Short Communication

INFLUENCE OF AROMATICS CONTENT IN THE FEED STREAM ON HF-CATALYST REGENERATOR AND LINEAR ALKYLBENZENES SULPHONATION REACTOR STABILITY

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Received 13 August 2016
Accepted 10 July 2017

ABSTRACT

The article presents results of experimental analysis of alkylaromatics composition in paraffins dehydrogenation process feed flow. It was shown that during the technological stages, as a result of dealkylation and polymerization processes, these substances adversely affect the equipment. At the HF-catalyst regeneration stage their presence leads to compression of inter-draining period, as heavy aromatics accumulate mainly in the column bottom. In sulphonation reactor it manifests itself as viscous component formation, sulphonation uniformity disfunction and compression of inter-washing period. Recommendations concerning the processes optimization depending on alkylaromatics composition in the feed flow are provided.

Keywords: sulphonation, alkylaromatics, viscous components, optimization.

INTRODUCTION

One of the main problems of alkylbenzene sulphonic acid (ASA) production is noncontrollable decrease in the product quality, namely, decrease of ASA content in the product flow below allowable value (96 mass %). Literary review showed that the main reason for ASA content decrease is disturbance of linear alkyl benzenes (LAB) conversion uniformity in sulphonation process [1 - 5]. This is caused by formation of highly viscous components (HVC) in the organic liquid phase that prevents SO_3 diffusion from gas to the liquid phase. The other problem is connected with HF-regeneration column parameters instability that occurs due to formation of heavy aromatics (HA) fluorides [6, 7].

The aim of the present research was to investigate the influence of alkylaromatics on HF- regeneration column and sulphonation reactor parameters stability using mathematical modelling.

As formation of HVC cannot be completely avoided, the other way to improve the ASA manufacturing process efficiency is to optimize the sulphonation reactor mode considering the aromatics content in dehydrogenation reactor and amount of tetralines entering the sulphonation reactor. The task of forecasting the inter-washing period of sulphonation reactor is also of great importance.

EXPERIMENTAL

The aim of HF-catalyst regenerator is to determine the temperature in the distillation column bottom, as its value is the performance indicator of chemical technological system on the whole.

The mathematical model of regeneration column bottom is as follows:

$$\begin{cases} \dfrac{dC_i}{dt} = \dfrac{C_i - C_i^0}{\tau} + \sum W_j \\ \dfrac{dT}{dt} = \dfrac{T - T_0}{\tau} + \dfrac{\eta}{\tau} + \sum_{j=1}^{n} W_j Q_j^{\text{c.r.}} \end{cases}, \quad (1)$$

where j = 8.9; t - astronomical time, s; τ - contact time, s; C_i and C_i^0 - current and initial components concentrations, relatively, mol/m^3; Wj - rate of chemical reaction, mol/s; T - temperature in the column bottom,

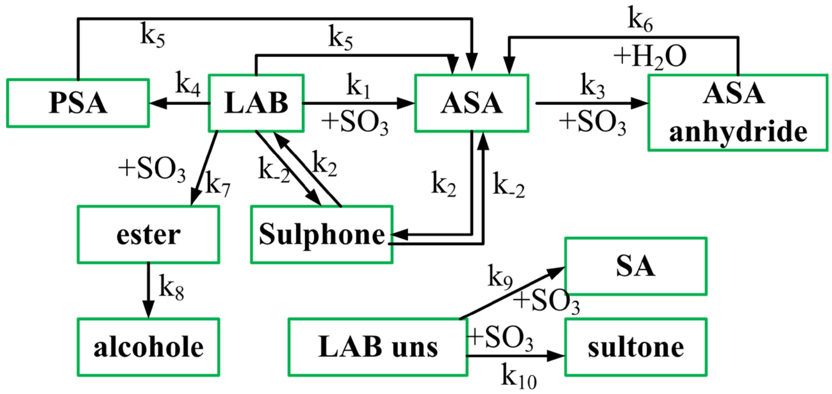

Fig. 1. Reaction network of sulphonation process (PSA - pyrosulphonic acid; LAB uns - unsaturated LAB; SA-acid, obtained by LAB uns sulphonation into side chain).

K; T_0 - initial temperature in the column bottom, K; $Q_j^{c.r.}$ - heat effect of chemical reaction, J/mol; η - change in the column bottom temperature due to decrease in HF evaporation rate because of HA fluorides formation.

The mathematical model of sulphonation reactor is analogical and considers reactions of active matter (ASA) formation, unsulphonated matter and H_2SO_4 formation, in accordance with presented reaction network (Fig. 1).

RESULTS AND DISCUSSION

Influence of aromatics on HF regenerator performance

According to previous research, HA of different types (HA-1 and HA-2) and tetralines are formed from aromatics entering the sulphonation rector with reagents from previous technological stages (Fig. 2).

Table 1. Dependence of column bottom filling period on the amount of aromatics in alkylation process raw materials (experimental data).

Date	Aromatics flow rate to alkylation, kg/h	Period of column bottom filling, days (calculations)
11.03.2011	303.7	12.7
10.06.2011	386.3	10.5
19.10.2012	436.1	9.0
03.07.2015	475.2	7.8
31.10.2015	502.1	7.3
13.07.2015	548.1	6.7
03.06.2015	627,6	6.5
1.06.2015	689.5	5.3
02.11.2015	804.5	4.6

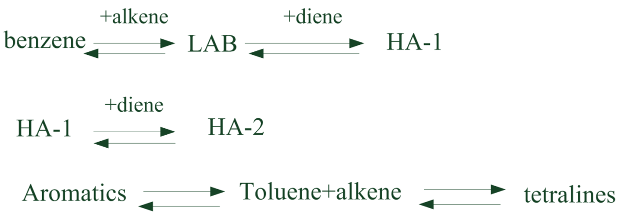

Fig. 2. Nature of HA.

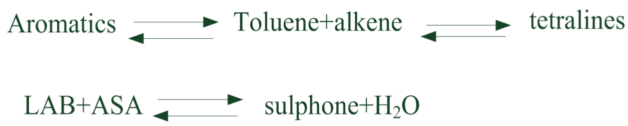

Fig. 3. Nature of highly viscous components.

In regeneration column these substances react with HF thus forming insoluble fluorides (HA-F).

The presence of aromatics in alkylation process raw materials leads to decrease in column bottom filling period (Table 1).

In November 2015, aromatics flow rate to sulphonation reactor was about 800 kg/h, and the period of column bottom filling fell by one half (Table 2).

Thus, the increase in aromatics content in alkylation reactor feed flow results in decrease of the period of column bottom filling due to formation of extra amount of soluble HF heavy components [8 - 10].

Table 2. Dependence of column bottom filling period on the amount of aromatics in alkylation process raw materials (forecast for 01.06.2015).

Aromatics flow rate to alkylation, kg/h (variation on a model)	Period of column bottom filling, days (calculations)
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

Influence of aromatics content on the sulphonation reactor performance

The main highly-viscous components formed in sulphonation reactor are tetralines (these substances are formed at the alkylation stage and enter the sulphonation reactor with the raw materials flow) and sulphones (formed in the sulphonation reactor).

On Fig. 3 the scheme of the compounds formation is presented. The content of tetralines in the LAB flow at the reactor entry is presented in Table 3. The formation of tetralines, which are highly-viscous, influences the product viscosity. The necessity of the reactor washing is connected with the decrease of the active matter content in the product flow (below 96 mass %) due to the viscosity increase and sulphonation uniformity disfunction. So, there is an obvious dependence of ASA color and inter-washing period duration on the amount of aromatics passed through the sulphonation reactor (Table 4).

If the amount of aromatics passed through the sulphonation reactor is essential, there is a sharp increase in the colour change (in accordance with the increase of viscosity). For example:

Table 3. Content of tetralines in the LAB flow at the entry of the sulphonation reactor.

Date	Content of tetralines in the LAB flow at sulphonation reactor entry, mass %
31.10.2015	3.5
17.09.2015	4.7
01.09.2015	5.1
14.10.2015	5.8

Table 4. Dependence of ASA color change and inter-washing period duration on the amount of aromatics passed the sulphonation reactor.

№	Period	Amount of aromatics passed through the sulphonation reactor, t.(experiment)	ASA color, Klett units (experiment)	
			Beginning of period	End of the period
1	08.01.2014-16.01.2014	51.8	10	22
2	04.03.2014-11.03.2014	56.7	11	20
3	06.04.2014-18.04.2014	51.2	10	16
4	29.12.2014-05.01.2015	47.1	9	13
5	03.07.2014-14.07.2014	112.7	11	52
6	07.08.2014-21.08.2014	107.4	11	39
7	08.04.2015-14.04.2015	34.5	10	15
8	14.04.2015-23.04.2015	57.6	9	12
9	21.06.2015-01.07.2015	53.5	10	17

Period 3 - 51.2 t aromatics - 12 days, Δcolor 6 Klett units;

Period 5 - 112.7 t aromatics -11 days, Δcolor 41 Klett units.

The usage of the mathematical model for LAB sulphonation process allows to calculate the dynamics of highly viscous components accumulation in dependence on the amount of aromatics passed through the sulphonation reactor and to forecast the date of necessary reactor washing.

CONCLUSIONS

It is possible to improve the efficiency of the ASA production technology in view of aromatics content in the dehydrogenation reactor feed and amount of tetralines entering the sulphonation reactor. It is also possible to forecast the reactor inter-washing period duration depending on the aromatics content (model calculations) and to optimize the alkylation reactor mode by fresh HF flow rate regulation depending on the raw materials composition and unsaturated LAB formation. The models application to the alkylation and sulphonation units allows to forecast the date of equipment mismatching and to prevent it.

Acknowledgements

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

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