

### STABILITY OF ALKYLATION AND SULPHONATION UNITS JOINT WORK IN ALKYL BENZENE SULPHURIC ACID MANUFACTURING

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#### Abstract

The presented paper is devoted to research on stability of alkylation and sulphonation units joint work in alkylbenzene sulphuric acid manufacturing. The reasons of equipment unstable operation and product quality deterioration in the stages of benzene alkylation with olefins and alkylbenzenes sulphonation were determined. Using the developed mathematical models of these processes uncontrolled temperature rise in the bottom of HF-catalyst regeneration column forecasting was carried out. Study of sulphonation and alkylation units stability in dependence on aromatics flow rate in alkylator was also performed.

**Keywords:** sulphonation; alkylbenzene sulphuric acid; film reactor; technological modes optimization.

#### 1. Introduction

Linear alkyl benzene sulphonates (LABS) are chemicals with saturated hydrocarbon chain of 10-13 carbon atoms linked to one of sulfonic acid groups. These substances are common anions used in detergents production. ABSA is obtained by flowing steps (fig. 1):

- 1) dehydrogenation of alkanes on Pt-catalyst with olefins obtaining;
- 2) hydrogenation of by-product (dienes);
- 3) alkylation of benzene with obtaining of linear alkylbenzenes (LAB) using HF as catalyst;
- 4) sulphonation of LAB with obtaining of ABSA.

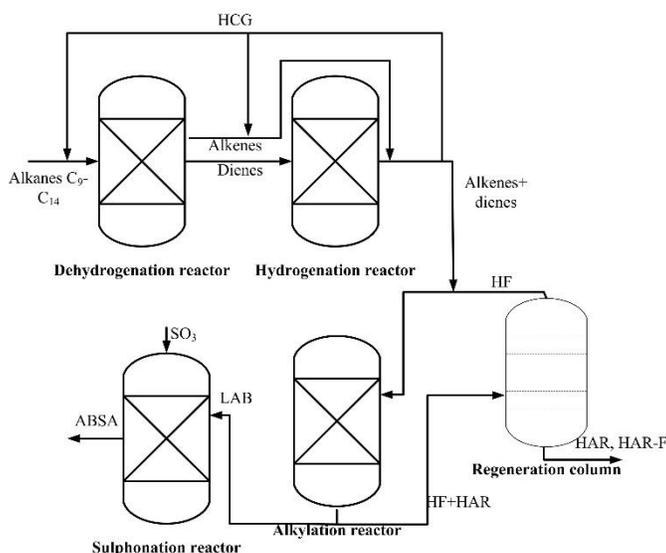


Figure 1. Flowchart of ABSA production: HCG - hydrogen-containing gas; HAR - high-aromatics; HAR-F - HAR fluorides

Given the impact of large number of different factors to work of coupled devices of technological scheme, study and optimization of these processes is of great complexity.

Research of causes leading to reactors stable operation violation and emergency situations in the workplace is of particular interest. As for HF- catalyst regeneration column, it is exposed to periodic disturbances in modes, which comprise the following: HF ceases boiling; there is uncontrolled temperature rise in the bottom of the column. The problem of sulphonation reactor is deterioration of main product –ABSA quality. At ABSA content below 96.1% in product flow they increase consumption of sulfur in sulfur trioxide  $\text{SO}_3$  production stage to increase the conversion of LAB. This increases the concentration of sulfuric acid in the sulphonation reactor product mixture above the allowable limit, necessitating stopping the production line for equipment washing. ABSA darkening also occurs, and this reduces the possibility for product commercialization.

To study the behavior of such systems in multi-factor changing of control parameters methods of mathematical modeling of chemical-technological processes are successfully used [1-2]. Thus, the aim of this work is to study the stability alkylation and sulphonation units joint work using the mathematical modeling method.

## 2. Experimental

### 2.1. Development of mathematical models for alkylation and sulfonation processes

Reaction networks and the kinetic models of the processes have been developed and presented in [4-6].

In the stationary regime change in  $i$ -th hydrocarbon concentration with reactor volume (contact time) the plug flow reactor model can be written as follows:

$$\frac{dC_i}{d\tau} = W_i$$

Assumption of ideal displacement regime in alkylation reactor was confirmed by calculation of Peclet criterion ( $403.7 > 200$ ). According to experimental data, characteristics of benzene alkylation reactor are similar to adiabatic. Then the heat balance equation in steady state can be written as follows:

$$\rho C_p \frac{dT}{d\tau} = \pm \sum_{j=1}^N (-\Delta H_j) W_j$$

Mathematical models of alkylation and sulphonation processes also give a good convergence of experimental and calculated data. Thus the developed computer programs are suitable for the refinery processes monitoring and optimization.

### 2.2. Establishing the reasons HF-catalyst regeneration column abnormality

HF regenerator column is a distillation column comprising 12 bubble cap trays and has an inner monel clad layer (up to 67% nickel and 38% copper). The HF feed stream is supplied to 7-th plate. The design of columns is shown schematically in fig. 2.

During the research following hypothesis on violation during HF-catalyst regenerator operation was done: violation of the column is due to formation of acid-insoluble layer on the surface of liquid in the bottom of the column, which prevents evaporation of HF and leads to uncontrolled increase in temperature. Lowering the temperature at the bottom of the cube is associated with formation of stagnant zones with different temperature profile that are formed due to termination of HF evaporation and convection violations. Additional cooling is associated with cold HF runoff in the column cube from the system.

This layer is formed from the substances that meet the following requirements:

- insoluble in HF;
- a density is less than that of HF;
- a viscosity is higher than that of HF.

Substances dissolved in liquid HF can be HAR-F. The alkylation process may be accompanied by olefins fluorination reaction, but these compounds are not detected in the

raw materials of regenerator column, as separated in the settler with the hydrocarbon phase and removed from the bottom of the stripper. This shows that hydrocarbon fluorides are formed directly in the regeneration column as a result of HAR hydrofluorination reaction.

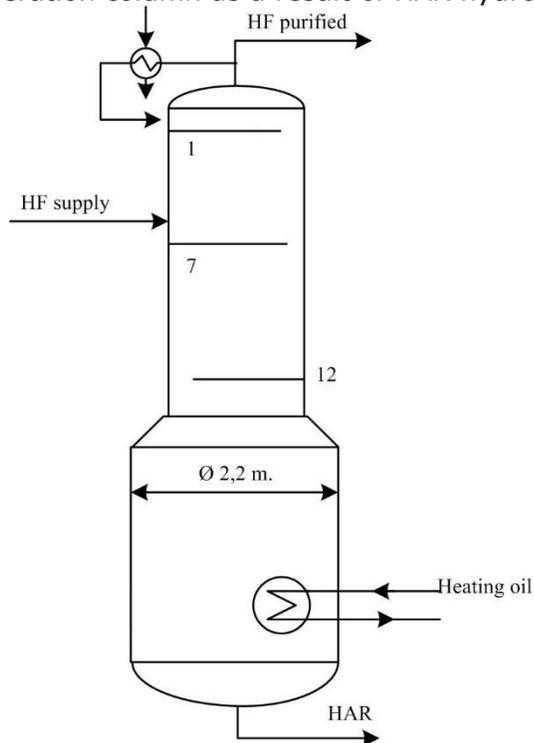


Figure 2. Design of HF regeneration column

### 2.3. Establishing the reasons of ABSA color deterioration

A literature review showed that, despite the fact that ABSA color is basically an aesthetic factor in sulphonates commercialization, more intense color can also be a qualitative indication of high degree of sulphonation. Anionic surfactants in aqueous solution are colored from yellow to reddish orange [7]. Klett color is defined by the formula  $R = (1000) (D) / 2$ .

To increase of color intensity in sulphonation process is caused by following factors:

- 1) high concentration of  $\text{SO}_3$  and high of  $\text{SO}_3/\text{LAB}$  molar ratio, which leads to dealkylation with formation of unsaturated hydrocarbons (alkenes), which polymerize forming resinous compound and thus deteriorate ABSA color;
- 2) temperature of ABSA and exhaust gas measured at the outlet of reactor should not exceed  $42^\circ\text{C}$ . At higher temperatures charred particles are formed and product color deteriorates [8];
- 3) increase of sulfuric acid in ABSA.

### 2.4. ABSA aging

An important role in the color change is the so-called ABSA aging acid in which there is an increase in sulphonation degree. It occurs in several stages [9]:

- 1) fast stage, which occurs in the first 10 minutes;
- 2) step which takes from 40-50 minutes to 4 hours;
- 3) stage, which takes from several days to several weeks, and is most obvious, if sulphonation process proceeds at severe conditions (high  $\text{SO}_3/\text{LAB}$  molar ratio, high coolant temperature).

According to [9], on pilot plant the concentration of sulphonated compounds in the end of the aging process is usually as high as 98% by weight. The content of sulfuric acid in this case may be reduced to 0.5% by weight.

There are many foreign patents, which provide information on ABSA color stabilization by its lightening. Typically, the lightening process is carried out by reacting of ABSA with proton reagent. Typical protic reagents: water, alcohols  $R(OCH_2CH_2)_n$ , glycerol, ethanolamine, diethanolamine and triethanolamine.

ABSA is treated by protic reagent in concentrations ranging from 0.50 to 15.0 wt. based on the ABSA weight. The most frequently proton reagents are used with concentration 4 - 10% by weight. Most preferred oxidizing agent is hydrogen peroxide, which can be used in various forms and concentrations. Selection form is an aqueous solution, at concentrations ranging from 0.10 to 70%, based on the total weight of the solution. A more preferred concentration is in the range of from 30 to 50%. ABSA reacts with protic reagent at a temperature from about 0 °C to about 80°C, for a time sufficient to obtain a homogeneous mixture with stirring. The most preferred temperature - from 25°C to 50°C. The resulting mixture has a color from 2 to 8 Klett units.

It is also noted that the color of resulting acid, however, is not sufficiently stable. It should be transformed into a sulfonic acid salt as soon as possible after clarification, otherwise it acquires dark again [10].

The proposed methods of ABSA color stabilization were tested and validated experimentally. It was also found that the ABSA color is in direct correlation with the share of aromatics in the dehydrogenation feed (fig. 3).

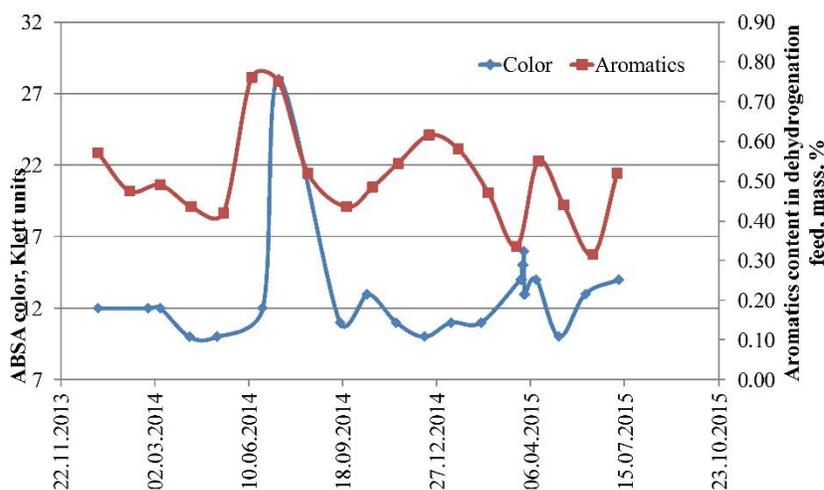


Figure 3. Change in ABSA color and concentration of aromatics in time

Aromatics in the feed negatively affects ABSA quality indicators, in particular, color. This can be explained by formation of highly viscous component in the reaction mixture resulting from aromatics dealkylation reactions with subsequent with alkenes polymerization forming tetralin homologues.

## 2.5. Establishing the reasons of ABSA quality decrease

The main indicator of ABSA quality is pure substance concentration in a mixture with non-sulfonated residue. Formation of non-sulfated residue of ABSA is determined by kinetic factor (target and side reactions during the sulphonation) and hydrodynamic (presence of high-viscosity component and  $SO_3$  diffusion to organic phase limitation).

According to the analysis (IR and mass spectroscopy) of non-sulfonated residue it is composed of following compounds: esters, alcohols, sulphones, sultones and SA. SA-isomers of sulphonic acids obtained by sulphonation of unsaturated LAB in the side chain.

The content of unsaturated aromatic compounds in reaction stream of sulphonation reactor is connected with LAB bromine index. Since unsaturated compounds are active in reaction of sulphonation in the side chain, the by-products are SA, which refer to nonsulfonated residue and have a higher viscosity than the desired product.

The most important condition for quality product obtaining is the uniform distribution of LAB on reaction cylinders surface. If uniform distribution does not occur, then the structure of the film is broken, causing both incomplete and extra LAB sulphonation.

Fig. 4 shows the material flows of alkylation and sulphonation reactors and HF regeneration column.

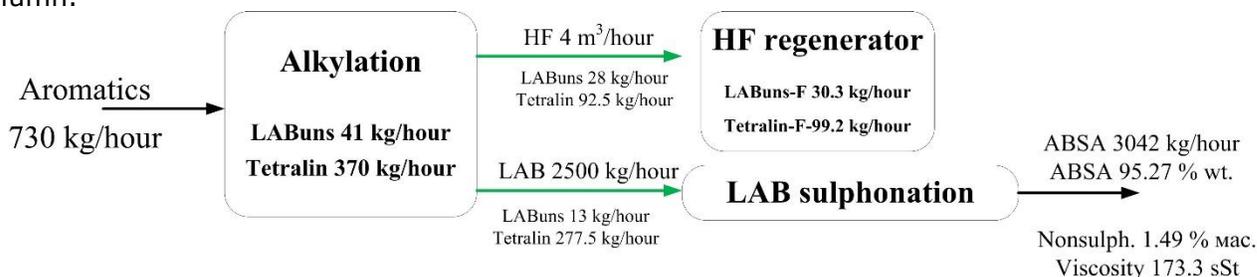


Figure 4. Material flows of "alkylation-sulphonation" block of ABSA production unit

The alkylation reactor feed contains 730 kg/hour of aromatics (experimental data). In alkylation reactor 41 kg/hour of unsaturated LAB and 370 kg /hour of tetralin homologues is formed. Proceeding from the time of regeneration bottom filling, tetralin flow to regenerator is about 92.5 kg/hour. Rest of tetralin (277.5 kg/hour) enters the sulphonation reactor forming highly viscous component. Amount of unsaturated LAB entering the LAB sulphonation reactor is calculated from the experimental value of LAB bromine index and is about 13 kg/hour. Remaining unsaturated LAB in amount of 28 kg/hour enters the HF regeneration column.

Thus, ABSA deterioration is related with two factors:

- increasing LAB bromine index that is the share of unsaturated LAB in the sulphonation reactor feed;
- formation of highly viscous component from aromatic compounds, resulting in increase of reaction mixture viscosity and decrease in sulphonation process uniformity.

### 3. Results and discussion

Using the developed mathematical models of alkylation and sulphonation processes series of calculations to study the stability of these ABSA production stages were carried out.

#### 3.1 Forecasting of uncontrolled temperature rise in HF regeneration column bottom using the mathematical model

Upon reaching the limiting mass of HAR-F in the bottom of the column there is a sharp and uncontrolled increase in temperature. The dependence of temperature on amount of HAR-F is shown in fig. 5.

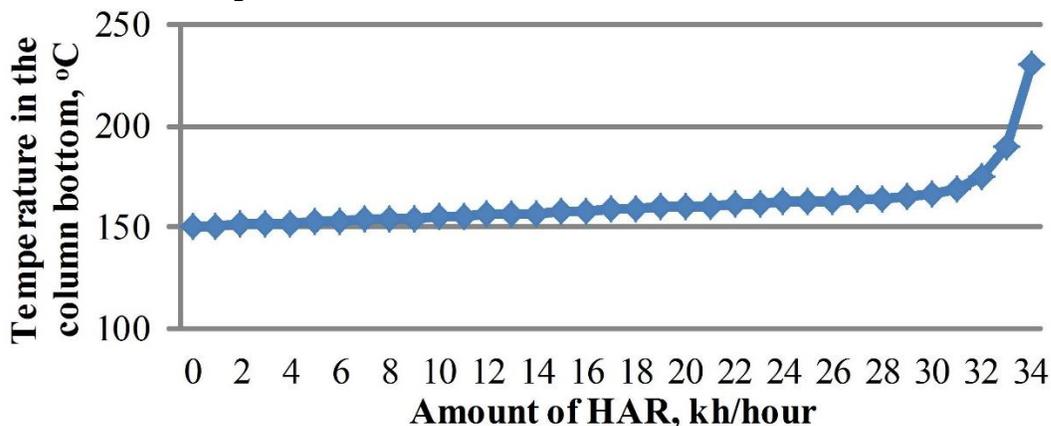


Figure 5. Dependence of temperature on amount of HAR-F in the column bottom

Algorithm for predicting violations in stable column operation was proposed. It consists in calculating the alkylation process parameters; calculating the HAR total amount; calculating the HAR flow rate to HF regenerator; calculating the amount HAR-F accumulated in the bottom of the column; temperature calculation in the column bottom. When the temperature reaches the limit value warning about possible violation in regenerator regime is given.

### 3.2. Dependence of alkylation and sulphonation units stability depending on the rate of aromatics flow rate to alkylator

With increasing aromatics flow rate to alkylation reactor amount of tetralines and HAR fluorides in the column regeneration increases. Preventative drainage of the columns excluded emergency situations. However, in case of its absence time of column stable operation would be reduced, as the critical HAR-F concentration would accumulated earlier.

Fig. 6 shows the dependence of ABSA viscosity (calculated from experimental values of its color) on the number of aromatics passed through sulphonation reactor in the period between reactor’s washings.

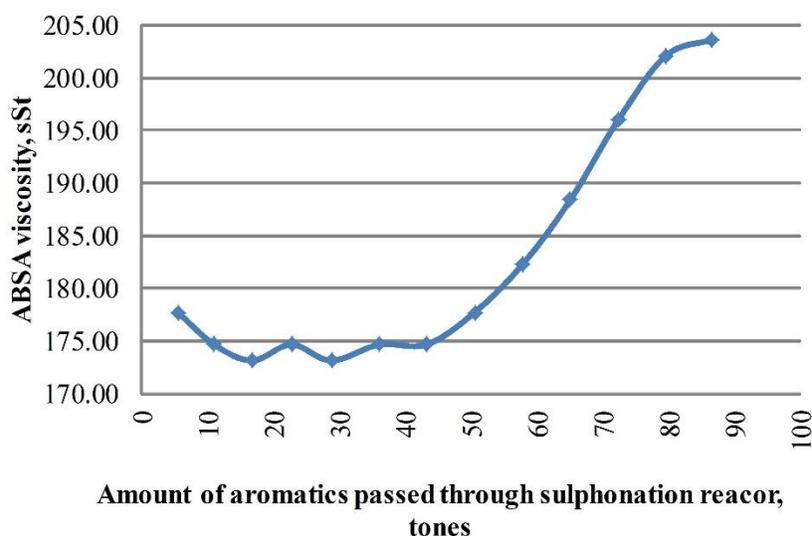


Figure 6. Dependence of ABSA viscosity on amount of aromatics

The sharp increase in viscosity at the end of period between reactor washings confirms accumulation of highly viscous component in the reactor. At the initial stage the diffusion of SO<sub>3</sub> to reactants is not difficult, therefore, the viscosity does not change significantly. With an increase in viscous component concentration the diffusion is hindered, increasing the rate of interaction between reagents of hydrocarbon phase. Thus, in such reaction between ABSK and LAB sulphones – one of the highly viscous components – are formed. So at the end of period between washings there is a sharp increase in mixture viscosity.

Tab. 2 shows the dependence of period between reactor washings duration on aromatics flow rate to alkylator.

Table 2. Dependence of period between reactor washings duration on aromatics flow rate to alkylator

Aromatics flow rate to alkylator, kg/hour	Period between reactor washings duration, days	Aromatics flow rate to alkylator, kg/hour	Period between reactor washings duration, days
300	17	550	9
350	15	600	9
400	13	650	8
450	12	700	7
500	10	750	6

When the flow rate of aromatics to alkylation reactor increases the concentration of highly viscous component in sulphonation reactor also increases. This leads to an growth of ABSA viscosity, its color deterioration and, as a consequence, to reduction of period between sulphonation reactor washings.

Fig. 7 shows changes in highly viscous component in sulphonation reactor accumulation dynamics at different aromatics flow rates to alkylator. Increasing of aromatics flow rates to alkylator results in reduction of highly viscous component critical value accumulation time.

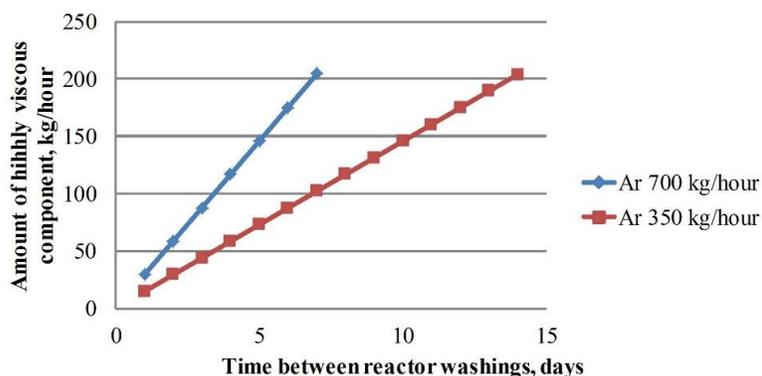


Figure 7. Dynamics of highly viscous component in sulphonation reactor accumulation

In turn, the high viscosity component accumulation in sulphonation reactor affects the ABSA share as follows (fig. 8).

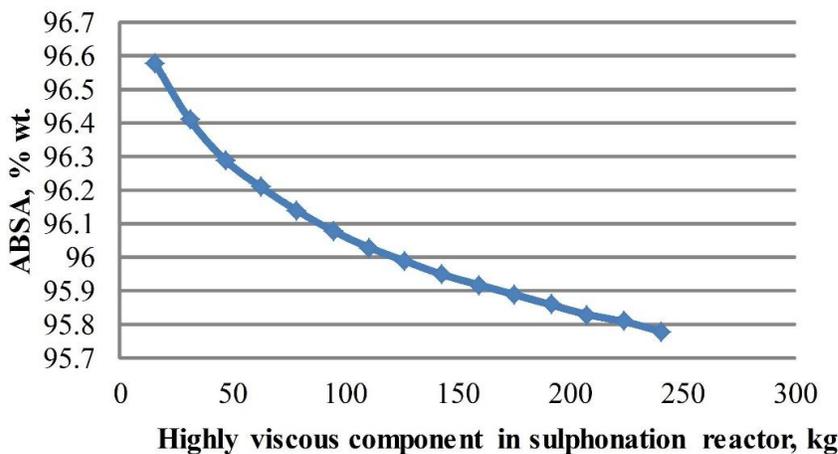


Figure 8. Dependence of ABSA share on amount of highly viscous component in sulphonation reactor

As can be seen from fig. 8, accumulation of highly viscous component leads to reduction of ABSA share, as sulphonation uniformity is disturbed when diffusion changes.

#### 4. Conclusions

1. The reason for HF-regeneration column stable operation violations is formation of HAR-F layer, preventing the evaporation of acid from the column bottom.
2. The possible reason for ABSA color deterioration is reactions of alkenes polymerization and process of acid "aging". Slowing of ABSA darkening process is possible by its treating with proton reagents: water, alcohols, glycerol, ethanolamine, diethanolamine and triethanolamine.
3. Deterioration of ABSA quality is due to two factors: the increase in LAB bromine index that is the share of unsaturated LAB in sulphonation reactor feed; formation of highly viscous

component from aromatic compounds resulting in increase of reaction mixture viscosity and sulphonation process uniformity reduction.

- Increasing of aromatics flow to alkylation reactor results in increase of tetralines and HAR-F concentration. This reduces the period of highly viscous component critical value accumulation and, consequently, reduces the ABSA share.

### List of symbols

$t$	time, sec;
$C_i$	concentration of $i$ -th component, mole/m <sup>3</sup> ;
$\tau$	contact time, sec;
$W_i$	rate of $i$ -th component concentration while chemical reactions change, mole/(m <sup>3</sup> ·sec).
$(-\Delta H_j)$	heat of $j$ -th chemical reaction, J/mole;
$W_j$	rate of $j$ -th chemical reaction, mole/(m <sup>3</sup> ·sec);
$C_p$	heat capacity of reacting mixture, J/(mole·K);
$\rho$	density of reacting mixture, kg/m <sup>3</sup> ;
$T$	temperature, K;
$D$	optical density of the sample at the desired concentration

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