



# Influence of alkylaromatic hydrocarbons on the efficiency of linear alkylbenzene sulfonic acid synthesis



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## HIGHLIGHTS

- The impact of aromatics and isoalkanes on alkylbenzene sulfonic acid formation was studied.
- Deactivation of Pt-catalyst caused by its coking was researched.
- The effect of highly viscous component formed from alkyl aromatics on sulfonation process was assessed.
- Mathematical model of sulfonation process considering process unsteadiness was developed.
- The yield and quality of ASA were improved.

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## ABSTRACT

ASA is the main ingredient of many commercial formulations for industrial and domestic synthetic detergents. Studying the work of the technological equipment that is used for manufacturing of the linear ASA allow us to conclude that alkylaromatic hydrocarbons in the product flow to hydrogenation reactor have significant impact on all technological stages. The aim of this work was to estimate the quantitative impact of alkyl components on ASA manufacturing efficiency and to improve the performance of the main equipment. The performed infrared (IR) and gas chromatography–mass spectrometry (GC–MS) analysis of the linear alkylbenzenes (LAB) and ASA samples indicate that the viscous components are tetralines and sultones as a part of unsulphonated matter. The developed mathematical model was used to reveal the following results and regularities of equipment modes: if the hydrogen/feedstock molar ratio at dehydrogenation stage equals 6/1, it is less optimal due to coke formation and requires increasing water supply. An increase of aromatics content in alkylation product flow leads to an increase in HF flow rate to the regeneration column. The optimal  $\text{SO}_3/\text{LAB}$  molar ratio increases along with content of aromatics in raw materials. The developed model of sulfonation process predicts the duration of reactor inter-washing period.

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## 1. Introduction

The increasing demand for detergents that give stable foam and are biodegradable requires new ways of improving the plants operational safety. As a rule, industries producing alkylbenzenes that can be sulfured to ASA are dangerous [1–7].

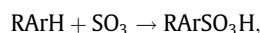
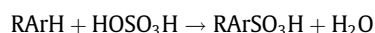
*Abbreviations:* Ar, aromatic hydrocarbons; ASA, linear alkylbenzene sulfonic acid; DAB, dialkylbenzenes; GC–MS, gas chromatography–mass spectrometry; HAR, heavy aromatic compounds; HAR-F, heavy aromatics fluorides; HCG, hydrogen containing gas; IR, infrared; LAB, linear alkylbenzene; LAB<sub>uns</sub>, LAB with unsaturated hydrocarbon chain; NAB, branched alkylbenzenes; PSA, pyrosulfonic acid; SA, sulfonic acid obtained after LAB<sub>uns</sub> sulfonation into side chain.

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The detergents residual content in the soil is an indicator of urbanization so that it is important, and, according to modern requirements, must be minimized [8–13]. In laboratory conditions the biodegradability is monitored by photocatalytic decomposition of detergent samples using ZnO at high temperatures [14] and other techniques [15–18].

The technology of multistage ASA preparation is in sequential dehydrogenation of *n*-alkanes to alkenes followed by alkylation of benzene in presence of HF catalyst. The obtained LAB is sulfonated with  $\text{SO}_3$  in the falling film reactor producing ASA [4].



here R – hydrocarbon radical from  $\text{C}_{10}$  to  $\text{C}_{14}$ , ArH – benzene.

**Nomenclature**

$C_i$	concentration of the $i$ -th component ( $\text{mol m}^{-3}$ )	$T_{cool}$	temperature of the coolant flow, K
$C_i^{in}$	initial concentration of the $i$ -th component ( $\text{mol m}^{-3}$ )	$T_{LAB}$	temperature of the LAB flow, K
$C_p$	heat capacity of reaction mixture ( $\text{J m}^{-3} \text{K}^{-1}$ )	$u_i$	reaction flow velocity ( $\text{m h}^{-1}$ )
$C_{p(cool)}$	heat capacity of the coolant ( $\text{J m}^{-3} \text{K}^{-1}$ )	$V$	reaction volume ( $\text{m}^3$ )
$C_{p(LAB)}$	heat capacity of the LAB flow ( $\text{J m}^{-3} \text{K}^{-1}$ )	$W_j$	reaction rate ( $\text{mol m}^{-3} \text{hr}^{-1}$ )
$C_{v.c.}$	concentration of highly viscous components ( $\text{mol m}^{-3}$ )	$x_i$	mass ratio of the $i$ -th component in the mixture (relative units)
$G$	feed flow ( $\text{m}^3 \text{h}^{-1}$ )	$Z$	the total volume of the recycled raw materials ( $\text{m}^3$ )
$G_{cool}$	coolant flow rate ( $\text{m}^3 \text{h}^{-1}$ )	$a_j$	a change in the $j$ -th reaction rate due to viscous component or coke accumulation
$G_{LAB}$	LAB flow rate ( $\text{m}^3 \text{h}^{-1}$ )	$-\Delta H_j$	heat of the $j$ -th reaction ( $\text{J/mol}$ )
$k_j$	reaction rate constant of the $j$ -th reaction ( $\text{h}^{-1}$ or $\text{m}^{-3} \text{mol h}^{-1}$ )	$\mu_i$	dynamic viscosity of the $i$ -th component of the mixture ( $\text{Pa s}$ )
$k_{Aj}$	reaction rate constant of the $j$ -th reaction in alkylation process ( $\text{h}^{-1}$ or $\text{m}^{-3} \text{mol h}^{-1}$ )	$\mu_{mix}$	dynamic viscosity of the mixture ( $\text{Pa s}$ )
$k_{Dj}$	reaction rate constant of the $j$ -th reaction in dehydrogenation process ( $\text{h}^{-1}$ or $\text{m}^{-3} \text{mol h}^{-1}$ )	$\rho$	density of the reaction mixture ( $\text{kg m}^{-3}$ )
$k_{Sj}$	reaction rate constant of the $j$ -th reaction in sulfonation process ( $\text{h}^{-1}$ or $\text{m}^{-3} \text{mol h}^{-1}$ )	$\tau$	contact time (h)
$L$	reactor length (m)	$\nu_{ij}$	stoichiometric coefficient of the $i$ -th substance in the $j$ -th reaction
$T$	temperature (K)		
$T^{in}$	initial temperature (K)		

There is a range of problems associated with ASA production, such as low conversion of LAB to ASA at the sulfonation stage, the need for periodic equipment washings due to contamination with sulfonation by-products, and deterioration of ASA biochemical degradability.

On the one hand, these problems are caused by shortcomings in the sulfonation reactor design. The paper [5] describes a new type of reactor developed by “Lion Fat and Oil Co.” Ltd. – a leader in the Japanese market of household chemicals and cosmetics. The principal difference of this reactor from the film one is as follows: 1) there is an ideal “isothermal sulfonation” due to “inert gas flow”, so that the air is fed between  $\text{SO}_3$  and falling organic film to assist the  $\text{SO}_3$  access to the raw materials; 2) there are special devices that distribute organic film of uniform thickness to the reactor walls.

The surveys such as that conducted by Lanteri (1978) focus on the need to rise product output by increasing the  $\text{SO}_3$  feed flow to ensure the process uniformity [19]. The problem solving is impeded due to the fact that the sulfonation is characterized by an increase in viscosity of the final product in comparison with the raw material and the high heat effect. It prevents the free contact of LAB with  $\text{SO}_3$  and reduces the overall sulfonation product flow rate. The  $\text{SO}_3$  supply is regulated by changing the sulfur feed flow to combustion to form  $\text{SO}_2$  with subsequent oxidation to  $\text{SO}_3$ . The optimal feed flow depends on the reaction mixture viscosity that is determined by concentration of by-products formed at the previous stages.

On the other hand, variability of raw materials composition promotes undesirable reactions at each stage of ASA manufacturing technology. High concentrations of undesirable alkylaromatic compounds in the dehydrogenation feedstock accelerate Pt-catalyst deactivation. At this stage, isoalkanes are converted to isoalkenes and then to isodienes. The last are converted to alkyl aromatics and coke structures.

During dehydrogenation stage branched alkylaromatics can split forming alkylaromatics with one methyl radical and light hydrocarbons. The resulting products flowing to the alkylation reactor promote acceleration of the heavy alkylates formation and lead to deterioration of ASA biodegradability.

In the last sulfonation stage the branched alkanes hydrocarbons may form unsaturated alkylaromatics which form produces undesirable sulfonic acids and esters.

The aim of this work was to estimate the quantitative impact of alkyl components content in the raw materials on the efficiency of ASA manufacturing with use of dehydrogenation, alkylation, and sulfonation mathematical models. This makes it possible to determine the optimal process conditions ensuring the high quality of ASA under the changing technological conditions and chemical composition of the feedstock.

## 2. Object and methodology of research

### 2.1. Description of the technology

A plant for LAB manufacturing includes a number of consecutive blocks:

1. Catalytic dehydrogenation of  $\text{C}_9\text{--C}_{14}$  alkanes over Pt-catalyst yielding a mixture of  $n$ -alkenes and  $n$ -alkanes;
2. hydrogenation of dienes over nickel-based catalyst;
3. HF alkylation of benzene with alkenes yielding LAB;
4. sulfonation of LAB with sulfuric anhydride to produce ASA.

A block diagram of LAB and ASA synthesis is shown in Fig. 1.

Dehydrogenation of  $\text{C}_9\text{--C}_{14}$  alkanes to the corresponding alkenes is the first stage of LAB and ASA production. The stage produces feedstock for synthesis of biodegradable detergents. Industrially, this process is carried out at the temperatures of 460–490 °C and pressure above atmospheric (0.2 MPa) over Pt-based catalyst. Besides the main reaction ( $\text{C}_9\text{--C}_{14}$  alkanes dehydrogenation), the other side reactions are possible under the process conditions (i.e. dehydrocyclization, aromatization, isomerization, cracking, and coking).

Synthesis of alkenes through benzene alkylation is carried out in the presence of HF acid catalyst at a temperature of 50–60 °C, pressure of 0.4–0.6 MPa, the benzene consumption in the reactor is maintained at around 17–22  $\text{m}^3/\text{h}$ , the flow rate of hydrocarbons into the reactor is 70–128  $\text{m}^3/\text{h}$ , the catalyst (HF) flow rate to the reactor is 105–192  $\text{m}^3/\text{h}$ . The sulfonation stage occurs at a temperature of 35–40 °C, the LAB flow rate to the sulfonation reactor is about 2400–2800 kg/h and the  $\text{SO}_3/\text{LAB}$  molar ratio is maintained at the level of about 1 mol/mol. The network of sulfonation reactor is presented in Fig. 2.

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