



Synthesis of heavy alkyl benzene sulfonate in a rotating packed bed combined with a stirred tank reactor



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ABSTRACT

This study presents the synthesis of heavy alkyl benzene sulfonate (HABS) via liquid–liquid reaction of heavy alkylbenzene (HAB) with dilute liquid sulfur trioxide (SO₃) in a rotating packed bed (RPB) combined with a stirred tank reactor (STR). The effects of different operating conditions including high gravity level (G), total liquid flow rate (Q_L), SO₃ concentration (ζ), SO₃ dosage (φ), reaction temperature (T) and reaction time (θ) on HABS content (η) were investigated, and the results revealed that high HABS content of about 88% was achieved under the optimal operating conditions including G of 59, Q_L of 62.8 L h⁻¹, ζ of 30%, φ of 1.1, T of 45 °C and θ of 4 min. The results indicated that the sulfonation reaction was basically achieved in the RPB of the combined reactor, and the time of the synthesis process was shortened.

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1. Introduction

Heavy alkyl benzene sulfonate (HABS) has a large molecular weight and is widely applied as heavy duty detergent, lubricant additive, corrosion inhibitor, oil-displacing agent and assistant plasticizer [1,2,7]. It is generally synthesized either via gas–liquid reaction of heavy alkylbenzene (HAB) with a SO₃ gas mixture in a falling-film reactor (FFR) or through liquid–liquid reaction of HAB with fuming sulfuric acid or dilute liquid sulfur trioxide in a stirred tank reactor (STR) [3–5].

However, owing to the high viscous property and boiling point of HAB as well as the fast sulfonation reaction process [4], gradients usually occur both in reactant concentration and temperature along the tubes of the FFR, resulting into coking phenomenon and oversulfonation during the gas–liquid sulfonation process [5,9,10]. Consequently, the liquid–liquid sulfonation process in STR or continuous stirred-tank reactor (CSTR) was developed to overcome the aforementioned problems associated with the gas–liquid sulfonation in FFR [8,10]. Nonetheless, due to

the low micromixing efficiency of these reactors, the micromixing time does not well match with the fast sulfonation reaction and hence the quantity and quality of the product are greatly compromised [6]. Therefore, a reactor with good micromixing and mass transfer performance is desirable for the liquid–liquid sulfonation process.

A rotating packed bed (RPB) is a novel efficient reactor that has been widely employed for intensification of micromixing and mass transfer processes [11,12]. The rotating packing in the RPB provides a strong shear force which incises liquid into very fine elements. The fine elements coalesce and further split many times as they pass through the packing. The frequency of fusion and splitting becomes much faster as the size of the fluid elements get much smaller, leading to a remarkable intensification of micromixing and mass transfer [13]. As a result, RPBs have successfully been applied to absorption [14], crystallization [15], polymer devolatilization [16], polymerization of butyl rubber [17], bromination [18], distillation [19,20], etc.

In view of the great intensification of micromixing and mass transfer in RPB and the short residence time in RPB (less than 1 s) [21,22] for the completion of sulfonation reaction, an RPB combined with an STR was adopted to enhance micromixing and mass transfer efficiency in the liquid–liquid sulfonation reaction of HAB with dilute liquid sulfur trioxide in an attempt to achieve higher HABS content in this study. The effects of

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Nomenclature

a	Packing specific surface area, m^2
d^-	Mean diameter of the droplet, m
G	High gravity level
g	Gravity acceleration, m s^{-2}
L	Length of the end-effect zone, m
M	Average equivalent weight of HAB, g mol^{-1}
N	Rotating speed, r min^{-1}
N_D	Number of droplets for each layer
N_L	Total layer number of packing
Q_L	Total liquid flow rate, L h^{-1}
Q_{HAB}	HAB flow rate, L h^{-1}
Q_{SA}	Sulfonating agent flow rate, L h^{-1}
r	Geometric average radius of the rotor, m
r_1	Inner radius of the rotor, m
r_2	Outer radius of the rotor, m
T	Temperature, $^{\circ}\text{C}$
t	Residence time between two adjacent packing layer, s
u	Radial liquid velocity, m s^{-1}
u_0	Initial velocity of jet flow, m s^{-1}

Greek letters

ε	Packing porosity
ε_L	Liquid hold up, $\text{m}^3 \text{m}^{-3}$
σ	Surface tension, mN m^{-1}
ω	Angular velocity of the rotor, rad s^{-1}
ρ	Liquid density, kg m^{-3}
τ	Mean residence time, s
ν	Kinematic viscosity of the liquid, $\text{m}^2 \text{s}^{-1}$
δ	Thickness of two adjacent layer, m
ζ	SO_3 molar concentration, %
φ	SO_3 dosage, %
θ	Total sulfonation time, min
η	HABS content

different operating conditions such as high gravity level (G), total liquid flow rate (Q_L), SO_3 concentration (ζ), SO_3 dosage (φ), reaction temperature (T) and reaction time (θ) on HABS content (η) were examined to obtain the optimal conditions.

2. Experimental section

2.1. Materials

The heavy alkylbenzene (Nanjing Pingao Oil Co. Ltd.) used in this study had the following properties including molecular weight of 323 to 381, mean molecular weight of 357.7, density of 0.871 g mL^{-1} and viscosity of $19.2 \text{ mm}^2 \text{ s}^{-1}$ at 40°C . It comprised 48% mono-aromatics, 27% dicyclic aromatics, 15% tricyclic aromatics, 5% polycyclic aromatics and 4.4% unidentified aromatics.

Liquid SO_3 used as the sulfonating agent was distilled from fuming sulfuric acid (55–60 wt.%) and then mixed with 1,2-dichloroethane (1,2- $\text{CH}_2\text{ClCH}_2\text{Cl}$, purity > 99%, Beijing Chemicals Ltd.) in different proportions. 1,2-dichloroethane was adopted as solvent owing to its stability and easy recovery. Other chemicals were of analytical grade supplied by Beijing Chemicals Ltd.

2.2. Apparatus and procedures

The RPB mainly consisted of a packed rotor, a fixed casing, and liquid/gas inlets and outlets. The schematic diagram of the RPB was

showed in Fig. 1, and the parameters of the RPB was showed in Table 1.

Fig. 2 illustrates the experimental set up used in this study. The sulfonating agent which comprised liquid SO_3 with different proportions of 1,2-dichloroethane was contained in tank 1 at $28\text{--}30^{\circ}\text{C}$ while HAB was placed in tank 2. The prepared materials from tank 1 and tank 2 were respectively pumped into the RPB at varying volumetric flow rate. The volumetric flow rate of HAB ranged from 6.4 to 38.4 L h^{-1} while that of SO_3 was adjusted according to its concentration and the molar flow rate of HAB. The two streams pre-mixed at the inlet of the RPB and were sprayed into the inner edge of the rotor. The reactant mixture was then ejected out of the packing and captured by the wall of the cavity region (in the radial direction), and finally discharged out of the RPB from the liquid outlet into the STR where the sulfonation reaction continued for a period of time. The reaction time in the STR ranged from 0 to 5.0 min.

2.3. Analytical methods

The analysis was performed using the standard methods of the surfactant industry (ASTM D 4711–2009). The sulfonic acids were determined by non-aqueous potentiometric titration with methanolic cyclohexylamine. There were two peaks during the titration process: the first peak corresponded to the neutralized sulfonic acids and the first proton of sulfuric acids, while the second peak corresponded to the neutralized second proton of the sulfuric acids. The weight percent of sulfonic acids (RSO_3H) was evaluated as follows:

$$\eta = \frac{(2V_1 - V_2) \times C \times M}{W \times 1000} \times 100\% \quad (1)$$

where, V_1 and V_2 represent the consumption volume of titrant at the first and the second end points (mL), respectively, C is the molar concentration of titrant, W is the sample weight (g), and M is the average equivalent weight of sulfonic acid. All the used data was the average value of triplicate samples and the relative error was within 4.7%.

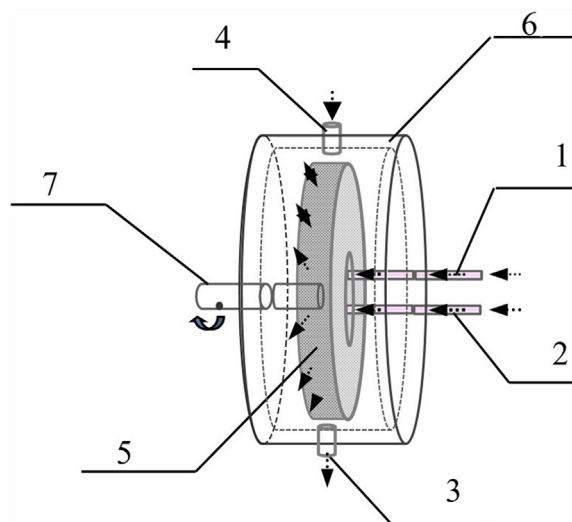


Fig. 1. Schematic diagram RPB for sulfonation experiment; 1-liquid inlet; 2-liquid outlet; 3-gas outlet; 4-gas inlet; 5-packing; 6-jacket for cooling water; 7-spindle.

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