

## Sulfonation of linear alkyl benzene (LAB) in a corrugated wall falling film reactor

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### Abstract

Sulfonation of a low molecular weight linear alkyl benzene (LAB) commercial cut with SO<sub>3</sub>–air mixtures was conducted in a corrugated wall falling film reactor (CWFFR). The aim of the study was to compare the performance of this reactor with that of a conventional smooth wall falling film reactor (SWFFR) of the same length. The influence of parameters such as the SO<sub>3</sub> to feed molar ratio, SO<sub>3</sub>-in-air concentration and geometry of the wall on the Klett color and active matter yield in the product was investigated. For low values of the SO<sub>3</sub> to feed molar ratio, a better color and a significant increase in the active matter content in the product were obtained with the CWFFR. Results also suggest a possible competition between turbulence induced by the corrugated wall and stagnation also caused by the wall. ©2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Sulfonation of LAB; Falling film reactor; Corrugated wall

### 1. Introduction

Due to their overall characteristics, the SO<sub>3</sub>–air sulfonation of various organic feeds is best conducted in falling film reactors. This type of reaction is highly exothermic [1–3] with very fast kinetics [4]. A more or less realistic assumption that mass transfer in the gas phase is the controlling step in the process has been reported in many studies [2,3]. In the case of linear alkyl benzene (LAB) sulfonation, not only does the desired reaction leading to the organic acid take place, but also parallel and consecutive reactions resulting in undesired products and color bodies. The combination of an instantaneous reaction, high exothermicity and a factor of 50–100 increase in viscosity means that temperature control of the organic phase during the reaction is the main problem. Some steps can be taken in order to achieve this control: dilution of SO<sub>3</sub> in air (volumetric levels of 4–8% are used) and an extensive cooling area in the reactor system (high ratio of cooling surface area to reactor hold-up volume). Thus, the bulk temperature of the organic phase and the liquid–gas interface temperature are kept as close as possible to the optimum temperature in order to avoid undesired reactions. There are at least seven main sulfonation reactor systems used worldwide for SO<sub>3</sub>–air sulfonation for which there is proven practical and documented experience. A great ma-

jority of these systems are multitube falling film reactors in which the liquid film is supported by a smooth tubular wall. However, many studies have proven the advantage of using corrugated tubes both from the heat and mass transfer points of view [5–11]. A French patent [12] describes a system in which annular baffles are mounted against the inner wall of a tubular falling film reactor. These baffles can also be mounted in a continuous wound spiral. The shape, dimensions and spacing between adjacent fins are conceived in such a way that no fluid stagnation may occur. In particular, the baffle height does not exceed the organic film thickness and the ratio of the height of the baffle to the baffle spacing may lie between 8 and 30. In the case of our corrugated wall falling film reactor (CWFFR), the inner wall of the reactor is approximately sinusoidal (Fig. 1), and the dimensionless number  $\delta = (a-b)/c$  (amplitude to wavelength of the solid surface ratio) is approximately 2.5. The assumption is made here that the application of such wavy tubes will contribute to the enhancement of both heat and mass transfer in the system and hence the overall product quality.

### 2. Experimental details

#### 2.1. Raw material

The LAB used in this study is a low molecular cut (C10–C13) of industrial origin with a viscosity of 7 cSt (at

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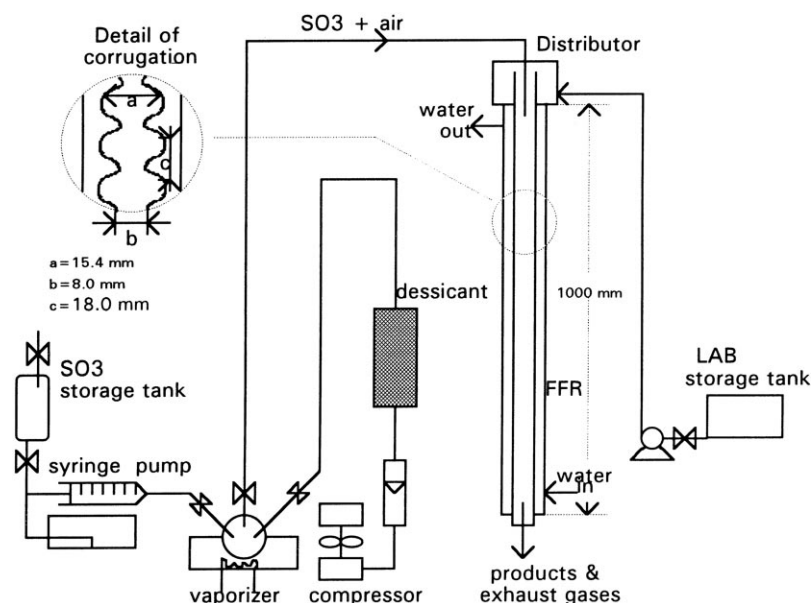


Fig. 1. Experimental apparatus.

20°C), a density of 0.855 (at 20°C) and a mean molecular weight of 240.5.

## 2.2. Experimental apparatus and procedures

A schematic diagram of the experimental apparatus is shown in Fig. 1. The basic part of this apparatus consists of a monotubular falling film reactor. Both liquid and gas reactants are fed in at the reactor top. The sulfonating agent  $\text{SO}_3$  is prepared in the laboratory through catalytic conversion of sulfur dioxide and stored in its liquid form at a temperature of about 30°C. It is then fed into the system with a syringe pump at the appropriate molar rate.

Before entering the reactor,  $\text{SO}_3$  is vaporized and mixed with a dried air stream at the desired volumetric concentration. Two borosilicate glass reactors of the same length (1 m) are used; one has a smooth wall of 8 mm, interior diameter. The second reactor has a corrugated wall. Details of the corrugation are also given in Fig. 1. Both reactors are fitted with a refrigeration jacket.

The LAB flow rate was fixed at  $269 \text{ ml h}^{-1}$  ( $0.956 \text{ mol h}^{-1}$ ) for all experiments and the  $\text{SO}_3$  and air flows were adjusted to obtain the desired  $\text{SO}_3$  to LAB mole ratio and  $\text{SO}_3$  mole fraction in the gas for each experiment. As the gas phase velocity is relatively low, no liquid entrainment in the gas was observed.

## 3. Results and discussion

At the end of each sulfonation run, a separate aging step of approximately 30 min is needed before the neutralization step. The Klett color (5% active matter solution, 10 mm cell,

N42 filter) and active matter content in the paste are finally determined. The experimental results are given in Table 1.

As can be seen from Fig. 2, the active matter content in the product obtained with the CWFFR is greater than that obtained with the conventional smooth wall falling film reactor (SWFFR). However, this content tends to decrease with increased  $\text{SO}_3$  to LAB molar ratio which means that parallel or consecutive reactions leading to undesired products may become important at high  $\text{SO}_3$  to LAB molar ratios. It is very difficult to compare the product quality using the Klett color criterion. This property is unfortunately not well correlated with other operative parameters.

For the SWFFR, the active matter content increases as the  $\text{SO}_3$  mole fraction in the gas decreases. For low values of the  $\text{SO}_3$  mole fraction, the gas phase volumetric rate is higher (higher  $\text{Re}_G$ ) and produces agitation of the gas–liquid interface which accounts for the observed higher conversion. Furthermore, we have assumed that the reaction rate is controlled mainly by diffusion of  $\text{SO}_3$  to the interface and it is known that the mass transfer coefficient in the gas phase ( $k_g$ ) is almost proportional to the gas velocity [1]. In the case of the CWFFR, the active matter content in the product fluctuates and is not correlated with the  $\text{Re}_G$ .

Taking into account the fact that a wavy flow increases agitation, we should expect a greater conversion in the case of the CWFFR. This has been observed only for low values of the  $\text{SO}_3$  to LAB molar ratio (Fig. 2).

A comparative study [13] of both reactors from the hydrodynamic point of view has shown that the mean residence time variance is much larger in the CWFFR, which indicates that fluid stagnation occurs and accounts for the large amount of dispersion in this type of reactor.

At this level of our investigation, we can only speculate on the positive effects of the corrugations, which simulate

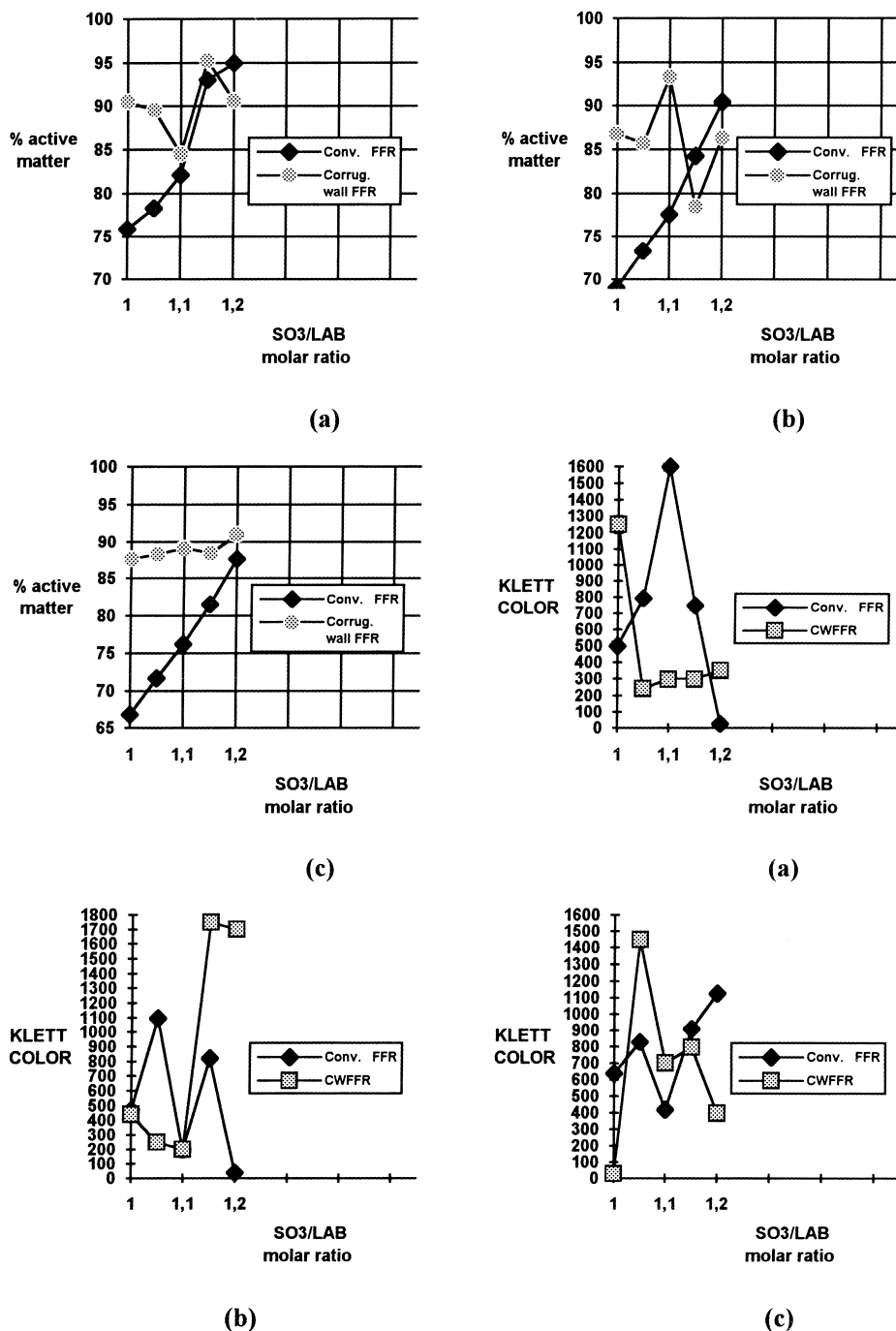


Fig. 2. Mean active matter and Klett color versus SO<sub>3</sub> to LAB molar ratio (SO<sub>3</sub> mole fraction: (a) 0.06; (b) 0.08; (c) 0.10).

a cascade of microstirred tank reactors expected to increase significantly heat transfer and conversion, and the negative effects of the possible product stagnation in the concave regions of the corrugations, which inevitably leads to undesired consecutive reactions and poor color products (charring). Other values of  $\delta$  and other corrugation shapes should be investigated.

In the case of our CWFFR, good results are effectively obtained for low SO<sub>3</sub> to LAB molar ratios for which a sig-

nificant increase the active matter content in the paste was observed. As this parameter increases, undesired reactions occur which lead rapidly to inconstant product quality.

Also, except for low SO<sub>3</sub> to LAB molar ratios ranging between 1.00 and 1.05, a complication of the geometry of the reactor wall supporting the organic film may not lead to a better product quality as was first assumed. This can be explained mainly by the presence of stagnant regions in the corrugated wall reactor, especially in the concave re-

Table 1  
Experimental results

SO <sub>3</sub> /LAB molar ratio	SO <sub>3</sub> -in-air conc. (vol%)	Reynolds number (gas phase) Re <sub>G</sub>	Mean active matter (mass %)		Klett color	
			Smooth wall reactor	Corrugated wall reactor	Smooth wall reactor	Corrugated wall reactor
1.00		999	75.9	90.5	500	1250
1.05		1051	78.3	89.5	795	240
1.10	6	1104	82.2	84.5	1602	300
1.20		1199	95.4	90.6	25	350
1.00		994	69.0	86.8	470	440
1.05		1046	73.3	85.7	1097	250
1.10	8	1098	77.6	93.3	200	200
1.15		1143	84.3	78.5	820	1750
1.20		1193	90.4	86.4	40	1700
1.00		989	66.8	87.7	640	27.5
1.05		1041	71.7	88.3	830	1450
1.10	10	1093	76.2	89.2	420	700
1.15		1137	81.5	88.5	910	798
1.20		1187	87.7	91.0	1125	398

gions of the corrugation, where undesired reactions may take place. The authors wish to thank Mr. Saïd Tebani for his important contribution in realizing the Pyrex corrugated wall tubular reactor.

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