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Letters to the Editor

Comment on "Optimisation of the Linear Alkyl Benzene Sulfonation Process for Surfactant Manufacture" and "Sulfonation Technology for Anionic Surfactant Manufacture": Falling Film SO_3 Sulfonation - Laminar or Turbulent Flow Controversy

To the Editor:

The continuous SO_3 falling film sulfonation (FFS) process has been firmly established on a worldwide basis as the preferred and dominant process for the manufacture of major anionic surfactants, because of its significant economic and operational advantages.[1,2] There appears to be an industry-wide misconception that the organic film in the process is in laminar flow, recently perpetuated by D. W. Roberts' articles in your journal,[3,4] and in several mathematical process models based on laminar flow assumptions.[4] This is an incorrect and absurd characterization of the operative physics of the process (while Roberts provided excellent reviews of the chemical reactions involved in the process and their kinetics, his explanation of the physics of the process is wrong).

Perhaps such investigators and mathematicians have never observed in glass tubes the violent mixing and *film turbulence* produced by the SO_3 reaction gas moving at, or near, hurricane velocity used in the process. I've spent almost 60 years working (40 years with my colleagues at Stepan Co.) in the field of SO_3 sulfonation, and I am a co-inventor of the world's first commercial FFS process, operational in 1960. Marvin L. Nussbaum (co-inventor) and I had observed that the high-velocity SO_3 reaction gas impacting on the flowing organic film created marked (or visual) turbulence in vertical cooling jacketed glass reaction tubes without the need to provide any mechanical agitation, with the resulting quality of derived products meeting or exceeding those obtained by other SO_3 or oleum sulfonation processes. Our subsequent process patents disclosed claims to *film turbulence* generated by the high-velocity reaction gas.[5]

The following points are offered in support of *film turbulence*.

(1) In the evolution of batch SO_3 sulfonation technology, it has been shown that with the awesome reactivity of SO_3 gas with organic feedstocks, which are prone to overreaction and charring, the best-quality products were obtained using the highest degree of agitation (or *turbulence*) and SO_3 air dilution. The same principles apply to continuous processes.

(2) A chemical engineering definition of laminar flow indicates that "the fluid may be considered as composed of thin layers which follow the contours of the surface without mixing with the adjacent layers, except as by mingling results from molecular diffusion".[6] In the absence of any mixing or *film turbulence* it would be impossible to achieve a controlled and satisfactory sulfonation.

(3) A U. S. Federal Court Judge in 1970, presiding over a FFS process infringement case (Stepan Chemical Co. vs Textilana and Allied Chemical Co.) relative to whether the organic film was in "quiescent" (laminar) flow or *turbulent flow*, evaluated expert witness testimony, high-speed photographic evidence, demonstrations of both simulated process conditions and an actual pilot-plant scale sulfonation in a cooling jacketed glass tube, ruled that the organic film was "*clearly turbulent*."[7]

(4) Plaintiff Stepan's accompanying courtroom photographic exhibits show an actual continuous SO_3 FFS of branched-chain detergent alkylate conducted in a water-cooled jacketed vertical glass tube (see Figure 1). The left side of this split-composite photograph shows the upper portion of the reactor tube, while the right side focuses on the bottom section of the reactor. Violent mixing, *marked turbulence*, and a continuing series of large, rolling waves and troughs moving down the tube are clearly observable.

(5) The estimated gaseous residence times in modern commercially available FFS systems fall between 0.09 and 0.19 s,[2] and since about 75−90% organic conversion occurs within the first one-third of the reactor length, that equates to about 0.03−0.05 s, underscoring that an extremely rapid reaction is involved. Such a high-speed reaction requires rapid, *turbulent mixing* to prevent over reaction and charring. Estimated liquid residence times of up to 30 s as characterized by Roberts[4] and others (including early publications by this author[2]) appear to be inconsistent with estimated film thickness profiles and is believed to be closer to 1 or 2 s.

(6) Commercially available continuous SO_3 FFS systems utilize 3−6% SO_3 gas in dry airstreams operating at about category 1 (33 m/s) to category 5 (70 m/s) hurricane velocities[2] to facilitate *film turbulence* and reaction.

(7) Patent and technical publications by suppliers of FFS systems such as Chemithon,[8] Mazzoni,[9] and Ballestra[10] cite the importance of *film turbulence* in the process.

(1) Knaggs, E. A. Development of Continuous Falling Film SO_3 Sulfonation Technology. *CHEMTECH* **1992**, 436−445.

(2) Knaggs, E. A.; Nepras, M. J. Sulfonation and Sulfation. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John Wiley & Sons: New York, 1997; Vol. 23, pp 146−193.

(3) Roberts, D. W. *Org. Process Res. Dev.* **1998**, *2*, 194−202.

(4) Roberts, D. W. *Org. Process Res. Dev.* **2003**, *7*, 172−194.

(5) Knaggs, E. A.; Nussbaum, M. L. U.S. Patent 3,169,142, 1965.

(6) Hougen, O. A.; Watson, K. M. *Chemical Process Principles*; John Wiley & Sons: New York, 1947; pp 973−974.

(7) Federal District Court of California, Los Angeles, Case 66-1259 DWW, Judge D. W. Williams, Finding of Fact, September 4, 1970.

(8) Brooks, R. J.; Brooks, B. U.S. Patent 3,427,342, 1969.

(9) Lanteri, A. U.S. Patent 3,931,273, 1976.

(10) Moretti, G. F.; Adami, I.; Nava, F.; Molteni, E. *The Multitube Film Sulphonation Reactor For the 21st Century*; Technical Literature, Ballestra SpA: Milan, Italy, 1999.

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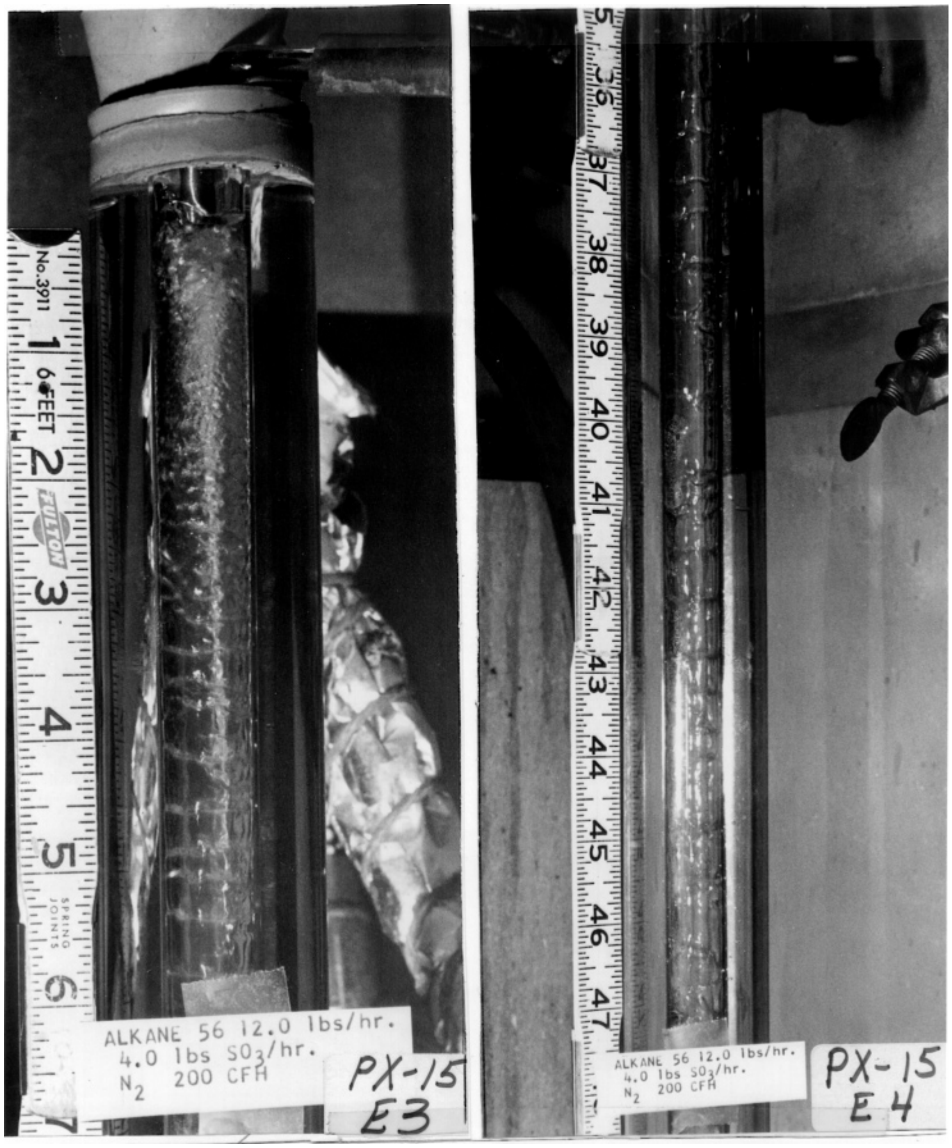

Figure 1. **Composite of two photographs showing actual continuous SO_3 sulfonation of branched-chain detergent alkylate using 5% SO_3 in a nitrogen gas stream in a cooling jacketed 1.1 cm i.d. × 122 cm glass reactor tube, alkylate flow 0.14 kg/(h × mm circumference), and gas velocity of 28.3 m/s. (Left)Top of reactor. (Right) Bottom portion of the reactor. (Photographs courtesy of Rodger L. Peters.)**

The remarkable ability of the continuous SO_3 FFS process to control and produce high conversion, high-quality products fundamentally rests on the requirement and function of the high-velocity reaction gas stream to generate substantial *film turbulence*, expanding the gas−liquid interface, providing for a very rapid SO_3 adsorption and reaction, resulting in a rapid increase in film temperature, thereby reducing film viscosity and aiding effective heat removal, all consummated in very short gas- and liquid-reactor residence times. The process is somewhat analogous to a hurricane blowing over a body of water although muted by the higher viscosity liquids.

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