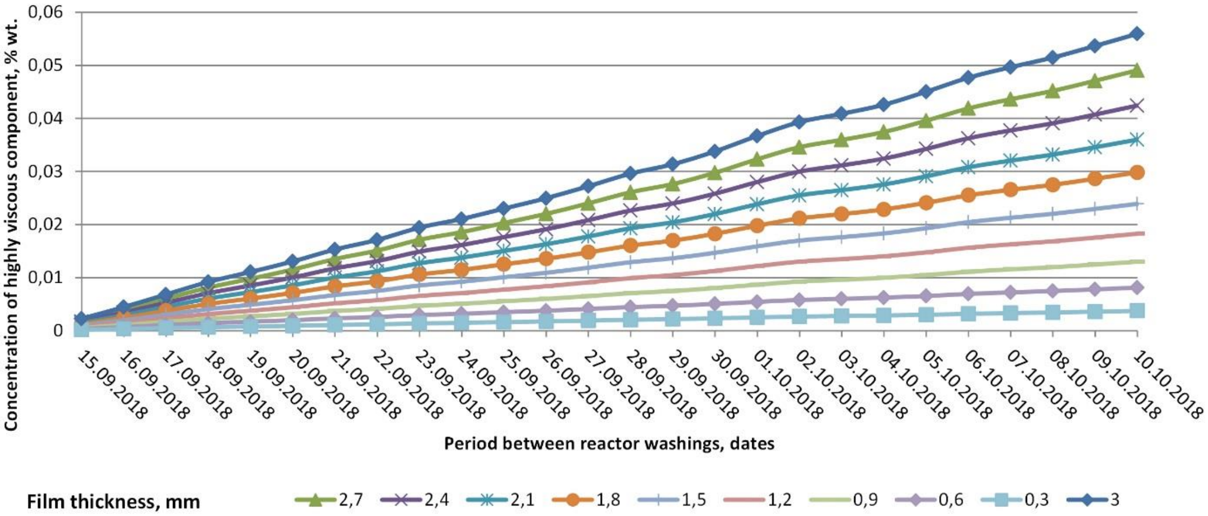

Figure 7. Dynamic of highly viscous component accumulation at a different film thickness

As can be seen from the graph, as the film thickness in the reactor increases, the concentration of the highly viscous component increases. This is because as the film thickness increases, diffusion of SO_3 molecules through the film thickness becomes difficult, and the reaction occurs only on its surface.

Thus, at a film thickness of 0.3 mm, the concentration of the highly viscous component on the last day of the period between reactor washings is 0.004 %wt., at 1.5 mm – 0,024 %wt., and at 3 mm – 0.056 %wt.

With increasing film thickness, the formation of H2SO4 increases. With film thickness in the reactor of 0.3 mm, the concentration of sulfuric acid on the last day is 0.16 %wt., while with

1.5 mm it was 0.68 %wt. and with 3 mm – 1.17 %wt. At the same time, the experimental value is 0.6%wt.

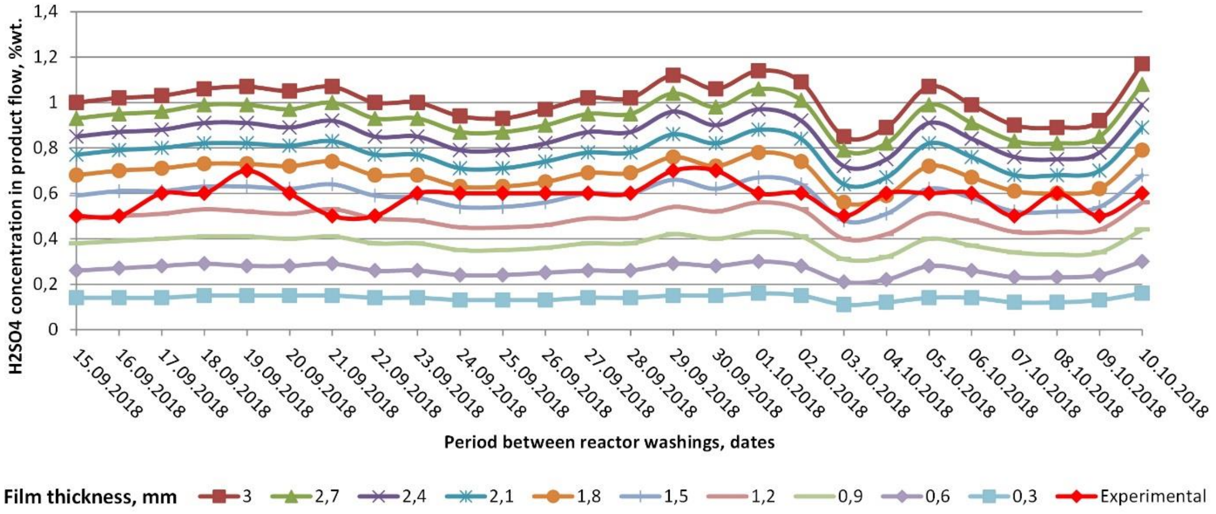

Figure 8. Dynamic of H_2SO_4 concentration at a different film thickness

With an increase in film thickness, the concentration of ASA decreases due to the formation of a larger amount of unsulfonated matter, which negatively affects the quality of the product flow, as shown in Fig. 9. With film thickness in the reactor of 0.3 mm, the concentration of alkylbenzene sulfuric acid on the last day is 97.94% mass., while with 1.5 mm it was 96.99 %wt. and with 3 mm – 97.59 %wt. At the same time, the experimental value is 97.59 %wt.

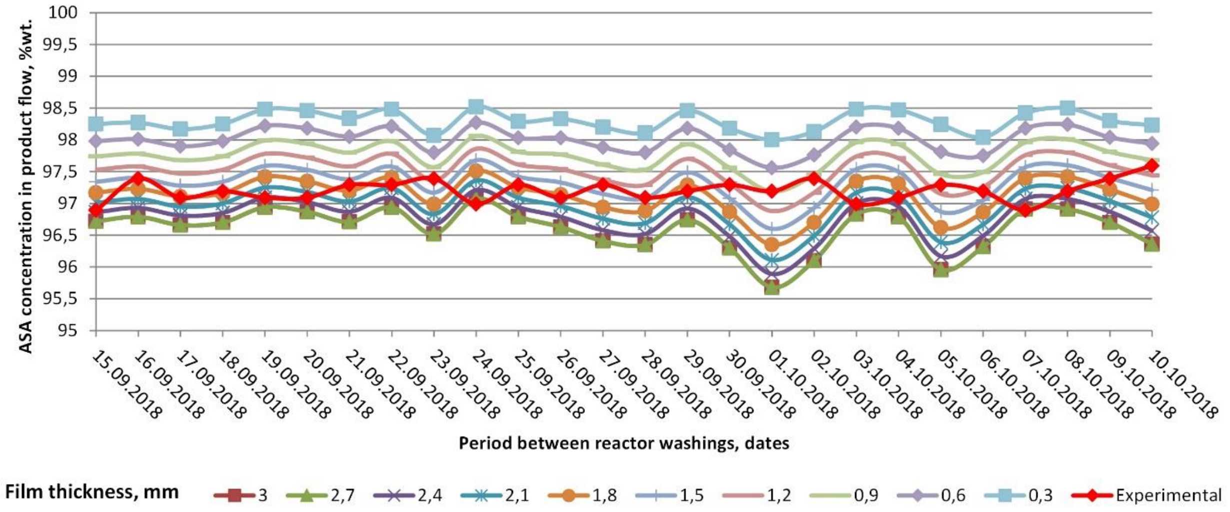

Figure 9. Dynamic of ASA concentration at a different film thickness

4. Conclusions

Thus, during the test calculations on the modeling system, it was noted that the dynamics of the experimental and calculated mass fractions of the necessary products of the sulfonation process, as well as their dependence on the film thickness inside the reactor tubes, are in good correlation, which indicates the adequacy of the model.

Also, the developed model makes it possible to predict the duration of the period between reactor washings, thus increasing its duration without harming the quality of the target product - increasing the economic efficiency of the LAB sulfonation process.

It was found that increasing the film thickness in the reactor has a negative effect on the duration of the period between reactor washings and the formation of the target component, ASA, since with increasing film thickness, the formation and accumulation of the highly viscous component is accelerated, which, accordingly, reduces the proportion of ASA. Also, as the film thickness increases, the proportion of unsulfonated matter in the product flow increases. This is because the reaction takes place only on the surface of the LAB film in the reactor.

Acknowledgements

The experimental calculations were carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant.

References

[1] Bannov PG. Processy pererabotki nefti. P.G. Bannov. M.: CNIITEHneftekhim. – 2001. – 625 p. [in Russian].
[2] Liquid Detergent Market by Nature (Organic and Conventional), Application (Laundry and Dishwashing), Distribution Channel (Online Sales Channels, Supermarket & Hypermarket, Departmental & Convenience Stores, and Independent Grocery Stores), and End User (Residential and Commercial): Global Opportunity Analysis and Industry Forecast, 2018 – 2025 [Internet] Available from: https://www.alliedmarketresearch.com/liquid-detergent-market
[3] BusinesStat Analyze of detergents market in Russia in 2011-2015, forecast on 2016-2020.[In Russian]
[4] Roberts D. Optimisation of the Linear Alkyl Benzene Sulfonation Process for Surfactant Manufacture. Organic Process Research & Development, 2003; 7: 172−184.
[5] Zaid TA, Benmaza K, Chitour CE. Sulfonation of linear alkyl benzene (LAB) in a corrugated wall falling film reactor. Chemical Engineering Journal, 2000; 76: 99-102.
[6] Ward RS, Diaper RL, Roberts DW. Relative Rates of Sulfonation of Linear and Branched Long-Chain Alkylbenzenes. Journal of Surfactants and Detergents, 2001; 4(3): 263–270.
[7] Roberts DW, Ward RS, Hughes PJ. Correlations of Relative Rate Constants for Sulfonation of Alkylbenzenes with Molecular Structure. Journal of Surfactants and Detergents, 1998; 1(2): 161–165.
[8] Moreno A, Bengoechea C, Bravo J, Berna JL. A contribution to understanding secondary reactions in linear alkylbenzene sulfonation. Journal of surfactants and detergents, 2003; 6(2): 137-142.
[9] Dolganova IO, Dolganov IM, Bunaev AA, Pasyukova MA. Nature of highly viscous component in the alkylbenze sulfonic acid technology and its influence on the process efficiency. Petroleum and Coal, 2019; 61(1): 25-31.
[10] Dolganova IO, Dolganov IM, Ivanchina ED, Ivashkina EN. Alkylaromatics in Detergents Manufacture: Modeling and Optimizing Linear Alkylbenzene Sulfonation. Journal of Surfactants and Detergents, 2018; 21(1): 175-184.
[11] Molever K. Monitoring the Linear Alkylbenzene Sulfonation Process Using High-Temperature Gas Chromatography. Journal of Surfactants and Detergents, 2015; 8(2): 199-202.
[12] Ahmadi AN, Mehdizadeh A, Jalili AH. Determination of Sulfonation Conditions of HAB as a By-product of Linear Alkylbenzene Production. Journal of Petroleum Science and Technology, 2015; 5(2): 45-50.

To whom correspondence should be addressed: Dr. Maria A. Pasyukova, Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia, E-mail: maria.pasyukova11@gmail.com