Research Article

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Continuous sulfonation of hexadecylbenzene in a microreactor

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Abstract: Heavy alkyl benzene sulfonates are inexpensive surfactants that are extensively used as oil-displacing agents during tertiary oil recovery. Among these, C_{16–18} heavy alkyl benzene sulfonates possess an excellent ability to reduce the oil-water interface tension. In this study, hexadecylbenzene sulfonic acid (HBSA) was synthesised in a continuous stirred-tank microreactor using a continuous method with 1,2-dichloroethane (EDC) dilution. Post-sulfonation liquid SO₃ solution was used as a sulfonating agent for hexadecylbenzene (HDB). The effects of reaction conditions, such as the SO₃:HDB molar ratio, sulfonation temperature and sulfonation agent concentration, on the yield and purity of the product were investigated. Optimisation of the reaction process yielded high-quality HBSA samples with a purity exceeding 99 wt%. The continuous sulfonation process significantly enhanced the production and efficiency in the case of a considerably short residence time (10 s) in the reactor, without the need for aging. The results of this study demonstrate significant potential for application in industrial production.

Keywords: microreactor, sulfonation, hexadecylbenzene sulfonic acid, liquid sulfur trioxide, surfactants

1 Introduction

Heavy alkyl benzene sulfonates are widely used in industrial washing owing to their good foam stability and detergency [1]. Hexadecylbenzene sulfonic acid (HBSA) is a heavy alkylbenzene sulfonic acid with 16 carbons on its side chain and can be used to synthesise sodium hexadecylbenzene sulfonate (SHBS). SHBS is known to effectively reduce the surface tension of liquids in alkaline environments. Therefore, it is used as an additive in high-end lubricant oil or as chemical oil-displacing agents for enhanced oil recovery [2].

Heavy alkylbenzene sulfonates are obtained by sulfonation, aging, hydrolysis and neutralisation of heavy alkylbenzene. Among these, the sulfonation reaction is a process that involves rapid and highly exothermic reactions. Reaction processes that are similar to sulfonation are typically temperature-sensitive and demonstrate a significant potential for use in conventional reactors [3]. The mainstay of industrial sulfonation reactors is a stirred-tank reactor (STR) [4]. The sulfonation reaction of alkylbenzene is limited to low temperatures owing to its critical safety [5] and the difficulty involved in achieving efficient mixing and good thermal control in conventional reactors. Despite this, accidents caused by sulfonation reactions occur occasionally. Moreover, uneven heat distribution within the reactor can lead to the formation of undesirable by-products and low yields [1].

Microreactors are a new type of reactor that has received increasing attention in the last two decades [6–8]. New methods and ideas are necessary to solve some of the technical problems concerning reinforcement during the process of SO₃ sulfonation reaction. Microreactors possess advantages, such as a small channel size and large specific surface area, which effectively increase the speed of energy transfer in the reactors, save energy and increase their internal production efficiency. Moreover, microreactors also exhibit high-safety performance characteristics [6,9,10]. They typically possess mass transfer capacities that are 1–2 orders of

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magnitude larger than those of conventional STRs and falling film reactors (FFRs) for sulfonation reactions [11–13]. Microreactors offer other benefits, such as uniform internal temperature distribution, ease of control of the reaction temperature, narrow residence time distribution and adequate operating safety. Therefore, microreactors are suitable for high-temperature sulfonation reactions with instantaneous and strong exothermic processes [13,14].

Common sulfonating agents include sulfonyl chloride, a sulfuric acid mixture with sulfur trioxide [15], sulfur trioxide [16] and sulfuric acid [17]. Among them, sulfonyl chloride is an active sulfonating agent. However, it causes a violent sulfonation reaction and produces hydrochloric acid. This can lead to a difficult post-treatment of the product [18]. When sulfuric acid or oleum is used as the sulfonating agent, water is produced, which inhibits the positive progression of the reaction. To solve this problem, it is often necessary to use a dosage of the sulfonating agent that is greater than the chemometric ratio. Sulfuric acid anhydride (SO_3) is used as a stable, inexpensive [18] and highly active sulfonating agent. It facilitates the sulfonation process with negligible waste acid generation. However, the high activity of SO_3 triggers a violent reaction with uncontrollable side effects. Therefore, currently, diluted SO_3 is often used in industries to control its reactivity. Gaseous SO_3 is typically diluted with dry air and nitrogen [19], and liquid SO_3 is diluted with non-protonic solvents, such as methylene chloride [20], MeNO_2 and PhNO_2 .

The main reaction and reaction processes are depicted in Figure 1. The sulfonation of SO_3 in aprotic solvents is an electrophilic substitution reaction.

In this study, a method for the continuous synthesis of HBSA in a microchannel reactor was investigated. Hexadecylbenzene (HDB) was used as the sulfonation substrate. Liquid sulfur trioxide diluted with 1,2-dichloroethane (EDC) was used as a sulfonation agent. Process conditions, such as reaction temperature, SO_3 :HDB molar ratio, sulfonate concentration, pipe flow rate and residence time, were investigated to elucidate their effects on the HBSA yield. These process conditions were optimised to achieve the required high-quality product specifications, maximise the product yield and reduce energy consumption during production. Our study provides substantial evidence for the development of a safe and green process for the continuous sulfonation of heavy alkylbenzene.

2 Materials and methods

2.1 Raw materials

In this study, HDB (99%, TCI) and diluted SO_3 were used as reactants for sulfonation. SO_3 was distilled from fuming sulfuric acid (~25 wt%, Alfa Aesar) by the addition of

Figure 1: Mechanism of sulfonation of alkyl benzene.

anhydrous P_2O_5 (98%, Alfa Aesar) between $\sim 180^\circ\text{C}$ and 200°C and subsequent dissolution in 1,2-dichloroethane (EDC; AR, Beijing Tongguang Fine Chemical Company) as the sulfonating agent. The exact SO_3 concentration was standardised using a 0.01 M NaOH volumetric solution (Macklin). HDB was subsequently dissolved in EDC in accordance with the ratio of the sulfonating agent to the substrate. EDC is a volatile organic compound that can be recycled using a 40°C rotary evaporation vacuum.

2.2 Experimental procedures

Figure 2 depicts the experimental setup featuring the continuous microreactor unit, which comprises two flat-flow pumps, a three-way micromixer, stainless-steel tubes of adjustable length and a water bath. The check valve in front of the mini-mixer ensures that the reactant does not flow back into the pump and storage tank and maintains a constant volume flow in the mixer. The inner diameter of the stainless-steel tube is 0.6 mm, and the length of the stainless-steel tube can be adjusted depending on the desired dwell test. To examine the effect of volumetric flow rate and reactor pipe length on product yield, an experimental device was designed, as illustrated in Figure 3. The length of the reactor can be varied by adjusting the valve.

All equipment were rinsed with EDC before the experiment began. Dry air was used to evacuate the liquid in the duct, which ensured that water was removed from the system and the reactants were not diluted by solvents. The sulfonation agent and formulated HDB solution were passed through both flat-flow pumps at the same flow rate, the micromixer and finally into the reaction pipeline. The product was collected at the end of each unit. EDC solvent

in the product was recovered by evaporation using a vacuum rotary evaporator. Dry air was subsequently used to blow away the remaining solvent.

2.3 Characterisation

The analysis of the products was mainly performed in accordance with Chinese national standards, such as GB/T 8447-2008, GB/T 6366-2012 and GB/T 3143-1982. The physicochemical indices of the different components, in accordance with the standards mentioned above, are listed in Table 1. According to these standards, the mass fraction of the active ingredient (HBSA) of a quality product should be higher than 97 wt% and the mass fraction and free sulfuric acid content of free oil, containing by-products and unreacted HDB, should be less than 1.5 wt%.

The content of the active substance in the product was determined by diphasic titration [21]. This involved the preparation of a 0.070 g/L TB (AR, Shanghai Guangnuo Chemical Technology) and 0.036 g/L MB (AR, Tianjin Damao Chemical Reagent Factory) solution. Each liter of acidic sodium sulfate solution contained 100 g of anhydrous sodium sulfate (AR, Shanghai Chemical Reagent Co., Ltd) and 12.6 mL of concentrated sulfuric acid.

Cetyltrimethyl ammonium bromide (CTAB, 0.004 mol/L; AR, Tianjin Damao Chemical Reagent Factory) was employed as the titrating solution. The accurate concentration of CTAB solution (c_1 , mol/L) was calibrated with 0.004 mol/L sodium dodecyl sulfate (SDS; GC, 99%, Aladdin) solution using the diphasic titration method.

An appropriate amount (m_{SI} , g) of the product was added into a beaker and dissolved using ultrapure water to facilitate the detection of HBSA contents in the final product. It was subsequently neutralised with a sodium

Figure 2: The schematic diagram of experimental setup.

Figure 3: The experimental apparatus is used to study the reaction residence time.

hydroxide solution. The filtrate was diluted to 1 L with ultrapure water. Thereafter, 10 mL of the solution was pipetted into five 150 mL conical flasks for testing. The following were also added to the conical flask: 5 mL TB, 5 mL acidic sodium sulfate solution, 10 mL ultrapure water and 15 mL dichloromethane (AR, 99.5%, General-Reagent). The colour of the dichloromethane layer in the lower phase was seen to gradually change from purplish-red to a flesh colour. At this stage, 4–6 drops of MB were added to change the colour of the dichloromethane layer to blue-green; CTAB was subsequently added, which turned the solution yellow-green, thus indicating the endpoint.

Using the volume of consumed CTAB solution (V_{CTAB} (mL)), the mass fraction of the active matter (X_1) can be calculated using Eq. 1:

$$X_1 = \frac{V_{\text{CTAB}} C_1 \times 326.49 \times 100}{m_{\text{S1}}} \times 100\% \quad (1)$$

The mass fraction of free oil was analysed using the petroleum ether extraction method. An appropriate amount (m_{S2} , g) of the product was added into a beaker, dissolved using a small amount of 95% (v/v) ethyl alcohol and subsequently neutralised with a sodium hydroxide solution. The solution was transferred into a stoppered cylinder;

the beaker was rinsed with water and the resulting liquid wash was added back to the cylinder. Petroleum ether (AR, Xuzhou Tianhong Chemical Trade; boiling point between 60°C and 90°C) was added to the cylinder after its contents were mixed. After allowing the cylinder to rest for a while to facilitate separation of the layers, the supernatant was siphoned into a pre-weighed flask (m_0).

The extraction process described above was repeated four times. The solvent recovery apparatus was installed, and the solvent was recovered in a water bath until no distillate was discharged. The flask was removed and placed in the water bath. A small amount of acetone (AR, Shanghai Chemical Reagent) was added to the flask, and a blow tube was inserted into the bottom of the flask. A stream of dry cold air was slowly circulated through the tube to remove traces of the solvent, and the flask was subsequently weighed (m_1). Then, the mass fraction of free oil (X_2) was calculated using Eq. 2:

$$X_2 = \frac{m_1 - m_0}{m_{\text{S2}}} \times 100\% \quad (2)$$

The content of free sulfuric acid was determined by titration. Dithizone (AR, Aladdin) was used as an indicator, and lead nitrate (c_2 , 0.010 mol/L; Zhongke Standard (Beijing) Technology) was used as the standard solution to titrate the buffered acetone solution of the sample. First, 1 mol/L HNO_3 and 40 g/L NaOH solutions were prepared. A dithizone-acetone solution consisting of 0.5 g dithizone dissolved in 1 L acetone was employed as the indicator. Dichloroacetic acid (AR, Sinopharm Chemical Reagent) and an ammonia solution (AR Beijing Tong Guang Fine Chemicals Company) were subsequently used to prepare an ammonium dichloroacetate buffer solution with a pH between 1.5 and 1.6, whose pH should be 3.9–4.3 in a 70–85% (v/v) acetone medium.

Table 1: Physicochemical indices obtained via GB/T 8447-2008

Components	Index	
	Superior product	Qualified product
DBSA (wt%)	≥97	≥96
Free oil (wt%)	≤1.5	≤2.0
Free sulfuric (wt%)	≤1.5	≤1.5

To measure the free sulfuric acid content in the product, approximately 1.0 g (m_{S_3}) of the sample was added to a beaker and dissolved in water. A certain volume of the solution was pipetted into a conical flask and 1 mL of dithizone solution was added to it. If the solution appeared green, sodium hydroxide solution was added dropwise until the solution started showing an orange-red colour and nitric acid solution was added dropwise to the solution showing green. Subsequently, 2 mL of the ammonium dichloroacetate buffer solution and 80 mL of acetone were added. The solution was titrated with a lead nitrate standard solution immediately after the addition of acetone, until the green colour of the solution turned into a dark red colour, which indicated the end-point. Using the volume of consumed lead nitrate solution (V_{Pb} (mL)), the mass fraction of free sulfuric acid (X_3) was calculated using Eq. 3:

$$X_3 = \frac{V_{Pb} c_2 \times 0.098 \times 5}{m_{S_3}} \times 100\% \quad (3)$$

The product was dried after solvent removal and was in the form of a white powder. The field structure of the product was observed using a field emission QUANTA FEG 400 scanning electron microscope (FEI Company).

3 Results and discussion

3.1 Effect of sulfonation temperature

The raw materials were fully preheated before mixing. The microreactor used in this study contained a stainless-steel tube with thin walls and a small diameter, which could gradually extract heat from the sulfonation reaction. Therefore, the temperature of the thermostatic water bath was used as the reaction temperature. Figure 4 depicts the effect of reaction temperature on the HBSA yield, free oil and free acid content. As the temperature increases from 40°C to 50°C, the yield of HBSA is seen to remain nearly constant at ~92.54 wt%. When the temperature increases to 60°C, the yield decreases to 90.90 wt% and subsequently increases. The images reveal no significant effect of temperature on the yield of HBSA.

To further illustrate the effect of temperature on the HBSA yield, an analysis of variance (ANOVA) was performed on the experimental data listed in Table 2.

The calculated ANOVA results are listed in Table 3.

The van't Hoff rule regarding homogeneous phase thermochemical reactions suggests that the reaction rate

Figure 4: Effect of reaction temperature on the yield of HBSA, free oil and free sulfonic acid, featuring an SO_3 :HDB molar ratio of 1.20:1, SO_3 mass fraction of 10 wt% and residence time of 10.18 s. The pale navy blue parts indicate the range of HBSA content in the superior products, and the pale yellow parts indicate the range of free oil and sulfonic acid content of the superior products.

increases by 2–4 times for every increase of 10 K in the reaction temperature. However, the ANOVA results reveal that the reaction temperature, or its increase, does not have a significant effect on the yield of the product, possibly because the process depends on mass transfer.

Figure 5 indicates that the temperature increases from 40°C to 50°C, and the content of free oil decreases significantly from 3.15 to 1.41 wt%. HDB, which is the main component of the free oil. As the temperature increases, the reaction proceeds further, and the conversion of HDB increases. As a result, the free oil content in the product reduces. The content of free oil in the product is seen to decrease to 0.84 wt% when the temperature increases to 90°C. At this point, HDB is almost completely converted. However, as the temperature increases from 40°C to 90°C, the sulfuric acid content is seen to gradually increase from 4.24 to 7.13 wt%. This implies that the high temperature facilitated a significant acceleration of

Table 2: HBSA yields at various temperatures

Reaction temperature (°C)	Yield (HBSA) (wt%)					$\bar{Y}$ (wt%)
40	92.58	92.64	92.21	92.72	92.54	
50	92.49	92.83	92.50			92.61
60	90.55	90.99	90.76	91.31	90.90	
70	91.67	91.62				91.65
80	91.80	91.97				91.89

Table 3: Variance analysis of HBSA yields at various temperatures

Source	df	SS	MS	F		Significance
Group	4	0.000722	0.00018085	0.000428	2.61	—
Error	10	4.225991	0.42259912			
Total	14	4.224446				

the side reaction, resulting in a large number of dark coloured by-products. This is consistent with experimental observations, such as the colour of the product, which was darker at higher temperatures.

It increases the resistance of the heat and mass transport of the liquid at temperatures above 60°C [1]. Moreover, at temperatures above 70°C, SO₃, which has a low boiling point, was observed to escape from the reactor by vaporising into a stream of small bubbles (Figure 5). This is because of the reduced solubility of sulfur trioxide in the alkylbenzene solution. Although the gasification overflow of sulfur trioxide reduced the sulfonating agent concentration, the generation, movement and rupture of small bubbles further agitated the reactants via the formation of eddy currents in the pipe and improved the solution mixing; this enhanced the mass transfer process, reduced the concentration of products at the reaction interface, and further improved the reaction speed. Overall, the reaction temperature does not have a significant effect on the product yield, which further demonstrates that mass transfer is a dominant factor in the sulfonation process. The preferred reaction temperature was selected as 50°C.

3.2 Effect of SO₃:HDB molar ratios

Theoretically, the sulfur trioxide sulfonation process involves a chemometric reaction. Because of SO₃ overflow and the side reactions, SO₃ in the system cannot effectively

participate in the reaction. The injection of a theoretical quantitative amount of sulfur trioxide would result in residual unreacted HDB in the reaction system. An excess amount of SO₃ over the theoretical value is required to maximise the product yield. However, excessive SO₃ can increase the quantity of spent acid in the product, thus increasing the load during the post-treatment. Therefore, controlling the SO₃ to HDB ratio is critical for determining the balance between product yield and reaction depth.

Figure 6 reveals that two different ranges of ratios of SO₃ to HDB influence the yield of HBSA, free oil and sulfonic acid. The HBSA yield increases gradually from 95.70 to 97.32 wt% when the SO₃:HDB ratio is in the range of 1.0–1.1, and the residual free oil and sulfonic acid decrease to the level of the valley point in the figure to 1.51 and 1.12 wt%, respectively. The synthesis of HBSA is reversible, and therefore, the equilibrium shifts rapidly towards the formation of HBSA during the increasing concentration of the reaction. Excess sulfur trioxide tends to transform HDB completely. At a 1.10:1 SO₃:HDB ratio, the HBSA yield reaches 97.32 wt%, which is near the peak shown in the figure and satisfies the GB standard. The free oil and sulfuric acid contents were both at the same level at 1.54 wt% or less. However, increasing the SO₃:HDB ratio has a negative influence on the formation of HBSA. A higher SO₃:HDB ratio (1.2:1) results in a lower HBSA yield of 92.61 wt%, which is even lower than the HBSA yield with the SO₃:HDB ratio of 1.0:1. Because the concentration of HDB decreases gradually in a system with an increasing SO₃:HDB ratio, the effective collision

Figure 5: Schematic of the reactor interior.

Figure 6: Effect of SO₃:HDB molar ratio on the yield of HBSA, free oil and free sulfonic acid, featuring a reaction temperature of 50°C, SO₃ mass fraction of 10 wt% and residence time of 10.18 s. The pale navy blue parts indicate the range of HBSA content in the superior products and the pale yellow parts indicate the range of free oil and sulfonic acid content of the superior products.

probability of the molecules reduces, resulting in a slower reaction speed. Another factor is the excess of sulfur trioxide, which accelerates super-sulfonation and increases the number of by-products. Moreover, the residual free oil exhibits a large increase from 2.02 to 5.34 wt%, as the SO₃:HDB molar ratio increases to 1.20. However, the increase in free oil content is only 0.49 wt%, i.e., from 1.05 to 1.54 wt%. SO₃ in extreme doses results in the by-product sulfone, which is difficult to eliminate in the post-production process; consequently, the HDBS yield decreases. Therefore, the continuous increase in the sulfur trioxide concentration was not conducive to an increase in the yield of the target product. Thus, an adequate SO₃:HAB molar ratio of 1.10:1 was selected as an optimal parameter for the sulfonation process.

3.3 SO₃ mass fraction

SO₃ is a highly reactive suspending agent and releases a large amount of heat when mixed directly with organic compounds. The presence of a solvent can reduce the viscosity and control the sulfonation activity of SO₃, thereby reducing the formation of by-products. However, too much solvent can excessively reduce the sulfonation activity, thereby reducing productivity and increasing the burden of solvent handling.

A high SO₃ mass fraction (up to 15 wt%) promotes the conversion rate of HBSA and decreases the residual free

oil and free acid content, as shown in Figure 7. When the SO₃:HDB molar ratio is 1.10:1, the SO₃ mass fraction is seen to increase from 5.0 to 10.0 wt%, and the product yield increases from 92.10 to 97.32 wt%. Meanwhile, the levels of free oil and sulfuric acid continue to decrease from 4.03 to 1.05 wt% and from 3.87 to 1.63 wt%, respectively. As the concentration of the sulfonating agent increases up to 15.0 wt%, the increasing trend of the active ingredient (HABS) in the product stabilises at 98.23 wt%. At this mass fraction of SO₃, the free oil and sulfate contents are 0.31 and 1.46 wt%, respectively. The sulfonating agent was used as a reactant and the increase in the concentration of SO₃ shifted the equilibrium in favour of the forward reaction, which facilitated the formation of HBSA. The content of HBSA reached the standard of a quality product and stabilised. However, an increase in the SO₃ mass fraction from 10.0 to 15.0 wt% did not significantly affect the residual sulfuric acid content in comparison with that from 5.0 to 10.0 wt%, because of an excess of SO₃.

The field structure of the product was observed using the field emission QUANTA FEG 400 scanning electron microscope. Prior to the hydrolysis step, a plate-like base structure is seen to be covered by a cross-needle-like structure, which is generated during the sulfonation process of the anhydride (Figure 8a and b). The needle-like particle structure disappears after the hydrolysis step. The anhydrides present are completely transformed

Figure 7: Effect of SO₃ mass fraction on the yield of HBSA, free oil and free sulfonic acid, featuring a reaction temperature of 50°C, SO₃:HDB molar ratio of 1.10:1 and residence time of 10.18 s. The pale navy blue parts indicate the range of HBSA content in the superior products, and the pale yellow parts represent the ranges of free oil and sulfonic acid content of the superior products.

during hydrolysis, as shown in Figure 8c and d. The needle-like structure was presumed to represent the α -phase SO_3 molecules, and this conjecture was confirmed by the change in its weight percent.

SO_3 was precipitated from the unreacted sulfonating agent in the form of needle-like SO_3 crystals adhering to the surface of the product. Excess SO_3 could be removed through methods, such as hydrolysis. When the SO_3 concentration is excessive in solvents, such as halogenated alkanes, the resulting cyclic trimer is known to affect the quality of the product [22]. Therefore, the optimal sulfonating agent concentration was selected as 10 wt%.

3.4 Flow rate and pipe length

SO_3 and HDB diluted with EDC were pumped at the same volumetric flow rate through a stratospheric pump during

the experiments. They were mixed via collisions in a T-shaped micromixer and subsequently entered the microreactor. As the volumetric flow rate increased ($\text{Re} > 10$), the effect of turbulence was enhanced, and the raw materials were mixed more rapidly and uniformly, thereby accelerating the sulfonation process. However, the increase in flow rate reduced the yield of the product, owing to the shorter residence time of the reaction.

The experimental setup designed to investigate the effects of flow rate and pipe length on the product yield is shown in Figure 3. Figure 9 illustrates the trends of the HBSA yields for different pipe lengths and total flow rate systems. Both pipe length and flow rate are seen to contribute to product generation because the yield is seen to increase with increases in the pipe length and flow rate. The HABS yields reached 99 wt% eventually.

Figure 10a reveals that the increase in path length has a positive effect on HBSA production at different flow rates. The peak yield of HABS is 99.85 wt% with a

Figure 8: (a and b) FE-SEM images of the product before and (c and d) after the hydrolysis step.

Figure 9: 3D graph of the relationship between pipeline length and HBSA yield under different long-distance pipeline lengths and total flow rates, featuring a reaction temperature of 50°C, SO_3 mass fraction of 10 wt% and SO_3 :HDB molar ratio of 1.10:1. The pale navy blue parts indicate the range of HBSA content in the superior products.

pipe length of 4 m and a total flow rate of 10 mL/min. The influence of the reactor length on the residence time of the material has been discussed earlier. At high flow rates (14–18 mL/min), the HBSA yield is noted to be stable when the pipe length is longer than 3 m. Even at a flow rate of 18 mL/min, the HBSA concentration is seen to stabilise with a pipe length of over 4 m. This is because of the higher mass transfer efficiency in the system at

high flow rates. However, the increased residence time triggers side effects, leading to a reduction in the active ingredient content of the product.

A longer residence time was observed to lead to a darker liquid product in a short time range. To investigate the effect of prolonged residence time on the colour of the product, the liquid product was mixed in a CSTR and subsequently underwent a reaction. The solution was subsequently removed to obtain HBSA powder. The colour of the HBSA powder obtained at different residence times is presented in Figure 11. When the residence time ranges from 0 to 120 min, the colour of the product is relatively stable and exhibits no visible changes. After a continuous reaction for 24 h, the colour of the HBSA powder is seen to gradually deepen to light brown. The product colour changes to a dark brown colour after 10 days. Although a longer residence time contributes to an increase in the yield, it also leads to per-sulfonation and the formation of a by-product, which is a significant source of the darker matter in the final product and affects the product quality.

Figure 10b shows the variation of HBSA yield with total flow rate at different lengths of the reaction tube. When the total flow rate is increased from 2 to 6 mL/min, the residence time becomes shorter; however, the HBSA yields increase by over 4.8% with different pipe lengths. Higher flow rates improve the mixing efficiency and facilitate the reaction process, which results in a continuous increase in flow rate and a slowdown in the growth of the

Figure 10: Effect of pipeline length on HBSA yield under different total velocity conditions. (a) Effect of total velocity on HBSA yield under various pipeline lengths and (b) a reaction temperature of 50°C, SO_3 mass fraction of 10 wt% and SO_3 :HDB molar ratio of 1.10:1. The pale navy blue parts indicate the range of HBSA content in the superior products.

Figure 11: Effect of different residence times on the colour of HBSA powder.

product yield. When the reactor length is 4 m, the yield is noted to decrease slightly after the total flow rate exceeds 10 mL/min. This is because an increase in the flow rate, which contributes to the mass transfer efficiency, results in a shorter residence time for a given pipe length and eventually, an incomplete response. In particular, a pipe length of 1 m and an increase in flow rate from 14 to 18 mL/min results in a decrease in product yield from 96.60 to 95.89 wt%. The residence time in this particular case (1.88 s) cannot ensure the completion of the reaction.

Overall, increasing the pipe length and total flow rate helped in the generation of reactants; the effect of the total flow rate in the system was more obvious. This further indicated that the sulfonation process was controlled by mass transfer, and the effect of residence time was less significant than that of the enhanced mixing effect.

3.5 Comparison of sulfonation processes

Table 4 presents a comparison of the experimental conditions and product specifications between the micro-reactor and FFR sulfonation processes [23]. The reaction temperatures and SO_3 :HDB molar ratios of the sulfonation process in the present study and FFR are similar; however, the residence time is shorter in the present study. Moreover, our continuous sulfonation process does not require aging. The content of active ingredients in the product can reach higher values, and the entire process does not necessitate any tedious post-treatment of the product. The sulfonation process described in the present study is also safer and more environmentally friendly.

Table 4: Comparison of sulfonation process conditions and product specifications of the continuous microreactor and FFR

Type of reactor	FFR	Micro-reactor
Reaction temperature	48°C	50°C
Aging temperature	60°C	—
Retention time	30–150 min	9.7 s
SO_3 /DDB molar ratio	1.07	1.10
Active matter (wt%)	95.84	97.2 (max 99.57)
Sulfuric acid (wt%)	0.89	1.05
Free oil (wt%)	1.78	1.63

4 Conclusion

The production of HBSA using HDB and liquid SO_3 in a microreactor was investigated in this study, and optimised experimental parameters were obtained. The temperature was noted to slightly influence the yield of HBSA because of the reduced reaction selectivity and forward equilibrium shift. However, it was also necessary to control the temperature because higher temperatures could lead to more by-products. The optimal SO_3 :HDB molar ratio was obtained as 1.10:1 and the mass fraction of SO_3 contributed to the increased yield of HBSA. Furthermore, the length of the pipe and the total flow rate were found to affect the residence time in the reactor. A longer residence time facilitated the completion of the reaction, and the yield of HBSA stabilised when the residence time exceeded 10 s.

The optimal reaction parameters obtained in this study were the following: a temperature of 50°C, SO_3 :HDB molar ratio of 1.10:1 and SO_3 mass fraction of 10 wt%. Under these optimised process conditions, a high-quality HBSA sample was obtained with a purity exceeding 99 wt%. Moreover, the short residence time (10 s) and the absence

of aging facilitate the highly efficient production of HBSA, and this process can yield objective economic benefits.

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