

### FORMATION OF HIGHLY VISCOUS COMPONENT IN LINEAR ALKYL BENZENES SULPHONATION REACTOR AND ITS EFFECT ON PRODUCT QUALITY

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#### Abstract

This article discusses reasons leading to formation of highly viscous component in linear alkylbenzenes sulphonation reactor of alkylbenzene sulphuric acid production. It was found that highly viscous homologs of tetralin are formed in aromatic compounds dealkylation reactions with subsequent polymerization of alkenes. Infringement of mixture viscosity negatively affects the uniformity of sulphonation process and reduces the quality of target product.

**Keywords:** sulphonation; alkyl benzene sulphuric acid; highly viscous component.

#### 1. Introduction

In Russia, the raw material for production of synthetic detergents are mixtures of alkylbenzene sulphuric acids (ABSA). Obtaining of ABSA consists of several technology-related processes: dehydrogenation of alkanes on Pt-catalyst with olefins obtaining; hydrogenation of by-product (dienes); alkylation of benzene with obtaining of linear alkylbenzenes (LAB) using HF as catalyst; sulphonation of LAB with obtaining of ABSA (fig. 1).

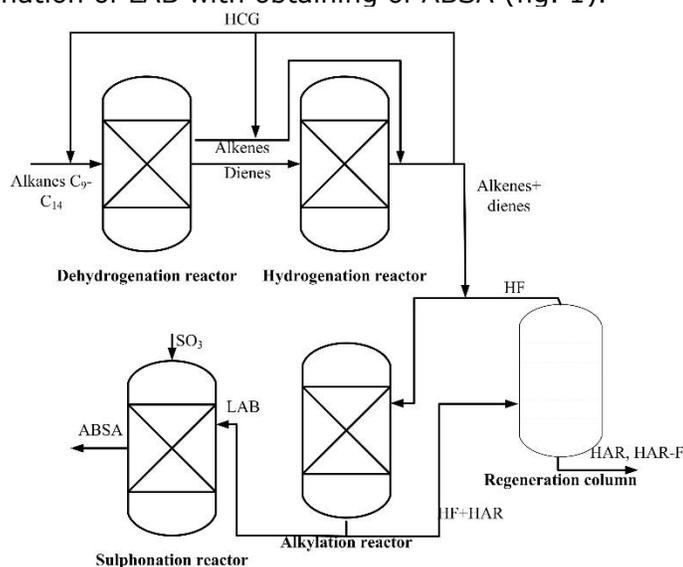


Figure 1. Flowchart of ABSA production: HCG - hydrogen-containing gas; HAR - high-aromatics; HAR-F - HAR fluorides

The significant demand for ABSA of high quality requires increased quality control not only for finished products but also for feedstock, which determines the optimal modes of each of production stages [1-3].

Sulphonation of linear alkylbenzenes occurs in a thin film reactor (fig. 2). A feature of this reactor is that the dosing of LAB must be permanent and uniformly distributed over the surface of reaction cylinder. At the same time, uniformity of reaction mixture is directly dependent on its viscosity. The content of highly viscous component in the sulphonation reactor raw material can lead to non-uniformity of the process and of LAB extra- and less- sulphonation reactions occurrence. Both have a negative effect on final product quality reducing ABSA content in product stream below the allowable - 96% by weight.

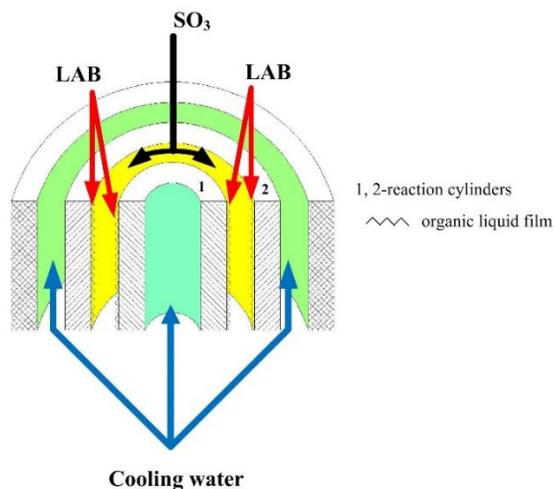


Figure 2. Design of sulphonation reactor

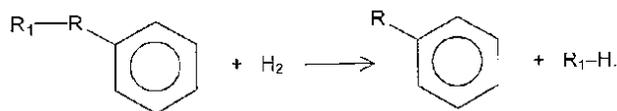
One of the main problems of sulphonation process is presence of highly viscous components in the raw materials of previous in technological scheme alkylation reactor. The aim of this research is to establish the nature of mentioned compounds, to describe the mechanism of their formation and to study the effect of ABSA viscosity on sulphonation process performance.

## 2. Experimental

### 2.1. The origin of highly viscous components in sulphonation reactor

Alkylaromatic hydrocarbons are fed with the raw material (are the part of desorbate and remain in C<sub>10</sub>-C<sub>12</sub> and C<sub>13</sub> fractions at pre-fractionation stage) of dehydrogenation process [4-7].

Alkylaromatic compounds may be split both in dehydrogenation and sulphonation stages forming light unsaturated hydrocarbon and alkylaromatic compounds with one methyl radical.



As a result of these reactions by-products are produced that:

- form heavy alkylation products (homologs of tetralin, indane, heavy aromatics *et al.*) in the alkylation step;
- in sulphonation stage light aromatics reacts less intensive than LAB with C<sub>10+</sub> sidechain, but is more prone to dealkylation with formation of short-chain olefins, capable to further polymerization.

Results of thermodynamic parameters calculation for possible reactions occurring at sulphonation stage show (tab. 1):

- The reaction of light aromatics with SO<sub>3</sub> is thermodynamically less likely and close to equilibrium, therefore, its sulphonation requires more contact time than sulphonation of

LAB with C<sub>10</sub> side chain. Therefore, most likely, this light alkylaromatics remains in nonsulphonated part.

- Light aromatics dealkylation reactions are thermodynamically more probable than reactions of LAB dealkylation. The result of these reactions is formation of low molecular weight olefins, very reactive in polymerization and forming a film of polymer compounds, that negatively effects the ABDA quality [9-10].

Table 1. Thermodynamic characteristics of LAB sulphonation process (T - 308 K, P - 0.04 MPa, C<sub>12</sub> radical)

| Nº        | Reaction  | ΔG, kJ/mole   | ΔH, kJ/mole   |
|-----------|---|---------------|---------------|
| 1         | LAB+SO <sub>3</sub> →ABSAs  | -233.3        | -209.8        |
| <b>2</b>  | <b>Ar+SO<sub>3</sub>→ABSAs</b>  | <b>-70.4</b>  | <b>-91.3</b>  |
| 3         | ABSAs+LAB ↔sulphones + H <sub>2</sub> O                                   | -1.3          | - 227.6       |
| 4         | 2 ABSAs+ SO <sub>3</sub> →ABSAs anhydride+ H <sub>2</sub> SO <sub>4</sub> | -47.7         | - 162.9       |
| 5         | LAB+2SO <sub>3</sub> → PSA  | -92.6         | -181.2        |
| 6         | PSA+LAB → 2 ABSAs   | -37.1         | -140.7        |
| 7         | ABSAs anhydride + H <sub>2</sub> O→2 ABSAs                                | -191.5        | -153.2        |
| 8         | LAB+SO <sub>3</sub> →ester+ H <sub>2</sub> O                              | -34.8         | -161.9        |
| 9         | ester+ H <sub>2</sub> O→alcohol   | -92.6         | -186.5        |
| 10        | LABuns+SO <sub>3</sub> →SA  | -274.5        | -197.8        |
| <b>11</b> | <b>Ar+SO<sub>3</sub>→ SA</b>  | <b>-132.7</b> | <b>-101.3</b> |
| 12        | LABuns +SO <sub>3</sub> →sultone  | -253.1        | -168.9        |
| 13        | LAB → benzene + alkene (C <sub>12</sub> )                                 | -10,4         | -83,3         |
| <b>14</b> | <b>Ar→ toluene + alkene C<sub>4</sub></b>                                 | <b>-57,4</b>  | <b>-64,1</b>  |
| <b>15</b> | <b>4 alkene→ homologs of tetralin</b>                                     | <b>-70.1</b>  | <b>-168.3</b> |

ABSAs – alkylbenzenesulphuric acid; PSA – pyrosulphuric acid; LABuns – LAB with unsaturated side chain; SA- the acid formed as a result of LABuns sulphonation in the side chain; Ar- aromatic compounds.

Thus, highly viscous component is formed in alkylation stage as a result of reactions 14 and 15 occurrence. According to reaction stoichiometry, from 645 kg/hour of aromatics about 334 kg/hour of tetralin homologues may be formed (at 100% conversion). This amount of highly viscous component is sufficient for ABSAs viscosity to reach the value of 187 cSt.

## 2.2. Mixture viscosity calculation

The viscosity depends on the cooling water temperature and viscosity of individual components of the mixture. Thus, in presence of highly viscous components in LAB the structure of reaction film is broken.

For mixture viscosity calculation the following empirical formula viscosity (Orrick-Erbar method of) was used.

$$\ln\left(\frac{\mu}{\rho \cdot M}\right) = A + \frac{B}{T} \quad (1)$$

where  $\mu$  – kinematic viscosity of the liquid, cSt;  $\rho$  – density of the liquid, kg/m<sup>3</sup>; M – molar mass, kg/mole; A and B constants are defined as the sum of group components given in Orrick-Erbar (tab. 2).

Table 2 The properties of substances at T - 308 K, P - 0.04 MPa

| Mixture component              | Molar mass, g/mole | Density, kg/m <sup>3</sup> | $\mu$ , cSt |
|--------------------------------|--------------------|----------------------------|-------------|
| Tetralin homologues            | 287                | 978                        | 726.1       |
| Indane homologues              | 273                | 971                        | 492.3       |
| Diphenylalcanes                | 322                | 879                        | 583.6       |
| ABSAs                          | 329                | 845                        | 163.8       |
| H <sub>2</sub> SO <sub>4</sub> | 98                 | 1630                       | 150.2       |
| SA                             | 329                | 852                        | 180.1       |

For highly viscous component in mixture with ABSK identification, viscosity of ABSK/non-sulphonated residue / H<sub>2</sub>SO<sub>4</sub> mixture was calculated with use of Kendall-Monroe method:

$$\mu_{mixture}^{1/3} = \sum x_i \cdot \mu_i^{1/3} \quad (2)$$

where:  $x_i$  – mass ratio of  $i$ -th component of the mixture;  $\mu_i$  – viscosity of  $i$ -th component, cSt.

Results of mixtures viscosities of «A» and «B» grade ABSA calculation are shown in tab. 3. Thus, consideration of tetralin homologues as ABSA highly viscous components allows obtain the most authentic values of mixture viscosity.

Table 3. Results of ABSA with highly viscous components mixtures viscosities calculation

| Mixtures (96.3 % of ABSA, 1.7% of highly viscous component, 1% of H <sub>2</sub> SO <sub>4</sub> ) | Mixture viscosity, cSt | Real viscosity of «A» grade ABSA, cSt |
|--|------------------------|---------------------------------------|
| ABSA/Tetralin homologues   | 169.5                  |                                       |
| ABSA/Indane homologues   | 169.7                  | 175.1                                 |
| ABSA /Diphenylalcanes  | 168.5                  |                                       |
| Mixtures (95% of ABSA, 4% of highly viscous component, 0.6 % of H <sub>2</sub> SO <sub>4</sub> )   | Mixture viscosity, cSt | Real viscosity of «B» grade ABSA, cSt |
| ABSA/Tetralin homologues   | 264.7                  |                                       |
| ABSA/Indane homologues   | 229.9                  | 266.4                                 |
| ABSA /Diphenylalcanes  | 244.2                  |                                       |

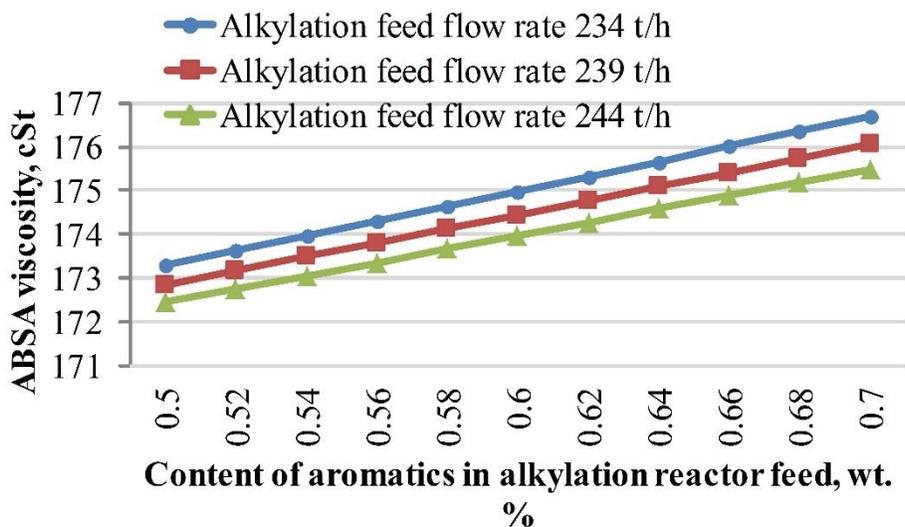


Figure 3. Dependence of ABSA viscosity on ratio of aromatics in alkylation reactor feed (T-303 K)

### 3. Results and discussion

All calculations presented below were carried out with use of mathematical model developed for alkylation and sulphonation processes and taking physical and chemical regularities of hydrocarbons transformations into account. Fig. 3 shows the dependence of ABSA viscosity on ratio of aromatics in alkylation reactor feed.

Thus ABSK viscosity depends on the content of aromatics in alkylation reactor feed. Knowing the controlled values of «A» grade ABSA viscosity we can set the allowable value of aromatics content at different feed flow rate to alkylation reactor.

Let's consider ABSA viscosity dependence on temperature in sulphonation reactor in the working temperature range (fig. 4). At average temperature in sulphonation reactor of 303 K and aromatic content in alkylation reactor feedstock ABSA viscosity is equal to 175 cSt. At higher temperatures there is decrease of mixture viscosity, however, this leads to intensification of side reactions of non-sulphonated compounds formation, i.e. to reduction of ABSA quality.

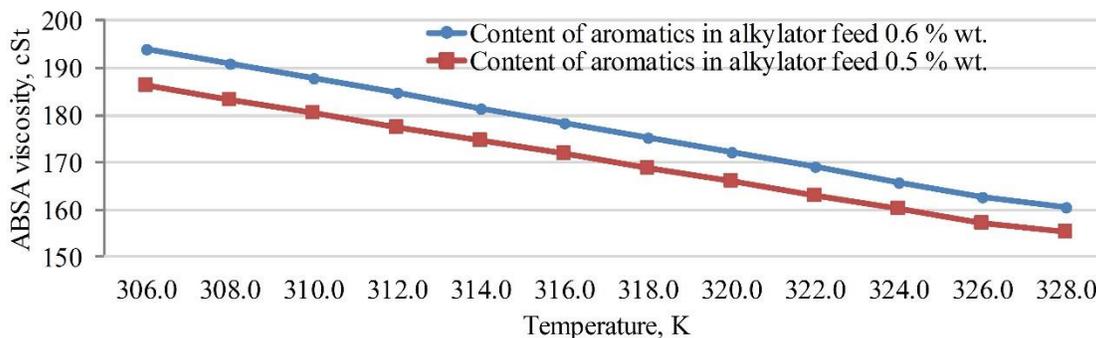


Figure 4. Dependence of ABSA viscosity on temperature in sulphonation reactor

Fig. 5 shows the dependence of ABSA mass ratio on its viscosity. From Fig. 5 it can be seen that the increase in ABSA viscosity leads reduction of its mass ratio in the product stream due to deterioration of sulphonation process uniformity.

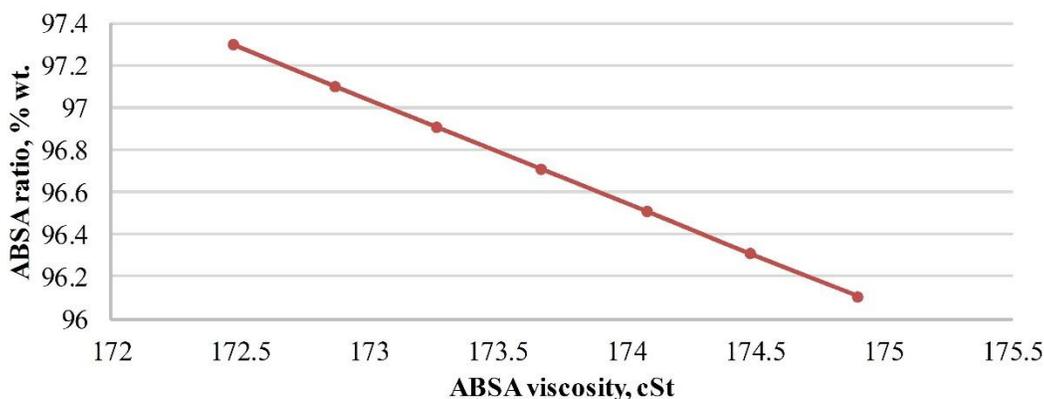


Figure 5. Dependence of ABSA mass ratio on its viscosity

#### 4. Conclusions

1. ABSA viscosity depends on content of highly viscous compounds formed from reactions of aromatics dealkylation followed by alkenes polymerization.
2. Knowing the controlled values of «A» grade ABSA viscosity we can set the allowable value of aromatics content at different feed flow rate to alkylation reactor.
3. Low aromatic content in alkylation reactor feedstock allows maintaining a higher feed flow rate to alkylator, i.e. increasing the production of LAB of desired quality.
4. The increase in ABSA viscosity leads reduction of its mass ratio in the product stream due to deterioration of sulphonation process uniformity, LAB extra- and less- sulphonation reactions occurrence because of  $\text{SO}_3$  diffusion coefficients in organic phase change.

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