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Sulfonation/Sulfation Processing Technology for Anionic Surfactant Manufacture

Jesús Alfonso Torres Ortega
Universidad de La Salle
Colombia

1. Introduction

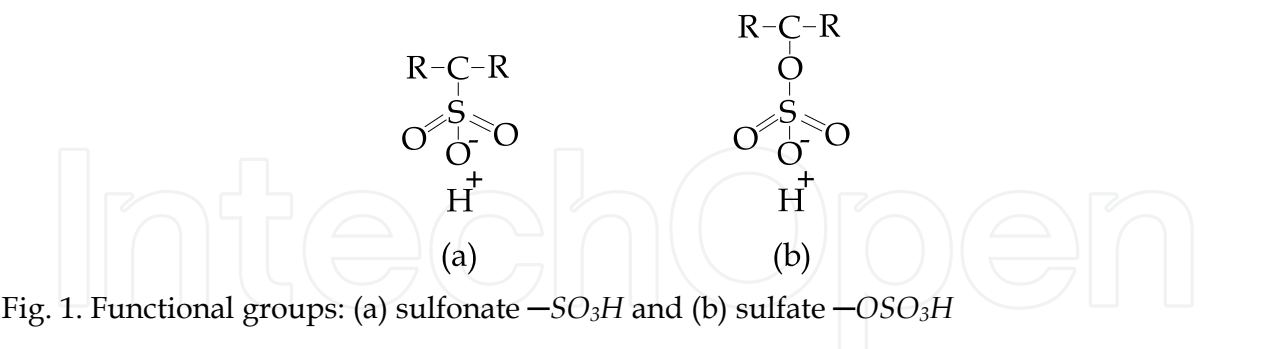
In 2008, global production of surfactants was 13 million metric tons reaching a turnover of US\$24,33 million at 2009, which means an increment of 2% from the previous year. Moreover, it is projected a strong growth ca. 2,8% annually till 2012 and between 3,5 – 4% thereafter (Resnik et al., 2010). Sulfonation plants are scattered around the globe in production units with capacities varying from 3.000 to 50.000 tons/year, mainly of anionic surfactants. At least 800 sulfonation plants are estimated to be currently in operation around the World. However, about 20% of the global production (2.500.000 tons/year of sulfonated anionic surfactants) is concentrated in the United States, Western Europe and Japan (Acmite Market Intelligence, 2010).

Anionic surfactants are the key component in a detergent formulation. A molecule of anionic surfactant is composed of a lipophilic oil soluble “tail” (typically an organic molecule C_{12} - C_{14}) and a hydrophilic water soluble “head” (such as SO_3^-). Mixtures of organic molecules, either from non-renewable resources, such as crude oil or from renewable sources, such as vegetable oils, are currently used as raw materials for household detergents. The cleaning process performed by anionic surfactants (active detergents) is described in the following way (de Groot, 1991):

- i. Wetting of the substrate and dirt due to reduction of surface tension;
- ii. Remotion of dirt from substrate;
- iii. Retaining the dirt in a stable solution or suspension.

Sulfonation is the term that identifies an electrophilic chemical reaction where a sulfonic group SO_3H is incorporated into a molecule with the capacity to donate electrons. The product of this chemical reaction is recognized as sulfonic acid if the electron donor molecule is a carbon. Sulfuric anhydride reacts easily with delocalized electronic densities as those present in aromatics groups or alkenes in general. These reactions produce a variety of products, including derivate polysulfones. On the other hand, the sulfating process involves the incorporation of the SO_3H molecules to an oxygen atom in an organic molecule to form C-O-S bonds and the sulfate group (Figure 1). Sulfates acids can be easily hydrolyzed, and for this reason an immediate neutralization is required after the sulfate group is formed (Foster, 1997). Although sulfonation and sulfating processes are employed industrially to obtain a wide range of products from hair dyes to pesticides and

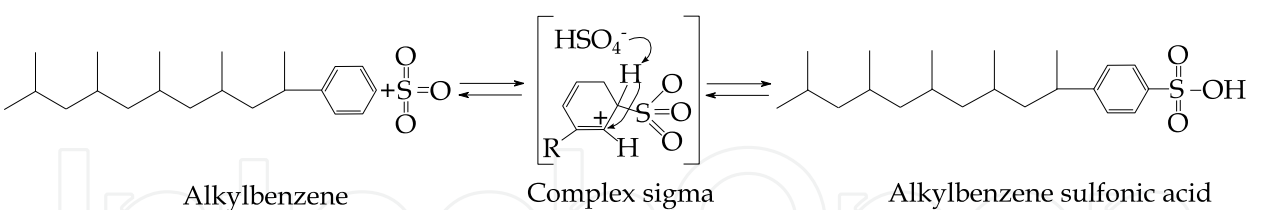
organic intermediates, their main applications are in the production of anionic surfactants (Foster, 2004).



2. Main anionic surfactants

2.1 Linear alkyl benzene sulfonate (LABS)

Linear alkylbenzene is the most common organic feedstock employee in the detergent industry (Figure 2). LABS of low molecular weight (230 – 245) lay in the category of anionic surfactants most used in all ranges of household detergent formulations. Dishwashing liquids are prepared from LABS of low molecular weight in combination with other anionic surfactant as Lauryl Ether Sulfate (LES) promoting high detergency, foam stability, degreasing capacity, and high stability in hard water (Zhu et al., 1998). Common concentrations of active detergents in liquid products are: LABS 10-15% (30%), Primary alcohol sulfate/LES 3-5% (10%), where values in brackets are the maximum for concentrated products (Table 1). LABS of high molecular weight (245-260) are the anionic surfactants more used in all ranges of household detergents formulation, but especially in heavy duty laundry products, sometimes in combination with nonionics alcohol sulfates from tallow and soaps (Mungray & Kumar, 2009).



2.2 Primary alcohol sulfates (PAS)

PAS are categorized in different groups regarding the number carbon that compose them: The so called lauryl alcohol sulfates C_{12} - C_{14} , the “tallow” alcohol sulfates (TAS) C_{16} - C_{18} , and the broader cut C_{10} - C_{18} alcohol sulfate comprising coconut fatty alcohol sulfates. The broad cut (C_{10} - C_{18}) alcohol sulfates presents cost/performance equilibrium in terms of detergency, solubility and foaming properties. This product can partially or totally substitute other anionic surfactants either in liquid or powder detergent formulations with adequate biodegradability and low “defatting action”, which is important for human tissue and delicate natural or synthetic fibers. The narrow cut (C_{12} - C_{14}) alcohol sulfates find their main application in a wide range of personal care products such as shampoos, bubble bath products, tooth pastes, dishwashing liquid, delicate products for laundry wash. The C_{16} - C_{18} alcohol sulfates (“tallow”) are used as sodium salts in the formulation of heavy duty laundry products for hand and machine washing. Their detergency power is up to 10% higher than LABS in a wide range of detergent formulations (de Groot, 1991). Furthermore, TAS shows controlled foam, which is important mainly at high temperatures, still keeping the advantage of softness in the wash of sensitive natural and synthetic fibers (Rosen, 2005). The physical detergency and biodegradability of primary alcohols can be affected by the carbon chain length distribution. Therefore, each new supply may require testing to determine whether the desired properties in the chosen application can be achieved. The mechanism for alcohol sulfation is thought to be similar to that for linear alkylbenzene sulfonation with $\Delta H = -150$ kJ/mol (Figure 3).

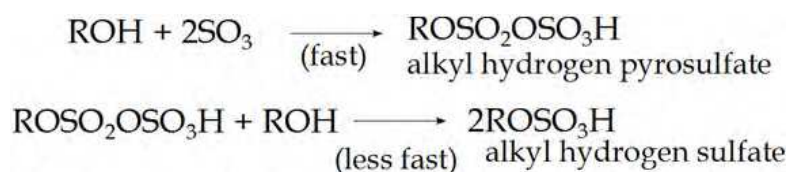


Fig. 3. Mechanism of alcohol sulfation (adapted from Roberts, 1998)

2.3 Alcohol ether sulfates (AES)

Primary alcohol ethoxylates are made by the addition of ethylene oxide to a primary alcohol in the presence of an alkaline catalyst (Boskamp & Houghton, 1996). The addition of the second ethylene oxide molecule to the alcohol is kinetically favored in comparison with the addition of the first ethylene oxide; hence the product of ethoxylation contains a distribution of ethylene oxide chain lengths attached to the alcohol along with the starting alcohol itself. Consequently the physical, detergency and biodegradation characteristics are affected not only by the carbon chain length distribution as is the case for primary alcohols, but also by the ethylene oxide distribution which in turn can be supplier depend (de Groot, 1991). The most common alcohol ethoxylates found as feedstocks for sulfation have an average of 2 to 3 molecules of ethylene oxide (2EO or 3EO).

During the sulfating of alcohol ethoxylates the by-products 1,4-dioxane may be formed (Figure 4). Although the formation of 1,4-dioxane is governed predominantly by sulfation and neutralization conditions and by the chemical composition of the feedstock, other factors such as the quality of the raw material also contribute. These factors must be considered during the store and handling of the alcohol ethoxylate feedstock.

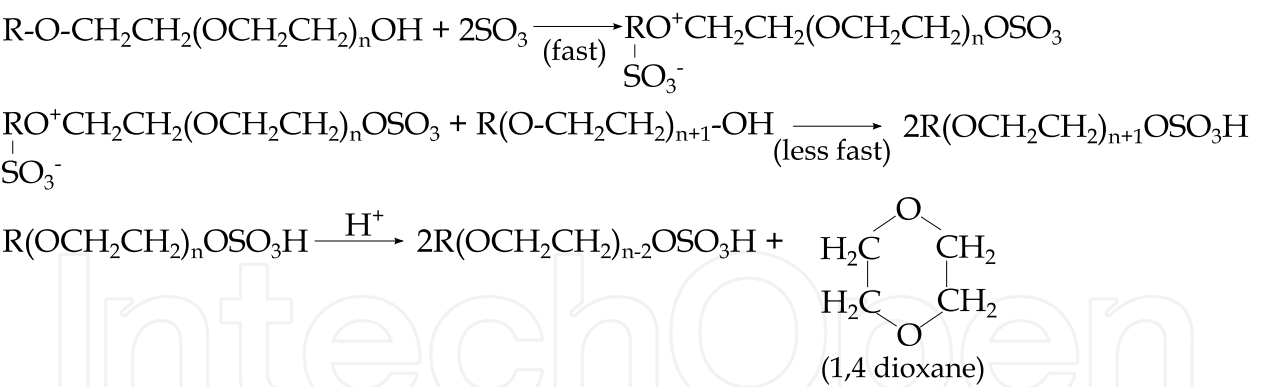


Fig. 4. Reaction scheme of ethoxylated alcohol sulfation (adapted from de Groot, 1991)

LES (C₁₂-C_{14/15} 2-3 ethylene oxide) can be considered as the most efficient anionic surfactant in terms of: superior detergency power, good tolerance for water hardness, and mildness on hands and fibers. The application therefore is wide: from household to personal care and cosmetic product. Unfortunately, sulfated alcohol ether sulfates show a limited stability to hydrolysis at high temperatures, and this restricts their use in heavy duty laundry powders, where high temperatures occur in the spray drying process of powder manufacture.

The high stability to calcium ions permits formulation of liquid detergents with limited or no addition of water “softeners” even in case of use in hard water (Matthijs et al., 1999). The optimum compromise of ethylene oxide addition to keep adequate foam levels and solubility/mildness ratio vary from 2 to 3 moles per mole of fatty alcohol. The most important worldwide application of AES 2-3 ethylene oxide (EO) are in dish washing liquid detergent, generally combined with LABS and in shampoos/bubble baths (Table 2).

	Liquids dish wash detergent	Shampoos/bubble baths
LES (C ₁₂ -C _{14/15} 2-3 EO)	5 – 10 %	10 – 30 %
LABS (low molecular weight)		15- 20%
Coconut Ethanol Amides (CEA)	2 – 3 %	2 – 3 %
Hydrotopes (Sodium Tolunene Sulfonate – Sodium Xylene Sulfonate) alcohol solvent		1 – 3 %
Other actives (i.e. amphoteric/nonionic)		5 – 10 %
H ₂ O, perfume, color, preservatives	Balance	Balance

Table 2. Applications worldwide of AES 2-3EO combined with LABS and in shampoos/bubble baths (de Groot, 1991)

2.4 Alfa-olefins sulfonates (AOS)

Alfa-olefins are a potential replacement for alkylbenzenes in detergent applications. Olefin sulfonation is highly exothermic with ΔH = -210 kJ/mol (Roberts, 2001). The neutralized product of alfa-olefin sulfonation requires hydrolysis to remove the sultones, which are skin sensitizers (Figure 5). Their exploitation, however, is largely limited to the Far East, Centre on Japan, at present. Commercial supplies of alfa-olefins are produced by the

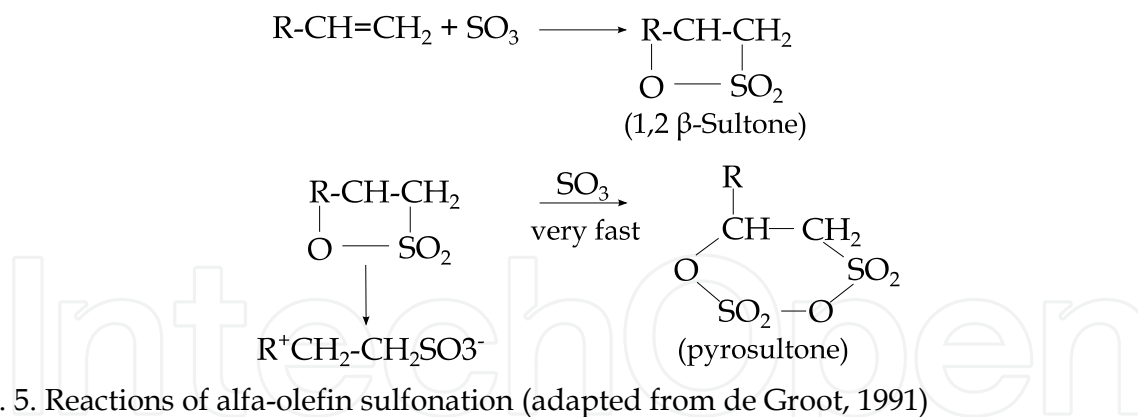


Fig. 5. Reactions of alfa-olefin sulfonation (adapted from de Groot, 1991)

oligomerisation of ethylene. The physical, detergency and biodegradation characteristics of alfa-olefins are affected by the carbon chain length distribution and therefore each new supply may require testing to determine whether the desired properties for the new chosen application can be achieved. The Lion Corporation, Japan, is one of the principal producers and users of alfa-olefin sulfonates. In addition to fabric washing powders, they also market fabric washing liquid, shampoos, tooth paste and foam bath products containing this active. In the USA, Minnetonka has utilized AOS in hand cleaners/liquid soaps. AOS is a potential replacement for alkyl benzene sulfonates in dish wash detergent liquids formulations with performance peaking at C₁₆ chain length (de Groot., 1991).

2.5 Fatty acid methyl esters sulfonates (FAMES)

FAMES are called to be the main feedstock for detergent formulating in the future due to their applicability in detergent formulations (Ingegar & Martin, 2001; Johansson & Svensson, 2001; Roberts & Garrett, 2000; Satsuki, 1998). Moreover, when it is derived from palm oil presents special biodegradable properties that place them over the surfactants derived from petrochemicals compounds. To date, the application of FAMES is under development in various detergent products, and their presence on the market is still highly restricted. The typical cut of FAMES (C₁₆-C₁₈) shows interesting surface activity (about 90% compared to LABS), high detergent, dispersing and emulsifying power in hard water, high lime soap dispersion and moderate foam levels. FAMES show high stability to pH and temperature hydrolysis. Therefore, they can be easily spray dyer and/or incorporated in detergent bars. Methyl ester sulfonates have a wide range of application and important biological properties. As aggregated value the FAMES can be used in cosmetics, as auxiliary agents in the production of fibers, plastics, and rubber, and in leather manufacture (Cohen et al., 2008; de Groot, 1991; Roberts et al., 2008; Stein & Baumann, 1975).

3. Sulfonation process used for the manufacturing of anionic surfactants

Sulfonation reactions can be carried out in different configurations, either liquid-liquid contact, or gas-liquid contact reactors, and a diversity of sulfonating reagents can be applied for the sulfonation process, such as: Sulfuric acid, SO₃ from stabilized liquid SO₃, SO₃ from sulfur burning and subsequent conversion of the SO₂ formed, SO₃ from boiling concentrated oleum and chlorosulfonic acid. However some reasons why SO₃/air in gas-liquid contactor (sulfonator) is becoming the predominant process for the manufacture of anionic surfactants are (Foster, 1997):

- i. Adaptability: All types of organic feedstocks, like alkylbenzenes, primary alcohols, alcohol ethers, alfa-olefins and fatty acid methyl esters, can be successfully transformed to high-quality sulfonate/sulfate active detergents using SO_3 /air as sulfonating reagent. Sulfonating reagents like sulfuric acid and oleum are less desirable because only alkylbenzene feedstocks can be converted to high-quality alkylbenzene sulfonic acids.
- ii. Security: Concentrated sulfuric acid, liquid SO_3 , and oleum (20 or 65%) are hazardous to be handled, transported, and storage. Sulfur, either in liquid or solid form, although less dangerous option as initial material for the manufacture of SO_3 , is still risky.
- iii. Price: SO_3 obtained directly from the sulfur combustion is the most economical option among all the others options mentioned above regarding transport, handle and storage.
- iv. Availability: Liquid SO_3 , 65% and 20% oleum and even sulfuric acid are not produced everywhere. Even close to sulfuric acid plants, it is not guaranteed the availability of all the gamma of oleum concentrations.

Several studies have been done about absorption along with exothermic reaction in a Falling Film Reactor - FFR (Mann & Moyes, 1977; Villadsen & Nielsen, 1986), particularly for dodecylbenzene and tridecylbenzene sulfonation. However, due to de complexity of processes taking place inside the FFR has not been completely elucidated, being of special interest today. The SO_3 -sulfonation is carried out in tubular reactors where the organic matter (liquid) wets the wall of the tubes while a gas stream containing the sulfonating reagent flows in co-current with the organic matter to avoid over-sulfonation (MacArthur et al., 1999). The simplest FFR configuration can be described as a two concentric tubes arranged in a vertical way (Figure 6).

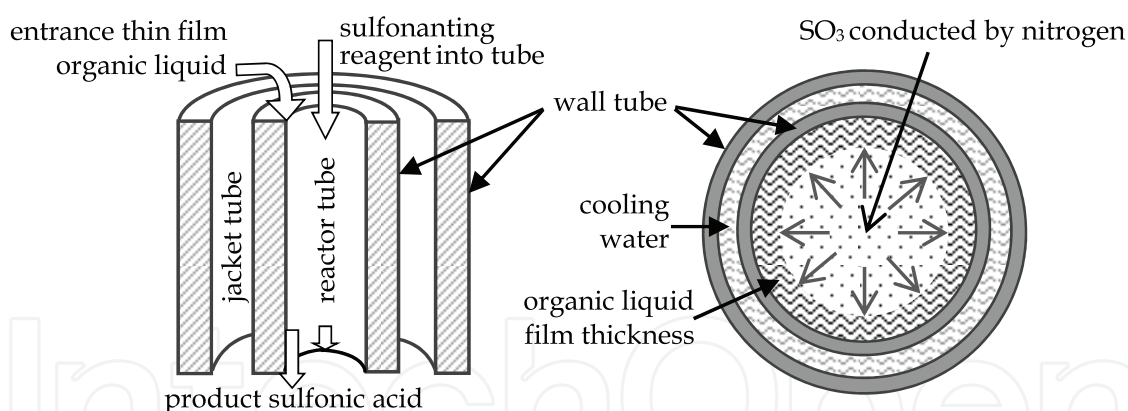


Fig. 6. Sketch of falling film reactor

Organic matter forms a thin film covering the inner wall of the inner tube. The film descends from the top of the reactor in laminar flow forming an annulus for whose interior a gas stream flows in turbulent regimen. In the first reaction section the concentrated sulfonate reagent get in touch with fresh organic matter. The reaction rate is high as well as the amount of heat released (150 – 170 kJ/mole). A coolant stream flows by the external wall of the inner tube in parallel with the reactant streams. As long as the reaction advances the viscosity of the liquid phase increases (ca. 100 times the initial value). The depletion of reactants reduces the reaction rate and the increase of viscosity slow down the mass transfer process in the film. In this point the co-current coolant, this has already removed a huge amount of heat from the first reactor zone, works as a heating current that controls the viscosity of the film.

Figure 7 shows a diagram of film SO_3 -sulfonation along with an additional step (bleaching) than could be required depending of the feedstock and characteristic of the final product. Depending on the type of organic feedstock and consequent organic acid, further reaction steps may be required before neutralization. Sulfonic acids of LABS are one of those materials that no require an aging step to reach full conversion. Moreover, a hydrolysis or stabilization step is required to convert anhydrides form during the sulfonation process. Alcohol and alcohol ethoxylate sulfonic acids, as well as FAMES, must be neutralized immediately after a delayed aging to avoid undesired by-products formed in side reactions.

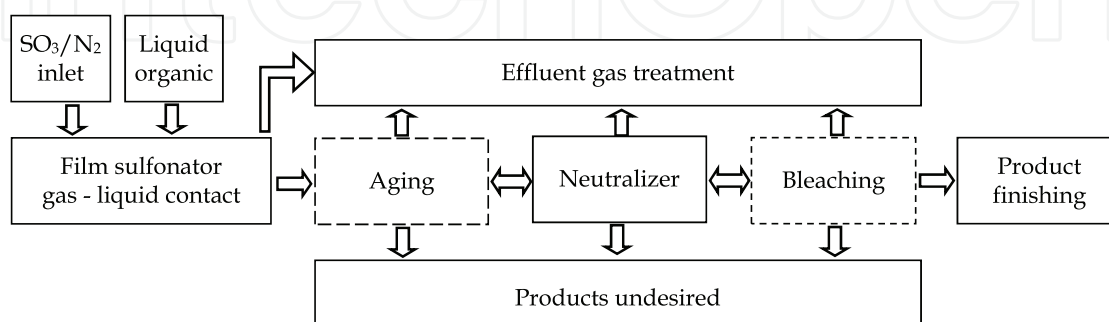


Fig. 7. Process diagram for film SO_3 -sulfonation

After aging and hydrolysis a stable product is obtained, then the neutralization stage can be carried out with many alkaline chemicals like caustic, ammonia and sodium carbonate. Neutralization with diluted caustic is recognized as instantaneous and highly exothermic it may form gel at high temperatures or undesired reactions may occur if micro-dispersion of organic acid in the diluted caustic phase fails. Various loop-type reactors, consisting of a circulation pump, homogenizer (where the acid is introduced in the circulating alkaline paste), and heat exchanger, are used for the complex neutralization step (Foster, 1997).

4. Phenomenological description of film sulfonation

Organic liquid flow through of the reactor wall in laminar regimen, the high flow of the gas phase by gravitational effects intensifies the formation of random waves all along the gas-liquid interface. Depending on the flow rate of organic liquid and gas stream the thickness of the film can increase or decrease up to twice its average value in the zone where the waves are present (Díaz, 2009). This induced turbulence affects the local values of concentration and temperature in the regions where appears, hence altering the mass transfer and temperature profiles in the film. Mathematical models which describe the sulfonation of tridecylbenzene in FFRs have been developed by Akanksha et al. (2007), Davis et al., (1979), and Johnson & Crynes, (1974), while Dabir et al. (1996), Gutiérrez et al. (1988) and Talens (1999) focused on dodecylbenzene sulfonation. Nevertheless, these models have been subject of debate due to the assumption that either the chemical reaction is limited to the gas liquid interface, the mass transfer of the sulfonating reagent in the gas phase is the rate determining step, and/or the flow profiles in the film are neatly laminar, neglecting the effects of the waves formed at the gas-liquid interface.

Recently Torres et al. (2009b) proposed a model for the methyl esters sulfonation that is appropriate for both laminar and turbulent films and it considers effects of wavy film

flow by using eddy diffusivity parameter. The eddy diffusivity models proposed by Lamourelle & Sandall (1972) for the outer region and modified by van Driest (1956) for the region near the wall were used. Effects of interfacial drag at the gas–liquid interface and the gas-phase heat and mass transfer resistance have also been considered in the proposed model. The model takes into account the variations of physical properties with temperature and predicts conversion profiles, gas–liquid interface temperature in the axial direction, and average liquid film thickness along the reactor length. Knowledge of temperature distribution along with the reactor is important for the product quality control, since for highly exothermic reactions under certain conditions can produce degradation of the products. The equations described in the following section account for the mass, momentum and heat transfer. In the development of these equations was considered the turbulent diffusivity for mass transfer coupled with chemical reaction, according to the theory of Yih & Seagrave (1978), and with heat transfer according with Yih & Liu (1983).

Finally some additional assumptions were made for the mathematical model:

- No entrainments of liquid droplets into gas or of gas bubbles into the liquid film occur;
- Fully developed film (entrance and exit effects to reactor are neglected);
- The liquid film is symmetric with respect to the reactor axis.

According with these assumptions the mathematical model is showed in the following sections.

4.1 Mass balance

Only three components are considered in the liquid phase: organic liquid, acid product and sulfonating reagent, therefore two microscopic balances are sufficient to determine the concentration profiles (Figure 8), where y varies from $y = 0$ (at the wall surface) to $y = \delta$ (at the liquid surface).

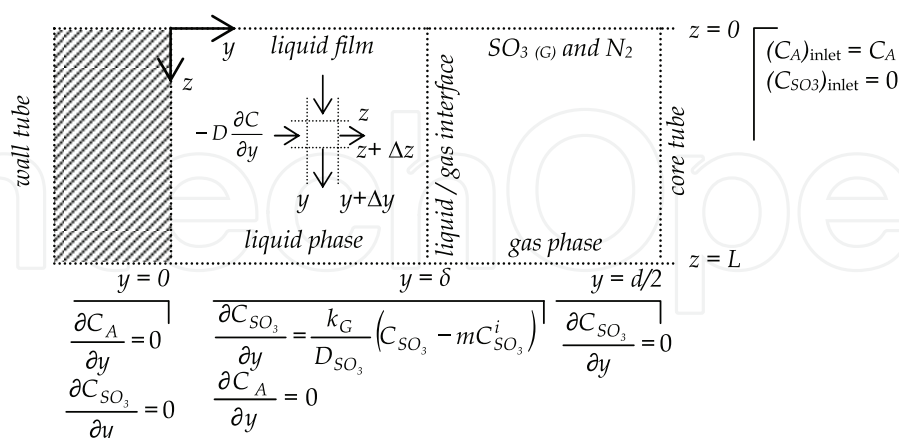


Fig. 8. Mass balance on finite volume includes the boundary conditions at the solid wall and liquid/gas interface

It is assumed that the mass balance for $SO_{3(G)}$ absorbing by the liquid (equation 1) can also be applied to reagent in the liquid phase where reaction occurs, then equation 2 is the steady state mass balance on the absorbing species A in liquid phase.

$$v_z \frac{\partial C_{SO_3}}{\partial z} = \frac{\partial}{\partial y} \left[(D_{SO_3} + D_T) \frac{\partial C_{SO_3}}{\partial y} \right] - r \quad \delta \leq y \leq \frac{d}{2} \quad (1)$$

$$v_z \frac{\partial C_A}{\partial z} = \frac{\partial}{\partial y} \left[(D_A + D_T) \frac{\partial C_A}{\partial y} \right] - r \quad 0 \leq y \leq \delta \quad (2)$$

As discussed by Knaggs, (2004), even if the liquid film is turbulent and does wavy flow then turbulent diffusivity cannot be neglected, this and turbulent viscosity in the liquid phase can be taken of work suggested by Yih & Liu (1983).

$$\frac{D_T}{\nu_T} = -0,5 + 0,5 \left\{ 1 + 0,64(y^{+2}) \frac{\tau}{\tau_w} \times \left[1 - \exp \left(\frac{-y^+(\tau / \tau_w)^{0,5}}{A^+} \right) \right]^2 f \right\}^{0,5} \quad (3)$$

$$\frac{\tau_w}{\tau} = 1 - \left(\frac{\tau_L}{\tau_G + \tau_L} \right)^3 \left(\frac{y^+}{\delta^+} \right) \quad (4)$$

Turbulent Schmidt number is evaluated from the Cebeci's modification of the van Driest model and is further modified as:

$$Sc_T = \frac{\nu_T}{D_T} = \frac{1 - \exp(-y^+(\tau / \tau_w)^{0,5} / A^+)}{1 - \exp(-y^+(\tau / \tau_w)^{0,5} / B^+)} \quad (5)$$

$$B^+ = Sc^{-0,5} \sum_{i=1}^5 C_i (\log_{10} Sc)^{i-1} \quad (6)$$

with $A^+ = 25,1$; $C_1 = 34,96$; $C_2 = 28,97$; $C_3 = 13,95$; $C_4 = 6,33$ and $C_5 = -1,186$. For non-volatile liquids such as methyl stearate, the vapor pressure is zero at working temperatures. At the interface, it is assumed that Henry and Raoult's laws are applicable to determine the SO_3 solubility. The Henry constant m , is determined from the SO_3 vapor pressure:

$$N_{SO_3}^G = k_G (C_{SO_3}^G - m C_{SO_3}^i) \quad (7)$$

$$\frac{k_G}{u} = 0,8 Sc^{-0,704} \quad (\text{McCready \& Hanratty, 1984}) \quad (8)$$

where the turbulent velocity is defined as:

$$u = \left(\frac{\tau_G}{\rho_G} \right)^{0,5} \quad (9)$$

4.2 Momentum balance

Axial liquid velocity v_z , can be found from the momentum equation after neglecting the pressure gradient and axial terms (Figure 9). The flow profile of the liquid falling is

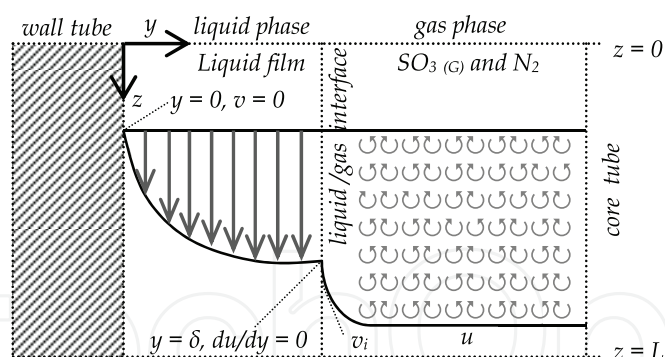


Fig. 9. Schematic representation of velocity profiles in laminar and turbulent regimes for both liquid and gas phase

predominantly laminar, while SO_3 flow is clearly turbulent and consequently the SO_3 is absorbed at the gas/liquid interface. In equation 10 for co-currents systems J is +1 and for counter current systems J is -1.

$$v_z = \frac{\rho_L g}{\mu_L} \left[y\delta - \frac{y^2}{2} \right] + J \frac{\tau_G y}{\mu_L} \quad (10)$$

For high gas flow where the shear force predominates over the gravitational force, the linear velocity distribution is:

$$v_z = \frac{\tau_G y}{\mu_L} \quad (11)$$

Calculation of τ_G based on the relations proposed by Riazi & Faghri (1986) shows that when the gas flow is turbulent, the effects of the interfacial drag cannot be neglected; τ_G can also be verified by means of experimental pressure drop data. In this way a set of parameters can be introduced and adjusted to minimize the deviation from a data set for sulfonation:

$$\Gamma = \frac{\rho_L g}{3\mu_L} \delta^3 - \frac{\tau_G}{2\mu_L} \delta^2 \quad (12)$$

$$\tau_G = C_f \rho_G u^2 \quad (13)$$

$$\frac{1}{C_f^2} = -4 \text{Log} \left\{ \frac{\varphi \delta}{3,7d} - \frac{5,02}{\text{Re}_G} \text{Log} \left(\frac{\varphi \delta}{3,7d} + \frac{13}{\text{Re}_G} \right) \right\} \quad (\text{Talens, 1999}) \quad (14)$$

$$\ln(\varphi) = 3,59 - 5,14 v_{iL} \quad (\text{if } v_{iL} < 0,175 \text{ ms}^{-1}) \text{ or } \ln(\varphi) = 20,55 v_{iL} - 0,93 \quad (\text{if } v_{iL} \geq 0,175 \text{ ms}^{-1}) \quad (15)$$

The initial value of the film thickness δ can be obtained through equation 16, after this value is calculated by iteration:

$$\delta = \left(\frac{3\Gamma\mu}{g\rho_L} \right)^{\frac{1}{3}} \quad (16)$$

4.3 Heat balance

For exothermic reactions such as sulfonation a large amount of heat may be released, the boundary conditions showed at Figure 10 is applying for the energy balance (equation 17).

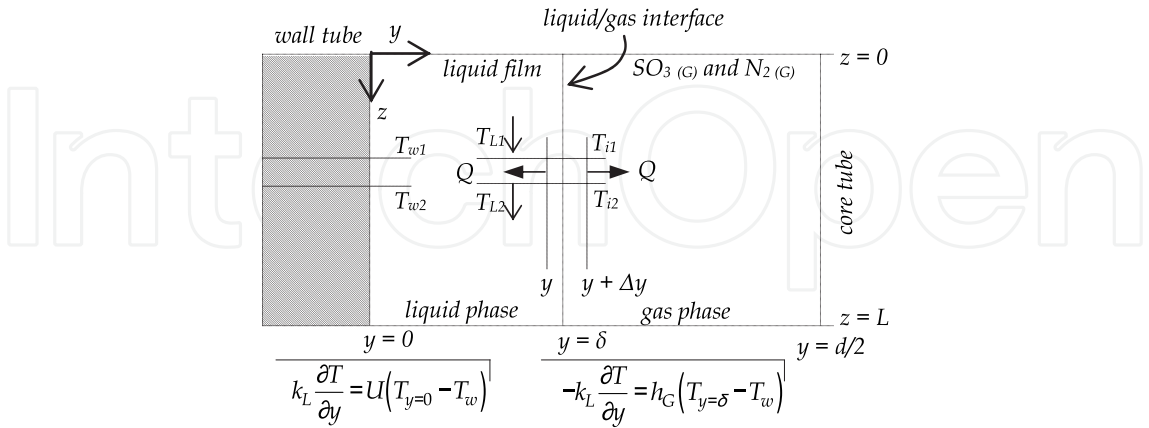


Fig. 10. Schematic representation of model for a segment heat balance

$$v_z \frac{\partial \rho c T}{\partial z} = - \frac{\partial}{\partial y} \left[-k_L \frac{\partial T}{\partial y} \right] + (\Delta H) r \tag{17}$$

$$\frac{1}{U} = \frac{1}{k_w \frac{d_{lm}}{d_{ex}}} + \frac{1}{h_w \frac{d_{ex}}{d_{in}}} \tag{18}$$

Heat transport equations follow the Prandtl analogy and are equivalent to those used for mass transfer.

$$\frac{h_G}{u} = 0,8 Sc^{-0,704} \tag{19}$$

5. Main parameters of film SO₃-sulfonation

An experimental set was developed to study the effect of follows factors: (i) mole ratio between SO₃ and organic liquid, (ii) wall temperature and, (iii) volumetric percentage of SO₃ in the phase gaseous. The variables representing the quality of the sulfonated product are: active matter, unsulfonated matter, acid value and color (Ahmad et al., 2007; Inagaki, 2001). The experimental matrix is presented in Table 3 and detailed information about the analysis is presented below (Torres et al., 2008b).

Conditions	value
SO ₃ /N ₂ inlet (gaseous sulfonate mixture), % vol/vol	3 - 7
SO ₃ /N ₂ temperature inlet, °C	50 - 60
SO ₃ /organic liquid, mole ratio	1:1 - 1,2:1

Table 3. Operating conditions used for the methyl ester sulfonation (Torres et al., 2009a)

5.1 Active matter

Increase of active matter in product was proportional to the increase of SO_3 /organic liquid mole ratio as well as the increase of SO_3 percentage in the gas stream. Slope changes observed with respect to the temperature are probably due to side reactions occurring at higher temperatures; the formations of undesired matters decrease active matter (Figure 11).

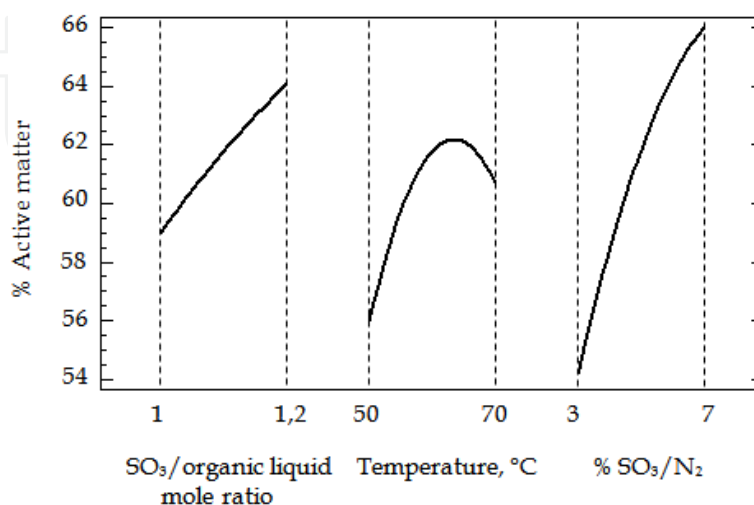


Fig. 11. Impact of the operation conditions on the degree of sulfonation

5.2 Unsulfonated matter

The impact of the experimental factors is initially inverse compared with the effect obtained with the active matter; however the SO_3 /organic liquid mole ratios beyond 1,1 produce an increase in the quantified unsulfonated matter. This change can be explained by over sulfonation of reactant and formation of side products. This assumption is consistent with the effects of temperature on the percentage of non-sulfonated matter (Figure 12).

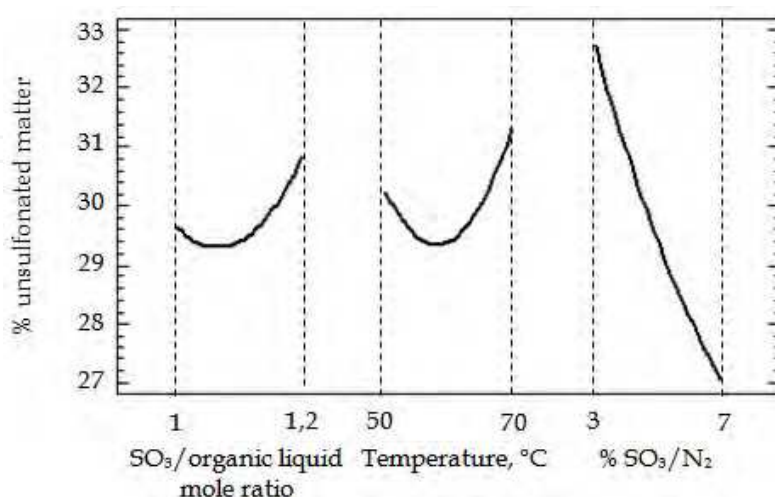


Fig. 12. Effects of the experimental factors on the unsulfonated matter

Over-sulfonated products do not have the same characteristics of the washing active substance and therefore are not identified as active matter but yet as free oil (unsulfonated).

Figure 12 proves that the unsulfonated matter percentage decreases the same as the sulfonating reagent in the gas mixture increases.

5.3 Acid value

Figure 13 shows the effect of the conditions process on acid value. Increase in the sulfur trioxide has a positive effect in agreement with expectations; also the increase of temperature in process enlarges the acidity in the product. Change in the slope can be explained by kinetics effects favored by temperature rising. Both the increase in the mole ratio and sulfur trioxide in the sulfonating mixture can be explained by the effectiveness of the reaction because an excess of SO₃ promotes the consumption of the same reactants for the generation of over-sulfonated matter.

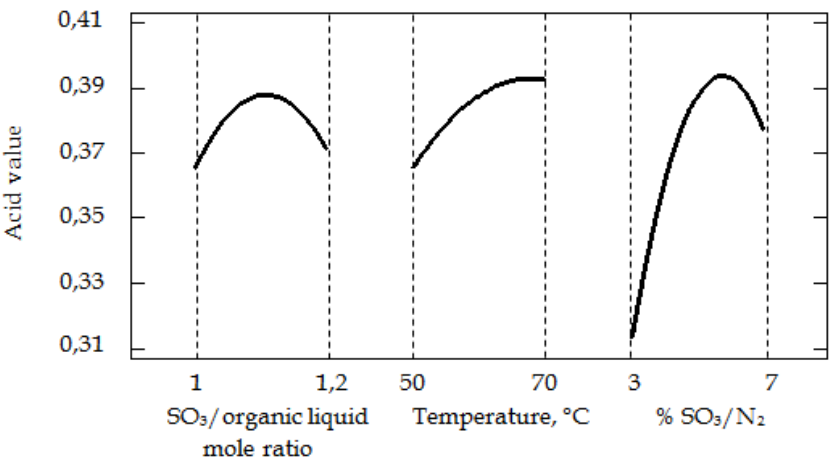


Fig. 13. Acid values obtain by changes of mole ratio, temperature and SO₃ inlet

5.4 Coloration

Figure 14 presents the trends for the coloration in the sulfonated product which intensifies the values of concentration of SO₃ some that the mole ratio and SO₃ content in the gas stream. All variables show a direct influence to the increase in color which is associated with

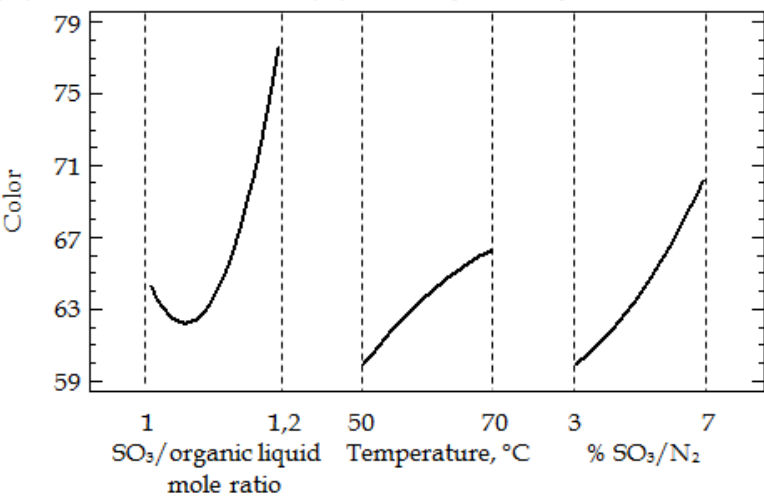


Fig. 14. Impact on coloration in the sulfonated product due to variations of process

higher sulfonation degrees. Although the coloration is identified mostly as an esthetic factor for the commercialization of sulfonates, higher colorations can also be a qualitative indicator of over-sulfonation. Anionic surfactants in aqueous solution have colors ranging from yellow to reddish orange (Inagaki, 2001).

6. Film SO₃-sulfonation applied

6.1 Sulfonation of methyl ester with SO₃

Use of methyl esters (ME) in the industry detergent, although under investigation and development since more than 25 years, has not yet expanded to high levels, mainly because the following reason:

- Controversial forecasts about availability of petrochemical feedstocks with related cost comparison via vs. natural sources;
- Viability of sufficient quality of sulfonation grade methyl esters;
- The process to produce high quality α -sulfonated methyl ester (SME) is generally more complex than that for alkyl benzene sulfonates;
- Application know-how is not yet completely availed and low FAMES solubility involves some restrictions in application, notably concerning the use in liquid detergent products and low temperature washing cycles.

Complex chemistry is not yet fully elucidated, but may be summarized as is shown in Figure 15 (Morales & Martínez, 2009).

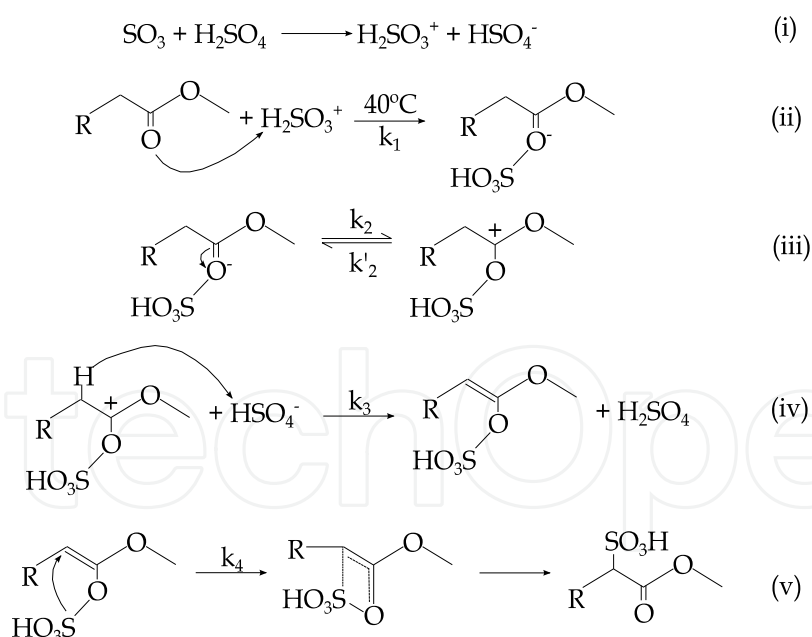


Fig. 15. Mechanism of methyl ester sulfonation in sulfonator (Torres et al., 2009b)

The methyl ester molecule is initially di-sulfonated in a relatively fast reaction accompanied with a high amount of heat released (Roberts, 2003). There is a third reaction stage considerably slower than the previous ones, where an SO₃ group is liberated (on aging). For some researchers, this SO₃ group just released would be especially active and therefore capable of directly sulfonating another methyl ester molecule in an alpha position. The

diffusivities of reagents are estimated from the Wilke-Chang equations and diffusivities in the mixture are estimated through the Vignes equation (Vignes, 1966). Generally, in methyl ester sulfonation the amount of intermediate III in the final product varies from 10-20% (Foster, 2004), but this amount can be reduced by a long and heated digestion (aging stage).

An experimental apparatus showed in Figure 16 was utilized by Torres (2009) for researching the parameters of film SO_3 -sulfonation of methyl ester derived from hydrogenated stearin palm, this apparatus was designed by Chemical Engineering Laboratory from Universidad Nacional de Colombia (Bogotá, Colombia).

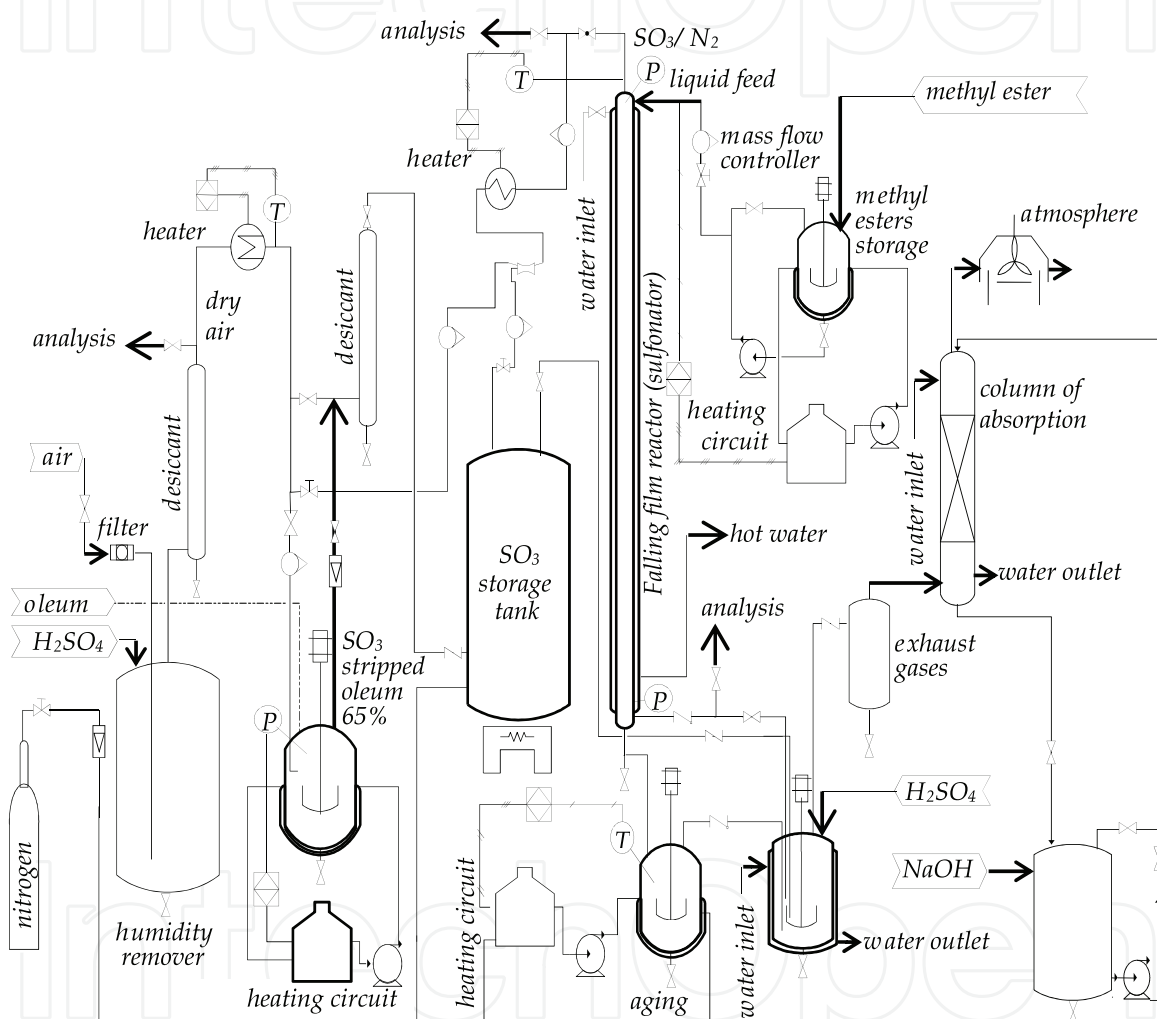


Fig. 16. Experimental apparatus for methyl ester sulfonation using a falling film reactor and SO_3 stripped from 65% oleum with dried air process

High degree of sulfonation is obtained in the aging step controlling simultaneously the temperature and residence time. At higher temperatures it is feasible to obtain higher conversion levels, whereas at low temperatures (below 80°C) the time required to reach high conversions is considerably long. These reactions are highly exothermic in order of 150 – 170 kJ/mole (including 25 kJ/mole of the absorption heat of gaseous SO_3). A kinetic model has been development by Roberts (2007) based on the proposal that two major intermediates are involved in aging (Figure 17).

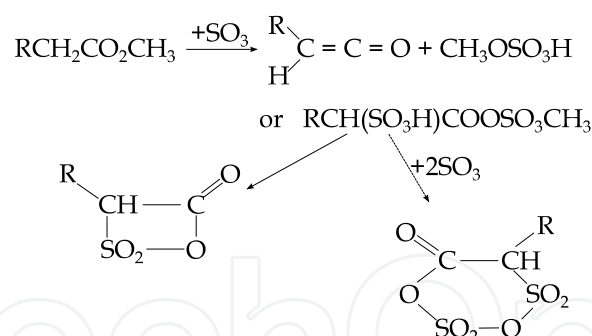


Fig. 17. Reactions in the aging step (adapted from Roberts, 2001)

$$k = Ae^{\left(-\frac{B}{T}\right)} \tag{20}$$

	$k_f, (\text{s}^{-1})$	$k_s, (\text{s}^{-1})$
$\text{Log}A$	12,10	11,52
B	12,060	12,130

Table 4. Values for equation 20 on aging stage (Roberts, 2008)

The overall conversion as function of time and mole ratio M of SO_3/ME is given by:

$$\% \text{ conversion} = 100M \left(\frac{1}{M_{100}} \right) - 0.25e^{-k_f t} - 0.167e^{-k_s t} \tag{21}$$

M_{100} is mole ratio for a conversion at 100%, after a delayed aging $M_{100} = 1,2$. These equations, for aging in a batch reactor system or in a plug flow systems, can be used as guidelines when setting initial conditions before fine-tuning plant operation to meet a required specification (Roberts, 1998). Methyl esters are less active than aromatic compounds to sulfonating due to the less electronic density of the aliphatic chains. The methyl ester sulfonation include a neutralization step to obtain monosodium salts of α -sulfo methyl esters as desire products (Kapur et al. 1978). If neutralization is immediate disodium salt is formed (see Figure 18a). However, if neutralization of the acid is delayed, the sulfo ester monodisodium salt is obtained as final product (see Figure 18b).

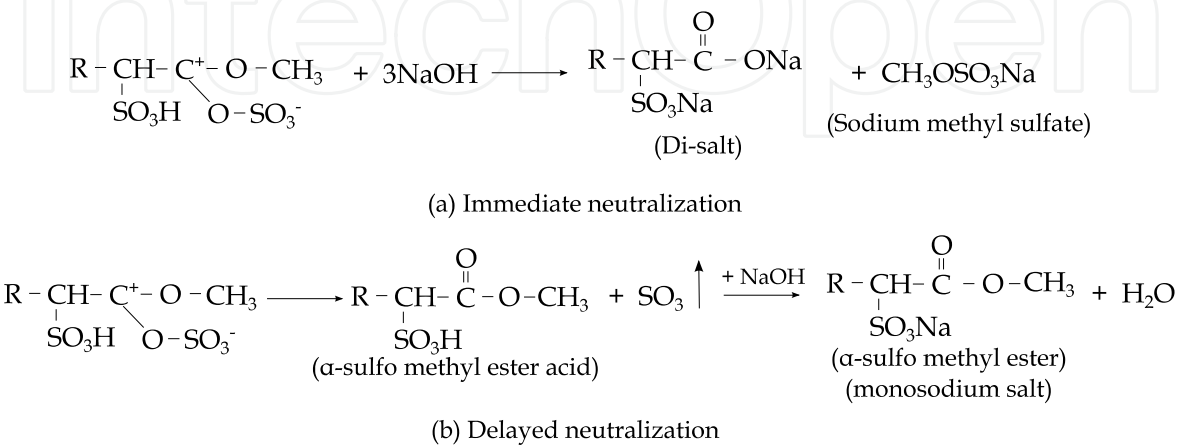


Fig. 18. Neutralization chemistry of SME (Torres et al., 2009b)

Generally, feedstock for the manufacture of FAMES containing unsaturated fatty acids and these has been attributed to the formation of polysulfone in the double bonds (Yamada & Matsutani, 1996). Unsaturated in methyl ester make it an olefin with a carboxyl methyl group at the end of the chain. Olefins are more rapidly sulfonated by SO_3 also unsaturated bound produces oversulfonation and oxidation of the olefin which competes with the saturated ester obtain product more colored, however the color can be improved by bleaching. Unsaturated make it an olefin with a carboxyl methyl group at the end of the chain. Olefins are more rapidly sulfonated also unsaturated bound produces oversulfonation and oxidation of the olefin which competes with the saturated ester obtain product more colored, however the color can be improved by bleaching (Figure 19).

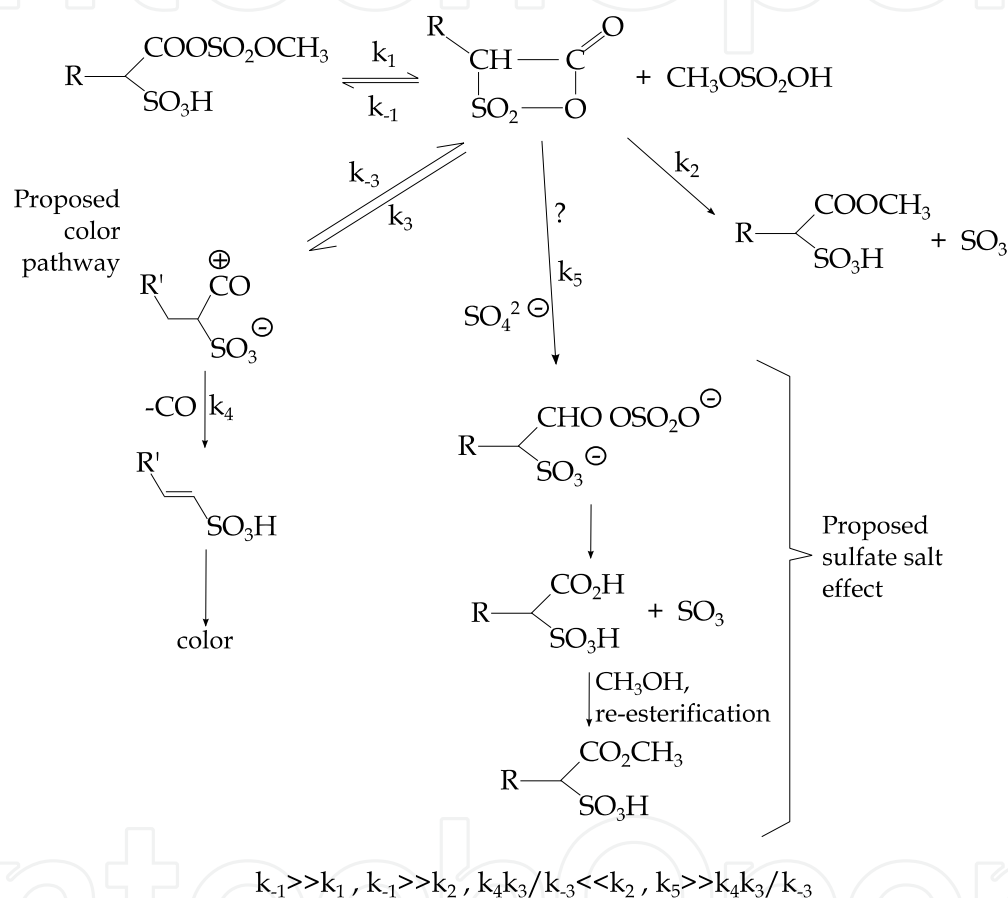


Fig. 19. Reaction scheme for the coloration in aging step (adapted from Roberts et al., 2008)

Mechanism proposed by Roberts (2007) suggests a reversible formation of β -dioxane cycle and $\text{CH}_3\text{SO}_3\text{H}$ this β -anhydride reacts opening its cycle, sintering itself, and losing a carbon monoxide to become an alkene sulfonic acid. This is formed mainly in reactions of sulfonation of α -olefins, these are very intensive in color when aged in the acid form (Clippinger, 1964).

6.2 Validation of model

The input variables more important for the conversion are: the length and diameter reactor, flow of liquid reactant, mole ratio between SO_3 and organic liquid, in this case methyl stearate derived of hydrogenated stearin from palm oil (Narváez et al., 2005; Torres

et al., 2005), and amount sulfur trioxide in the gas phase (SO_3/N_2), finally the temperature of the process. This mathematical model permits to calculate the profiles of interfacial liquid temperature, liquid film density, liquid viscosity for any column height and longitudinal profiles of conversion. The proposed model may be suitable for use in design and operation of industrial film reactors. To ensure convergence of the system of equations then transformation of the equations proposed by Agrawal & Peckover (1980) was chosen following the same development by Talens (1999). The set of equations resulting from the mass, momentum and heat transfer is solved numerically. Figure 20 shows schematic view from the top of a reactor: the liquid is evenly distributed around the wall, and the gas mixture is injected through the center of the column. The interfacial temperature is affected by the SO_3 amount in the gas mix. It is clear an increase of interface temperature result of the SO_3 excess in the gas flow. The temperature of the reagents is a key control variable to avoid undesirable side impact that damage the product mainly by strong coloration.

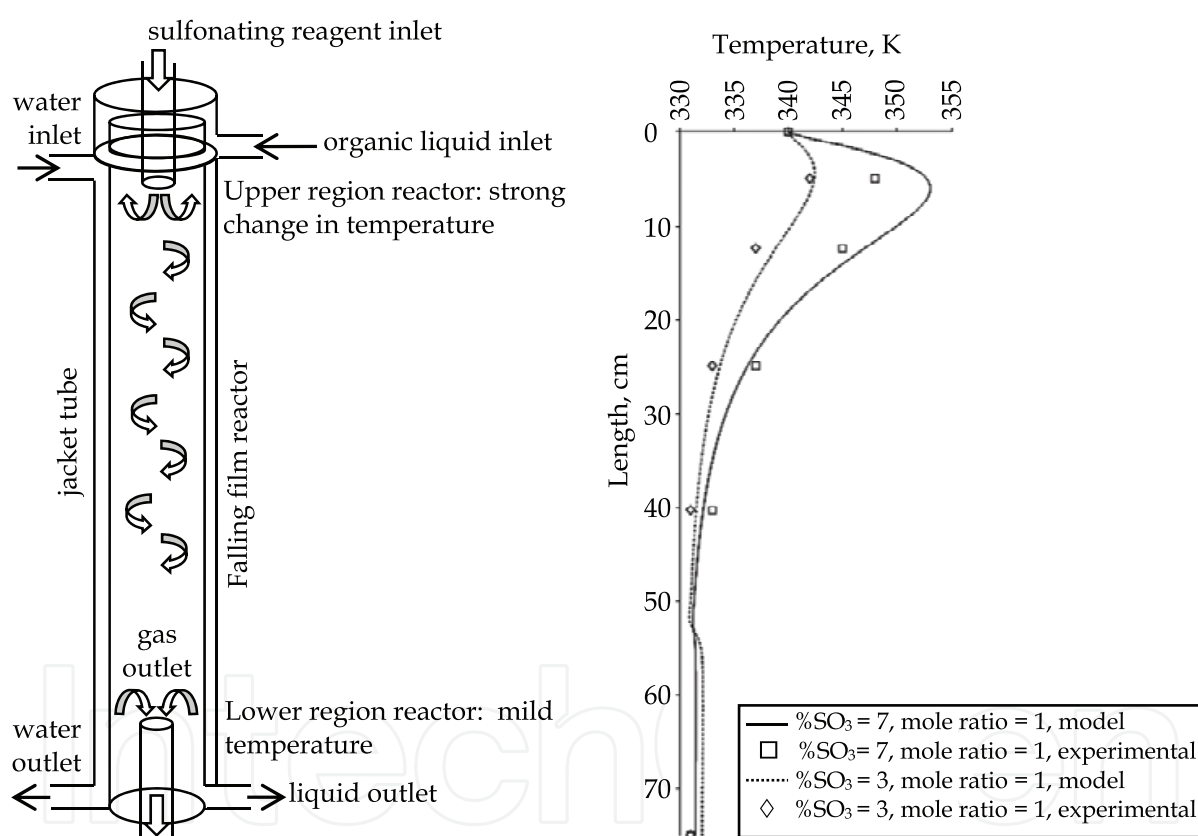


Fig. 20. An example of interfacial temperature profiles fall in the reactor longitudinal

Other example of the results provided by the model for longitudinal conversion profile from top of the reactor (expressed as percentage of active matter) is shown in Figure 21(a). The input values of the model are: SO_3/N_2 percentage at 5%, $\text{SO}_3/\text{methyl stearate}$ mole ratio at 1; T_G , T_L and T_w at 343 K, 333 K and 313 K, respectively. This figure shows schematically the fast conversion region at the top of the reactor (associated with gas phase control) and slow conversion region at the bottom (linked with liquid phase control). The washing active substance was determinate using a two titration technique with Hyamine 1622 as the titrant reagent and methylene blue as indicator (Tsubochi et al., 1979; Milwdsy & Gabriel, 1982;

Battaglini et al., 1986; Schambil & Schwuger, 1990). The progress of the reaction is decisive for sulfonation degree expressed as amount active matter.

Physicals and chemicals properties used in model are listed in Table 5.

Parameters	Correlation
Kinetic in sulfonator, kmol/m³s (Torres et al., 2008a)	$r = -kC_{SO_3}C_{ME}$ (22)
	$k = 1,14 \times 10^{19} e^{-\left(\frac{14.350}{T}\right)}$ (23)
Diffusivity, m²/s (Wilke & Chang, 1955)	$D_{SME-ME} = 3,12 \times 10^{-11} \frac{T_L}{\mu_L^{2/3}}$ (24)
	$D_{ME-SME} = 6,288 \times 10^{-11} \frac{T_L}{\mu_L^{2/3}}$ (25)
	$D_{SO_3} = 2,031 \times 10^{-10} \frac{T_L}{1000\mu_L^{2/3}}$ (26)
Gas thermal conductivity, J/msK (Davis et al., 1979)	$k_G = 0,0279$
Heat capacity of liquid, J/kmolK (Broström, 1975; Reid et al., 1987)	$c_L = 507,300 + 101,010x$ (27)
Heat capacity of gas mix, J/kmolK (Same at nitrogen)	$c_G = 29,82$
Liquid mixture density, kg/m³ (Talens & Gutiérrez, 1995; Broström, 1975)	$\rho_L = 980 + 192x - 0,66T_L$ (28)
Liquid thermal conductivity, J/msK (Davis et al., 1979)	$k_L = 0,276$
Surface tension, N/m (de Groot, 1991)	$\sigma = 0,046$
Viscosity of methyl esters mix, kg/ms (Torres & Sánchez, 2008)	$\mu_{ME} = 8 \times 10^{-6} e^{\frac{1949,6}{273+T_L}}$ (29)
Viscosity of methyl esters sulfonic acid, kg/ms (Talens & Gutiérrez, 1995)	$\mu_{SME} = 1,36 \times 10^{-8} e^{\frac{5700}{T_L+5,88}}$ (30)
Viscosity of gas mix, kg/ms (Same at nitrogen)	$\mu_G = 1,9 \times 10^{-5}$
Viscosity of liquid mix, kg/ms (Broström, 1975; Talens & Gutiérrez, 1995)	a) $0 < x \leq 0,25$: (31) $\mu_L = 2,72 \times 10^{-6} e^{\frac{2980}{T_L+3,86x}}$
	b) $0,25 < x \leq 0,6$: (32) $\mu_L = 3,7 \times 10^{-9} e^{\frac{4850}{T_L+1,035x}} + 0,003$
	c) $0,6 < x < 1$: (33) $\mu_L = 3,7 \times 10^{-9} e^{\frac{4850}{T_L+5,22x}} + 0,003$
All thermal conductivity, J/msK (Davis et al., 1979)	$k_w = 16,3$

Table 5. Correlation to estimate heat and mass transfer coefficients and properties of organic liquid and gas mixture (Torres & Sánchez, 2009)

The model was constructed to predict the sharp increase in the conversion that takes place in the first stage inside of the falling film reactor. It confirms that the mass transfer is initially controlled by the resistance in the gas phase. After due to several factors the resistance occurs in the liquid phase. Figure 21(a) presents the conversion profile in the film reactor from the model, experimental results showed conversions lower than those predicted by the reactor model in upper reactor region. This is due that the model assumes a fully developed flow and entrance effects of the streams to the reactor are neglected. However, the model is able to predict adequately conversions downstream for longer lengths. In the bottom of reactor is a small jump in the conversion predicted by the model, perhaps due to kinetic effects that reach importance by the consumption of reactants.

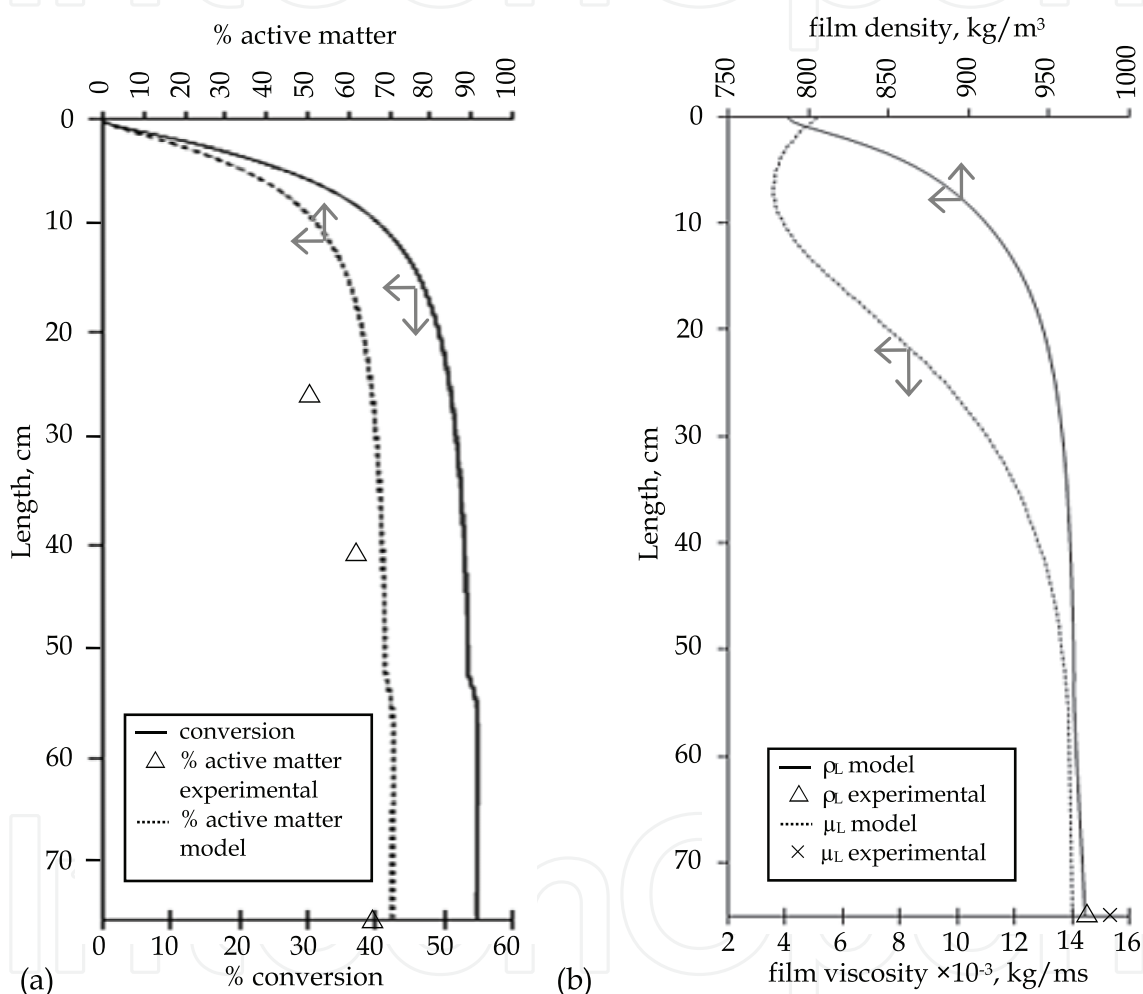


Fig. 21. (a) Longitudinal conversion profile for SME and (b) density and viscosity model estimated by the model

The most important outlet data obtained by solving the mathematical model are conversion, density and viscosity of the product. The density and viscosity of the effluent, downstream in the reactor film, estimated by the mathematical model is similar to that obtained experimentally, as shown in the Figure 21(b). The increase of temperature produces a decrease in viscosity enhancing the solubility of SO₃ in the liquid, and causing a decrease in film thickness. These variations are the result of abrupt change in composition and release of heat in the initial part of the reactor, which produce an increasing of the temperature in this

area. Same phenomena occur with the film thickness. The jump in conversion takes place in the top reactor, the temperature rises considerably and reduces the viscosity of the liquid, even canceling the effect of viscosity then in the bottom reactor increases composition and the interfacial velocity. Subsequently, the reduced generation heat and descent of the temperature is increase the viscosity again.

7. Conclusions

Transfer rates in the gas phase are affected by changes in the tubular reactor. Increases uncontrolled in the gas flow could drag some liquid into the gas phase. Therefore the gas velocity has to be set at the point where no liquid drops can be pulled to the gas phase. Temperature is a critical parameter in the quality control of the sulfonated products. Although inlet streams' temperature should be adjusted above room to enhance the reaction and avoid the solidification of the organic matter, an adequate control is required due to the high release of heat attributed to the sulfonation reaction. The SO_3 /organic liquid mole ratio requires rigorous control. Excess of SO_3 enhance side reactions and extended reaction times will also enhance side reactions.

The comparison obtained for this same process with petrochemicals compounds indicates that the model could be applied to any film sulfonation but adjusting the parameters and specific conditions, such as the physicochemical properties of the compounds used, since the sulfonation process described in this work is one of the more complicated cases. Although some of the physical and chemical properties of mixture are obtained of a similar form, these should be tested and approach to achieve convergence of the model; these yielded the best results in the mathematical model of falling film reactor.

The model predicts two distinct transfer areas. The first is characterized by an abrupt increase in conversion and temperature, in which the controlling step depends initially of the gas phase and in accordance with the extent of the sulfonation reaction, the viscosity fluid increases, the film thickness is also higher and the film velocity decreases, then the liquid phase becomes the controlling stage with a mild increase of the temperature and conversion. The mathematical model proposed for a film SO_3 -sulfonation fits adequately the trend of experimental results, so it is now possible to make a prediction on the conversion in a falling film reactor, because the profiles of temperature, density, viscosity and conversion are consistent with experimental results that satisfy the conditions to minimize the strictest mathematical calculations mistakes due to the usage of numerical solutions.

8. Notation

A	pre-exponential factor, s^{-1}
A^+	a van Driest constant
B^+	a van Driest parameter
C	concentration, kmol/m^3 ; van Driest constants
c	heat capacity, $\text{J}/(\text{kmolK})$
C_f	friction factor, dimensionless
D	diffusivity, m^2/s
d	reactor diameter, m
f	damping factor, $f = e^{-1.66(1-\tau/\tau_w)}$
g	acceleration due to gravity, m/s^2

ΔH	reaction enthalpy, J/kmol
h	heat transfer coefficient, J/(m ² sK)
k	reaction rate constant, m ³ /kmols; thermal conductivity, J/msK; mass transfer coefficient, kmol/m ² s
L	reactor length, m
M	mole ratio SO ₃ /ME
m	Henry constant, (kmol of SO ₃ /m ³ of gas)/(kmol of SO ₃ /m ³ of liquid)
N	mass flux of gaseous reactant, kmol/m ² s
P	pressure, atm
Q	heat of reaction, J/mol
r	reaction rate
Re	Reynolds number, dimensionless: $Re_G = \rho u(d - 2\delta)/\mu$; $Re_L = 4\Gamma/\mu$.
Sc	Schmidt number, dimensionless
T	temperature, K
U	global heat transfer coefficient, J/(m ² sK)
u	turbulence characteristic velocity of gas, m/s
x	conversion expressed as molar fraction of the sulfonic acid, dimensionless
v	axial velocity of liquid film, m/s
y	transversal coordinate (from wall toward the liquid free surface)
y^+	non-dimensional distance to the wall: $y(\tau_w g/\rho)^{1/2}/\nu$
z	axial coordinate

Greek letters

Γ	volumetric flow rate of the liquid per unit wetted perimeter, m ² /s
δ	film thickness, m
δ^+	dimensionless film thickness, $\delta^+ = \delta u/\nu$
φ	roughness enhancement factor, dimensionless
μ	liquid viscosity, kg/ms
ν	kinematic viscosity, m ² /s
ρ	liquid density, kg/m ³
τ	interfacial shear stress, N/m ²
σ	Surface tension, N/m

Subscripts

A	absorbing specie
ex	exterior
G	gas phase
i	interface
in	interior
L	liquid phase
lm	logarithmic mean
T	turbulent
w	wall

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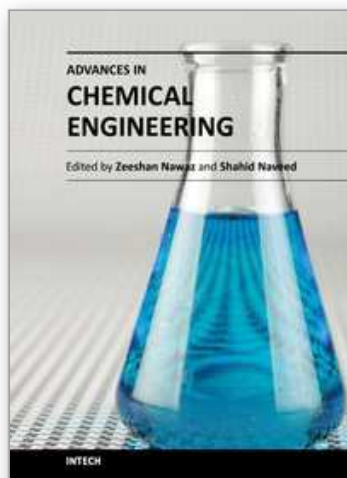
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Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the state of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic modeling. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided into two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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University Campus STeP Ri
Slavka Krautzeka 83/A
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InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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