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Procedia Engineering 152 (2016) 73 – 80

Procedia Engineering

www.elsevier.com/locate/procedia

International Conference on Oil and Gas Engineering, OGE-2016

Application of mathematical modeling for optimization of linear alkylbenzenes sulphonation modes in film reactor

Ivanchina E.[a], Ivashkina E.[a], Dolganova I[a], Dolganov I[a], Krutey A.[a*]

[a] *Tomsk polytechnic university, 30, Lenina av., Tomsk, 634050, Russian Federation*

Abstract

The methodological aspects of development and application of mathematical modeling system for optimization of multistage petrochemical production on the example of linear alkylbenzene sulphuric acids obtaining complex processes at LLC "KINEF" were reviewed. It was shown that creation of mathematical modeling system includes a sequence of reaction network development stages, reactor kinetic modeling, model theoretical and experimental studies, studying regularities of reactor modes and proposing recommendations for raw material composition improving.

Peer-review under responsibility of the Omsk State Technical University

Keywords: sulfonation; alkylbenzene sulphuric acids; mathematical model; sulphonation reactor of sulfonation; kinetic model

1. Introduction

Linear alkylbenzene sulphonates (LABS), which are chemicals with saturated hydrocarbon chain of 10-13 carbon atoms linked to one or two sulpho-groups. These materials are common anions used in the production of detergents. The raw material for detergents production is alkylbenzene sulphuric acids (ASA), which are obtained as follows: 1) dehydrogenation of paraffines; 2) hydrogenation of byproducts diolefines to monoolefins; 3) alkylation of benzene with olefins to linear alkylbenzenes (LAB) using HF-catalyst which is regenerated in a column-type apparatus; 4) LAB sulphonation to ASA [1, 2].

* Corresponding author. Tel.: +7-923-431-11-21; fax: +7-3822-56-38-65.
E-mail address: alex_krutey@mail.ru

Peer-review under responsibility of the Omsk State Technical University
doi:10.1016/j.proeng.2016.07.631

Process technological scheme is presented in Fig. 1.

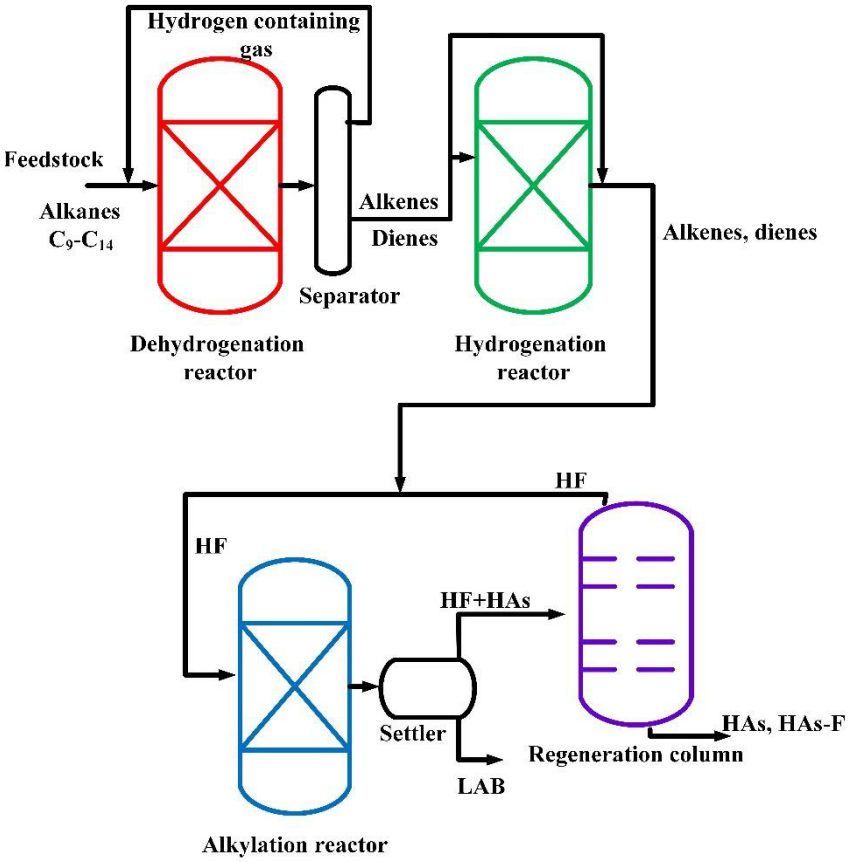

Fig. 1. Block diagram of ASA production: HAs are heavy aromatics; HAs-F are heavy aromatics fluorides.

Table 1. Characteristics of research subject (sulphonation reactor).

Characteristic	Parameters
Technological modes	LAB flow rate 2500–3000 kg/h, SO_3/LAB molar ratio – 1 mole/mole, LAB temperature – 25–35 ^oC, coolant temperature 25–30 ^oC
Raw materials composition, % wt.	LAB – 25.2–26
	SO_3–68.5–70
	Tetralines–4–6.3
Products flow rate and quality	Active matter content (minimum 96%); H_2SO_4 content (maximum 2%); unsulphonated matter (maximum 2%); color (maximum 80 Klett units)

LAB sulphonation stage defines ASA quality indicators (color, viscosity, active matter concentration), which are strictly specified. Thus, active matter content in the final product is to be given at least 96 wt.%, and unsulphonated compounds content (no more than 2 wt.%).

During the plant operation, the ASA quality changes. When ASA concentration is below 96.1% wt., consumption of sulfur at sulfur trioxide SO_3 obtaining stage is increased, to increase conversion of LAB. This increases the concentration of sulfuric acid in sulphonation reactor product mixture above the permissible limit, and causes the need to stop the production line for equipment washing.

Efficacy of sulphonation process flow ultimately determines ASA composition and, accordingly, the quality of the synthetic detergents. Therefore, maintaining optimal conditions of LAB sulphonation process is important and urgent. The difficulty of optimization is multifactor technology and mutual influence of processes and phenomena in coupled devices. These tasks are successfully solved with use of mathematical modeling methods of chemical-engineering processes and developed computer modeling systems that take changes in feedstock composition, catalyst activity and large number of control parameters into account [3-14].

2. Study subject

The aim of this work is development of mathematical model for LAB sulphonation process of LAB and its application to sulphonation process optimization.

3. Experimental

The first phase of mathematical modeling is development of sulphonation process reaction network [15-20].

With application of quantum-chemical PM_3 method, implemented in Gaussian 98 program, we performed calculations to determine the thermodynamic probability of reactions occurrence in sulphonation process, based on reaction network.

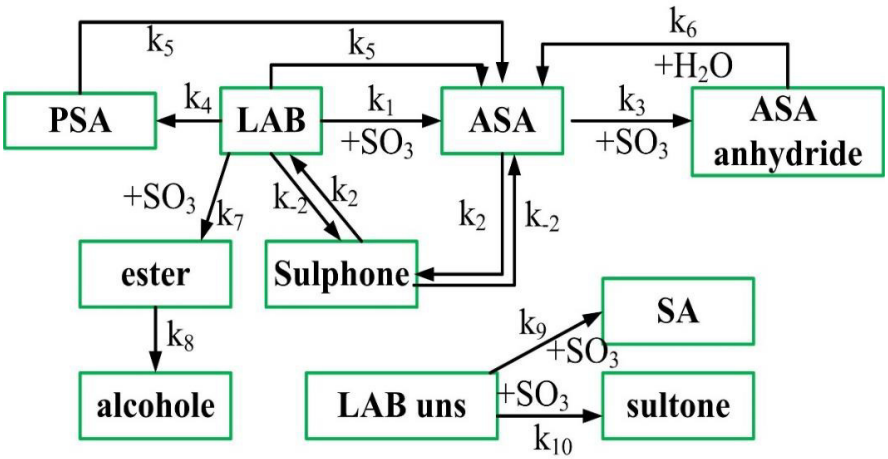

Fig. 2. Reaction network of sulphonation process.

Here PSA is pyrosulphonic acid; LAB uns are unsaturated LAB; SA is an acid, obtained by LAB uns sulphonation into side chain.

Reaction 2 is opposing as unsulphonated mater is mainly formed by sulphones; according to thermodynamic analysis, reaction of these substances formation is opposing at specified conditions.

On the base of this network the reaction rates expressions of sulphonation process were developed.

$$
\begin{aligned}
W_1 &= k_1 \cdot C_{LAB} \cdot C_{SO_3} \\
W_2 &= k_2 \cdot C_{ASA} \cdot C_{LAB} \\
W_{-2} &= k_{-2} \cdot C_{unsulf.matter} \cdot C_{H_2O} \\
W_3 &= k_3 \cdot C_{ASA} \cdot C_{SO_3} \\
W_4 &= k_4 \cdot C_{LAB} \cdot C_{SO_3}^2 \\
W_5 &= k_5 \cdot C_{PSA} \cdot C_{LAB} \\
W_6 &= k_6 \cdot C_{ASAanhydride} \cdot C_{H_2O} \\
W_7 &= k_7 \cdot C_{LABuns} \cdot C_{SO_3}
\end{aligned}
\qquad (1)
$$

Mathematical model of the sulphonation process with the assumption of perfect mixing mode is as follows:

$$
\begin{cases}
\dfrac{\partial C_i}{\partial \tau} = \dfrac{C_i - C_i^0}{\tau} + \sum W_j \\
\rho\ C_P \dfrac{\partial T}{\partial \tau} = \dfrac{T - T_0}{\tau} + \sum_{j=1}^{n} W_j Q_j^{\text{c.r.}}
\end{cases}
\qquad (2)
$$

Initial conditions: t=0, C_i=C_{0i}, T=T_0.

Ci is concentration of i-th component, mole/l; *kj* is rate constant of j-th reaction, l/(mole·sec); τ is contact time, sec; *Qj* is heat effect of chemical reaction, J/mole; *Wj* is rate of chemical reaction, m^3/(mole·sec); *Cp* is mass heat capacity of reaction mixture, J/(kg·K); ρ is density of reaction mixture, kg/m^3; *T* is temperature, K.

4. Results and discussion

With an increase in aromatics flow rate to alkylation reactor, the amount of fluorides and tetralines formed in the regeneration column increases, according to the reactions:

Aromatics→ toluene + olefin C4 (aromatics dealkylation)

nToluene → tetralines (olefins polymerization)

tatralines, LABuns, DABuns+HF→ HAs-F (heavy alkyl aromatic hydrofluorination).

Table 2 shows the influence of aromatics flow rate to alkylation on duration of HF regeneration column bottom filling period.

Table 2. Influence of aromatics flow rate to alkylation on duration of HF regeneration column bottom filling period.

Aromatics flow rate to alkylation, kg/h	Duration of HF regeneration column bottom filling period, days
300	12.8
350	11.3
400	10.0
450	9.0
500	8.2
550	7.5
600	6.9
650	6.3

700	6.0
750	5.5

In sulphonation, reactor aromatics, along with the sulphones, form high-viscosity component, the accumulation of which violates the uniformity of sulphonation process, making diffusion of SO_3 into the reaction film more difficult.

Fig. 3 shows the concentration of active matter on amount of high-viscosity component formed in the sulphonation reactor.

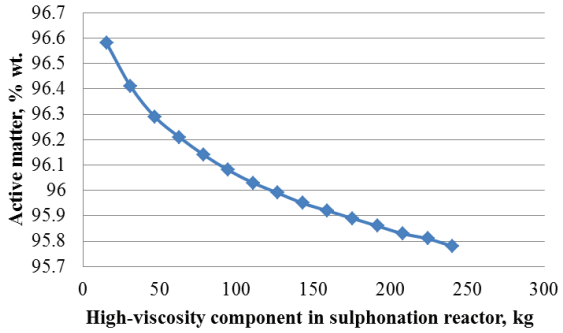

Fig. 3. Dynamics of active matter concentration change on high-viscosity component content in sulphonation reactor.

With accumulation of high-viscosity component, active matter ratio falls below the permissible value - 96% by weight. To prevent the reduction of commercial product quality, we recommend changing the flow of sulfur in the sulphonation reactor (i.e. SO_3/LAB molar ratio) in proportion to accumulation of high-viscosity component (Fig. 4).

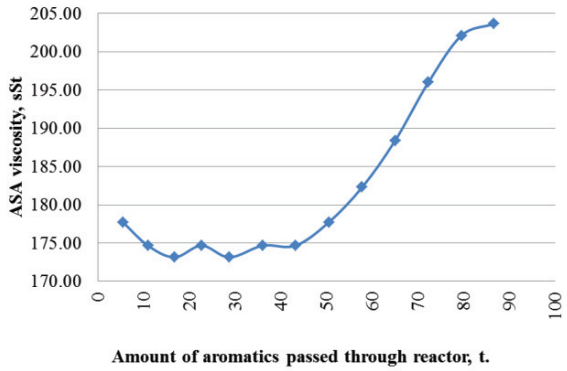

Fig. 4. Dependence of ASA viscosity on amount of aromatics passed through reactor.

The sharp increase in viscosity at the end of the inter-draining period indicates accumulation of high-viscosity component in the reactor. At the initial stage, diffusion of SO_3 to the reactants is not difficult; therefore, the viscosity does not change significantly. With an increase in high-viscosity components amount in the system diffusion is hampered and the rate of reaction between reactants in the hydrocarbon phase increases. In such a reaction

(interaction between LAB and ABSK) sulfones are formed, i.e. one of the high-viscosity components. Therefore, at the end of the inter-draining period there is a sharp increase in the mixture viscosity.

In the developed modeling system, mixture viscosity depending on the concentration of high-viscosity component (hvc) is calculated by the formula:

$$\mu = e^{\alpha \cdot Ccvc.} \cdot 10^{10^{(I-23.097)/34.468}} \quad (3)$$

Here I is viscosity index, α is coefficient, considering the influence of high-viscosity component concentration on the mixture viscosity.

The regularities incorporated in the mathematical model of sulphonation process allow predicting the time viscosity reaches its critical value (175 sSt), i.e. the time of required reactor washing with high accuracy (Table 3).

Table 3. Actual and predicted dates of sulphonation reactor washings.

Starting date of the cycle	Actual date of washing	Predicted date of washing (model calculations)
1.09.2015	17.09.2015	15.09.2015
17.09.2015	2.10.2015	2.10.2015
2.10.2015	14.10.2015	16.10.2015
14.10.2015	26.10.2015	26.10.2015
26.10.2015	9.11.2015	7.11.2015
9.11.2015	25.11.2015	23.11.2015
25.11.2015	11.12.2015	9.12.2015

Maintaining effective LAB sulphonation process conditions requires consideration of simultaneous influence of such parameters as content of aromatics in sulphonation reactor feedstock and SO3 /LAB molar ratio on active matter concentration (Fig. 5).

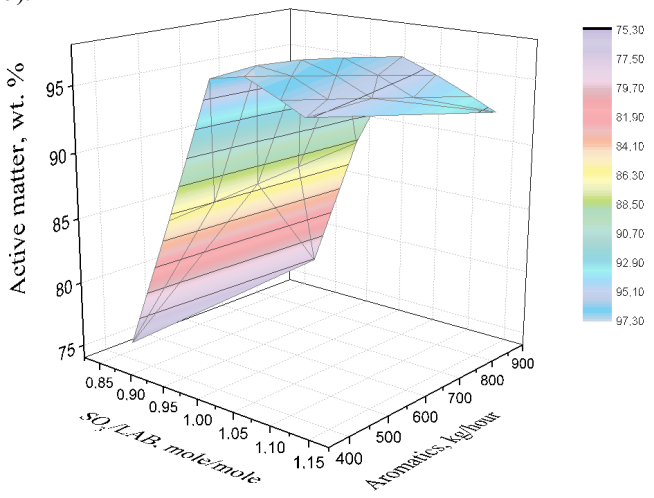

Fig. 5. Dependence of ASA viscosity on amount of aromatics passed through reactor.

The use of these regularities allows to maintain optimum technological modes of sulphonation process according to composition of the feedstock, as well as to predict the date necessary reactor washing when the concentration of high-viscosity component becomes critical.

5. Conclusions

1. Increased concentration of aromatic hydrocarbons in dehydrogenation process feedstock, first, increases concentration of high-viscosity components (homologs of indane, tetralines - by-products of alkylation process). The increase of ASA viscosity decreases LAB conversion at sulphonation stage.
2. Aromatics presence in raw materials decreases the duration of equipment stable operation both at the alkylation (due to accumulation of Has-F), and sulphonation steps (due to accumulation of high-viscosity components).
3. Taking components transformation mechanisms at sulphonation stage into account allows predicting the date of reactor washing with accuracy of 2 days.
4. Using of mathematical model allows controlling the technological mode, in particular, SO3 /LAB molar ratio, in dependence on sulphonation reactor raw materials composition.

Acknowledgements

The reported study was funded by RFBR, according to the research project № 16-33-60022.

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