

NATURE OF HIGHLY VISCOUS COMPONENT IN THE ALKYL BENZENE SULFONIC ACID TECHNOLOGY AND ITS INFLUENCE ON THE PROCESS EFFICIENCY

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Abstract

The purpose of this article is to study the composition of feedstock and products of the process of production of linear alkylbenzene sulfonic acid as a main component of synthetic detergents. Light aromatic compounds, contained in sulfonation feedstock, form a highly viscous component as a result of dealkylation and polymerization reactions. This component is able to accumulate in the sulfonation reactor reducing efficiency and uniformity of the process and the duration of period between reactor washings.

Keywords: *alkylbenzene sulfonic acid; sulfonation; highly viscous component; mathematical modeling.*

1. Introduction

Alkylbenzene sulfonic acid (ASA) is chemical 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 following steps [1-3]:

- 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) sulfonation of LAB with obtaining of ASA.

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.

Aromatic compounds of unknown nature contained in feedstock make it difficult to simulate and optimize the sulfonation process. During sulfonation these compounds lead to the formation of highly viscous component, which is critical for the process in a thin film of organic phase. The uniformity of its distribution in the reactor is disturbed, the diffusion of SO₃ molecules in organic phase is hampered, the product color deteriorates, content of active component is reduced [4-5].

The purpose of this work is to prove aromatics content in LAB and composition of active matter based on laboratory analyses of the selected samples, and analysis of trends of sulfonation parameters during the period between reactor washings using mathematical model.

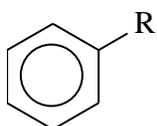
2. Experimental

2.1. Proving the aromatics content in LAB and composition of active matter based on laboratory analyses of the selected samples

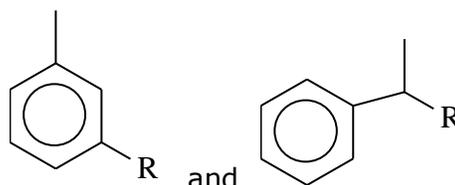
The most probable composition of aromatics coming with strippant C₁₁H₁₆, C₁₂H₁₈, C₁₃H₂₈, isomers C₁₁H₁₆, C₁₂H₁₈, C₁₃H₂₈, probably 2-methylnaphthalene, 1-methylnaphthalene). Analysis of the content of organic compounds in feedstock of dehydrogenation reactor was carried out on the magnetic mass spectrometer Thermo Scientific™ DFS (Germany) (Tab. 1).

Table 1. Results of hydrocarbon group analysis of the feedstock for dehydrogenation process, wax fraction C₁₀–C₁₃ (mixing unit)

Compound	Content, % wt.			
	06.06.2014	18.11.2014	24.06.2015	11.06.2015
Alkanes				
C ₁₀ H ₂₂	13.131	15.885	11.583	10.647
C ₁₁ H ₂₄	22.083	23.768	27.370	25.051
C ₁₂ H ₂₆	30.135	27.951	25.791	33.179
C ₁₃ H ₂₈	29.105	24.116	31.265	29.120
C ₁₄ H ₃₀	0.644	0.635	0.637	0.456
n-alkylbenzenes				
C₁₁H₁₆	0.039	0.077	-	-
C₁₂H₁₈	0.019	0.170	-	-
C₁₃H₂₈	0.044	0.189	-	-
C ₁₆ H ₂₆	0.009	0.035	-	-
C ₁₇ H ₂₈	0.031	0.036	-	-
C ₁₈ H ₃₀	0.020	0.015	-	-
C ₁₉ H ₃₂	0,012	0,009	-	-
Methylalkylbenzenes (branched alkylbenzenes)				
Σ isomers C₁₁H₁₆	abs.	0.344	0.004	0.001
Σ isomers C₁₂H₁₈	0.028	0.678	0.001	trace
Σ isomers C₁₃H₂₀	0.014	0.857	0.001	trace
Σ isomers C ₁₆ H ₂₆	0.032	0.087	-	-
Σ isomers C ₁₇ H ₂₈	0.098	0.088	-	-
Σ isomers C ₁₈ H ₃₀	0.090	0.104	-	-
Σ isomers C ₁₉ H ₃₂	0.086	0.077	-	-
Σ isomers C ₂₀ H ₃₄	0.047	0.038	-	-
Σ isomers C ₂₁ H ₃₆	0.023	0.021	-	-
Other hydrocarbons				
2-methylnaphthalene	0.036	0.189	-	-
1-methylnaphthalene	0.027	0.071	-	-
Σ isomers of dimethylnaphthalene	0.009	0.229	-	-
Unidentified compounds (probably isoparaffines)	4.238	4.331	3.348	1.546



n-alkylbenzenes, where R is the n-alkylbenzene radical (C₅–C₁₃)



linear and branched radical, more detailed composition is impossible to determine due to the low content of compounds in the sample

The most probable composition of aromatics coming with strippant C₁₁H₁₆, C₁₂H₁₈, C₁₃H₂₈, isomers C₁₁H₁₆, C₁₂H₁₈, C₁₃H₂₈, probably 2-methylnaphthalene, 1-methylnaphthalene).

Unidentified compounds mostly consist of saturated hydrocarbons, individual composition is impossible to determine due to the low content of compounds in the sample (probably isoparaffines).

Obviously, feedstock of the dehydrogenation process includes wide variety of aromatic compounds that entered the inlet of the dehydrogenation reactor, both from the stage of adsorptive extraction of paraffins at Parex unit (with strippant: C₁₁H₁₆, C₁₂H₁₈, C₁₃H₂₈, isomers C₁₁H₁₆, C₁₂H₁₈, C₁₃H₂₈, probably 2-methylnaphthalene, 1-methylnaphthalene), and with recycle of unreacted paraffins after alkylation (LAB circulation).

In addition, a large number of different isomers prevail in the sample of feedstock for 18.11.2014 – 2,294% compared with the sample for 06.06.2014 (0,418 %). It is also worth

emphasizing that both samples contain a significant number of unidentified compounds probably isoparaffines (4,238% – 06.06. and 4,331%–14.11), the sample of 2015 contain less of them. There are no isomers of $C_{11}H_{16}$ in dehydrogenation feedstock for 06.06, while for 18.11. their concentrations is 0,344 %. In samples for 2015 traces of these isomers were found.

According to the experimental studies of samples of feedstock for 2015 using the method of chromatography-mass spectrometry traces of linear and branched alkylbenzenes were found in new samples, despite of the results for 06.06.2014 and 18.11.2014. Probably previous samples were contaminated. Or inefficient operation of Parex unit in 2014 led to difference in feedstock composition in 2014 and 2015.

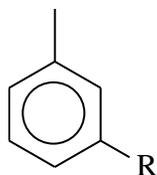
Analysis of Parex strippant composition in June 2014. showed high aromatic content (average concentration in strippant is 1 % wt., average concentration in dehydrogenation feedstock in fraction C_{10} – C_{12} , is 0,67 % wt. and average concentration in fraction C_{13} is 0,72 % wt.). According to the results of IR spectroscopy there are 5,25% unidentified compounds contained in LAB, probably short chain aromatics.

LAB samples were analyzed using gas chromatography – mass spectrometry (GC-MS), Tab. 2.

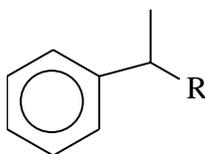
Table 2. Results of hydrocarbon group analysis of LAB

Compound	Content, % wt.			
	06.06.2014	18.11.2014	LAB E-602 11.06.2015	FC-212 24.06.2015
Methylalkylbenzenes (linear alkylbenzenes)				
$C_{16}H_{26}$	2.155	2.323	2.729	2.704
$C_{17}H_{28}$	3.997	4.159	4.191	4.205
$C_{18}H_{30}$	3.959	4.165	4.326	4.429
$C_{19}H_{32}$	2.681	3.129	3.339	3.472
Σ AB isomers C_{16}	8.118	7.764	8.889	8.495
Σ AB isomers C_{17}	24.363	22.351	18.632	19.008
Σ AB isomers C_{18}	28.858	28.859	26.251	25.535
Σ AB isomers C_{19}	23.156	24.051	22.725	22.818
Unidentified compounds (probably tetraline and indane homologues, polyalkylaromatics)	2.713	3.199	8.918	9.334

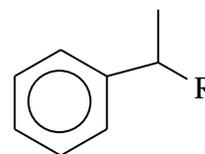
Methylalkylbenzenes are compounds of this structure:



where R is the n-alkyl radical (C_9 – C_{12}), or compounds of such type;



where R is the n-alkyl radical (C_8 – C_{11})



where R is isomer of alkyl radicals (C_8 – C_{11}), radical isomerism is impossible to establish without appropriate standards.

Σ isomers of alkylbenzenes are mostly possible isomers of such structure

Accessory substances in LAB (tetraline and indane homologues, polyalkylaromatics), are most probable included in «Unidentified compounds» due to the complexity of their identification. Experimental studies of active matter of ASA were carried out using GC-MS, and showed its composition mostly contains unconverted alkylbenzenes $C_{13}H_{27}$ and $C_{12}H_{25}$, their concentration is maximum.

The results of study were used in development of the unsteady mathematical model of sulfonation process which has prediction and optimization functions [6-11].

3. Results and discussion

3.1. Analysis of LAB and active matter composition

Thus, despite the presence of aromatic hydrocarbons was detected in ASA samples (aromatic ring in target and by-product), the target product ((C₉-C₁₄)-C₆H₄-SO₃H), by-products: pyrosulfonic acid ((C₉-C₁₄)-C₆H₄-SO₂-O-SO₃H) and sulfones (((C₉-C₁₄)-C₆H₄-SO₂-C₆H₄-(C₉-C₁₄)), active matter mostly consists of unreacted LAB (PhC₁₂H₂₅ and PhC₁₃H₂₇). Presence of sulfo compound is not confirmed.

Previously completed researches showed that during operation of the sulfonation film reactor highly viscous component forms and accumulates. Highly viscous component contains of tetralins and sulfones. Tetralines are formed both at the stage of sulfonation as a result of interaction of LAB and ASA, and at the previous stages of dehydrogenation and alkylation. This leads to a regular increase in the viscosity of the organic liquid film and as a result to the difficulties of diffusion SO₃ to the reagents and disturbing the uniformity of the sulfonation process. Therefore, the efficiency of the sulfonation process depends not only on ASA viscosity (the amount of accumulated highly viscous component), but also on a current aromatic content in feedstock (LAB), and operational parameters at previous stages. Thus, the decrease in molar ratio at the dehydrogenation stage leads to decrease in degree of dehydrogenation of diolefin by-products, increasing the amount of aromatic structure in the sulfonation reactor feedstock.

Indirect parameter which shows the amount of accumulated highly viscous component is pressure of ASA recycle. By the end of the period between reactor washings it increases dramatically, this signals that concentration of viscous component reaches a critical value and indicates the necessity of reactor washings.

The mathematical model of the sulfonation process considers dynamics of highly viscous component accumulation and allows predicting changes of the main indicators of product quality during the period between reactor washings and also its duration. It also allows making recommendations on increasing in duration of the period between reactor washings while maintaining the required product quality as well as recommendations on optimal sulfur supply to the sulfonation reactor depending on the amount of the current concentration of highly viscous component. The more aromatics contains in the feedstock of the sulfonation reactor the more viscous component is formed, the contents of tetralines in LAB and the contents of tetralines and sulfones in ASA grows. When ASA is recycled viscous component is at the entrance of the switchgear, at the same time permeability of the flow is disturbed and the pressure increases. Trends of considered parameters correlate with each other. With maximum aromatic content in LAB – 8.35 % wt. there is maximum pressure of ASA recycle - 225 kPa (for 11.06.2016). This confirms a link between the pressure of ASA recycle as an indicator of necessity of the reactor washings with accumulation of highly viscous component formed from aromatics. The deposition of viscous component occurs not only on the film inside the reactor but also at the entrance to the reactor. This is confirmed by correlation between the pressure of ASA recycle and its color which is indirect parameter of viscosity.

As calculations showed at the dehydrogenation stage the aromatic dealkylation reaction is more likely to form paraffines. The aromatic dealkylation reaction to olefins is reversible. Dehydrogenation of short-chain olefins to diolefins are less thermodynamically probable. Hydrogenation of light aromatics is less thermodynamically probable to dienes, probable to cycloalkanes, and also thermodynamically probable hydrogenation of naphthalene derivatives to bicyclic aromatic compounds (Tab. 2).

As a result of the reactions by-products (short-chain olefins) and aromatic compounds are formed, which:

- 1) At the alkylation stage form heavy alkylation products (tetraline and indane homologues, polyalkylaromatics, etc.);

2) At the sulfonation stage light aromatics less intensively enters the reactions of sulfonation, than LAB with the C₁₀₊ side chain, but more confirmed to dealkylation with the formation of short-chain olefins capable of further polymerization.

The results of calculation of the thermodynamic parameters of possible reactions at the stage of sulfonation show:

- 1) light aromatics reacting with SO₃ is less thermodynamically probable and close to equilibrium. Therefore a longer contact time is required for the sulfonation of light aromatics than of LAB with the C₁₀₊ side chain.
- 2) light aromatics dealkylation reactions are more thermodynamically probable, than LAB dealkylation reactions. The result of such reaction is formation of low molecular weight olefins with high reactivity in polymerization process with the formation of a polymeric compound film that deteriorates the quality of ASA.

3.2. Trends of sulfonation parameters during the period between reactor washings

Besides the main controlled parameters of the sulfonation process the mathematical model allows to calculate dynamics of accumulation of highly viscous component during the period between reactor washings (Fig. 1).

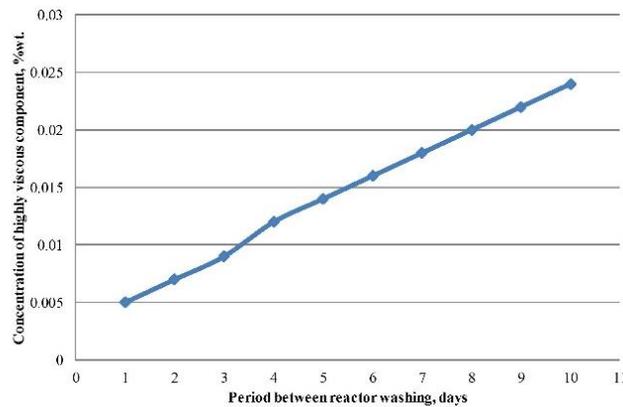


Figure 1. Dynamics of accumulation of highly viscous component during the period between reactor washings

The figure shows that during the period between reactor washings highly viscous component accumulates, which shows the deactivation of reaction medium. This additionally confirmed by trend of calculated sulfonation parameters during the period between reactor washings (Fig. 2).

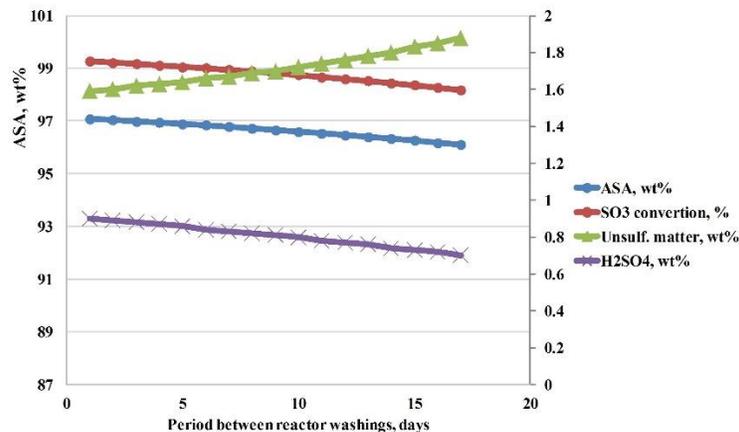


Figure 2. Trend of calculated sulfonation parameters during the period between reactor washings

The decrease in share of ASA and H₂SO₄ associated with a decrease in reaction rate due to the deactivation of reaction medium with highly viscous component accumulation. Therefore, the reaction is not completed, and unreacted LAB transferred to the active matter. The conversion of SO₃ is reduced by reducing amount of SO₃ involved in target reaction.

The represented dependences fully correlate with experimental data. The effect of aromatic content on duration of period between reactor washings is represented in Tab. 3.

Table 3. The effect of aromatic content on duration of period between reactor washings

Date	Aromatic content in LAB, % wt.	Period between reactor washings, days	Real sulfur supply for combustion, kg/h
05.01.2017	4.0	14	376.04
	4.2	14	
	4.4	13	
	4.6	13	
	5.8	12	
	5.0	12	
	5.2	11	
	5.4	10	
	5.6	10	
	5.8	9	
	6.0	9	

Amount of days before washing depends on aromatic content in LAB. The more aromatics contained in LAB, the less period between reactor washings as viscous components are accumulated.

4. Conclusions

It was shown that during operation of the sulfonation reactor highly viscous component accumulates, which contains of tetralins and sulfones. Tetralines are formed both at the stage of sulfonation as result of interaction of LAB and ASA, and at the previous stages of dehydrogenation and alkylation. This leads to a regular increase in the viscosity of the organic liquid film and as a result to the difficulties of diffusion SO₃ to the reagents and disturbing the uniformity of the sulfonation process. Therefore, the efficiency of the sulfonation process depends not only on ASA viscosity (the amount of accumulated highly viscous component), but also on a current aromatic content in feedstock (LAB), and operational parameters at previous stages. Thus, the decrease in molar ratio at the dehydrogenation stage leads to decrease in degree of dehydrogenation of diolefin by-products, increasing the amount of aromatic structure in the sulfonation reactor feedstock.

Indirect parameter which shows the amount of accumulated highly viscous component is pressure of ASA recycle. By the end of the period between reactor washings it increases dramatically, this signals that concentration of viscous component reaches a critical value and indicates the necessity of reactor washings.

The developed mathematical model of the sulfonation process which considers dynamics of highly viscous component accumulation is able to predict changes of the main indicators of product quality during the period between reactor washings and its duration. It also allows to make recommendations on increasing of the period between reactor washings duration while maintaining the required product quality as well as recommendations on optimal sulfur supply to the sulfonation reactor depending on the amount of the current concentration of highly viscous component.

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