

HYDRODYNAMIC EFFECTS ASOCIATED TO METHYL ESTER SULPHONATION IN FALLING FILM REACTORS

EFFECTOS HIDRODINAMICOS ASOCIADOS A LA SULFONACION DE ESTERES METILICOS EN REACTORes DE PELICULA DESCENDENTE

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ABSTRACT: Falling film reactors (FFR) are widely used in industry, mainly in those processes which require an efficient heat exchange. Although, these devices have been studied for several years, there is not yet a full understanding of their behavior. This is due to the fact that the performance of the FFRs can be easily influenced by hydrodynamic factors which affect transport phenomena in the reactor. In this study, an experimental analysis of hydrodynamic factors influencing a FFR is presented, paying special attention to hydrodynamic phenomena such as the phases' flow regimens and the residence time for the sulphonation of methyl ester (ME) from palm oil with SO₃. The results show that along with the SO₃/ME ratio the hydrodynamic of both phases (gas and liquid) present in the reactor have a strong influence over the sulphonation efficiency

KEYWORDS: sulphonation, falling film reactor (FFR), Hydrodynamic, Methyl esters (ME)

RESUMEN: Los reactores de película descendente (FFR por sus siglas en ingles), son dispositivos ampliamente usados en la industria, principalmente en aquellos procesos que requieren una eficiente transferencia de calor. A pesar que los FFR han sido estudiados por varios años, aun no se ha llegado a una comprensión completa de los procesos que suceden en el reactor. Esto se debe principalmente a factores hidrodinámicos, los cuales afectan los fenómenos de transferencia a lo largo del proceso. En este estudio se presenta un análisis experimental de la influencia de factores hidrodinámicos en un reactor de película descendente, analizando principalmente los fenómenos hidrodinámicos tales como los regímenes de flujo en las fases involucradas y tiempos medios de residencia, para la sulfonación de ésteres metílicos derivados de estearina hidrogenada de palma con SO₃. Los resultados mostraron que el comportamiento hidrodinámico en el reactor influencia fuertemente la eficiencia del proceso de sulfonación al mismo nivel que la relación molar SO₃/ME.

PALABRAS CLAVE: Sulfonación, reactor de película descendente (FFR), hidrodinámica ésteres metílicos (ME)

1. INTRODUCCIÓN

Falling film devices are widely used in industry, they are designed to allow energy and mass transfer between two non-miscible fluids without dispersion of one in the other. The principal applications of these devices include cooling towers, absorption columns, and reactors which are useful in processes either with high reaction heat, or where the temperature is a critical control parameter like in sulphonation or chlorination reactions [1].

Although, these devices have been widely used for a long time, there is not yet a full understanding of their behavior. This is because there are operational characteristics associated with the hydrodynamic behavior, which affect the rates of heat and mass transfer, hence the kinetics of the reactions [2]. To date, there is no consensus on any universally accepted correlation for the transport phenomena taking place in the interface and the hydrodynamic parameters of the thin film, valid over a wide range of Reynolds numbers [3]; mainly because the interface is affected by waves present in the liquid film that make the hydrodynamics

unsteady, influencing the film thickness, velocity distribution, wall shear stress and the mass and heat transport rates [4].

These waves, which can be formed either by the effects of gravity or by the shear stress caused from the high speed gas flowing in co-current with the liquid phase [5, 6], complicating significantly any description of a smooth laminar flow regime for the liquid film and producing a turbulent regime for the gas phase. Waves on a laminar film cause a certain amount of liquid mixing near the surface, and this considerably affects the rate of mass transfer and the interfacial area, since some degree of turbulence arises from eddy currents [5] (although, the appearance of waves at low flow rates does not mean that the flow is turbulent [7]).

In the case of sulphonation in FFR, different models have been developed; mainly in the case of linear alkyl benzene sulphonates (LABS). Johnson and Crynes (1974) [8] were the first ones who proposed a mathematical description of the FFR sulphonation, modifying the Gilliland-Sherwood equation Eq (1) and the Nusselt equation Eq (2) to calculate heat and mass transfer coefficients. This model assumes that the reaction takes place only on the gas liquid interface, therefore, the process rate is controlled by SO_3 diffusion from the gas bulk to the interface, in this way concentration and temperature axial profiles are calculated [9]. Although, this model describes experimental results well, film thickness and the different parameters that affect it were not considered [1].

$$Sh_G = 0.046 \left((Re_G)^{0.83} \right) \left((Sc_G)^{0.44} \right) \quad (1)$$

$$Nu_G = 0.046 \left((Re_G)^{0.8} \right) \left((Pr_G)^{0.35} \right) \quad (2)$$

Davis et al. 1979 [10], tried to describe completely the fluid-dynamic process determining the film thickness velocity profiles in the liquid phase. Based on the same considerations made by Johnson and Crynes (1974), the instantaneous reaction rate and process is controlled by the SO_3 mass transfer in the gas phase rather than in the liquid phase, Davis included the liquid properties dependence with temperature to calculate the falling film thickness and heat transfer in the liquid where a linear temperature profile was assumed in a radial direction. However, the assumptions made by Johnson and Crynes (1974) and adopted by Davis and coworkers can be applied only at the top of the

reactor. While the reaction proceeds, the viscosity of the liquid film increases with the presence of sulphonate matter. Therefore, both the mass transfer of SO_3 and reaction rate decreases downstream in the reactor as the conversion increases [5, 9].

In 1988, Gutierrez et al. [9], suggested a mathematical model for the linear alkyl benzenes LAB's sulphonation in a FFR getting a 95% of prediction confidence regarding experimental values. In the development of this model mass transfer in both phases (liquid and gas) were considered. Hence, the reaction is considered to take place not just in the interface but in the bulk of the liquid phase. In the first section of the reactor, the process rate is limited by the SO_3 mass transfer from the gas bulk to the interface and by the reaction rate. At this point the liquid viscosity and temperature are low enhancing the solubility of SO_3 in the liquid. As the conversion in the reactor increases, the transport phenomena in the liquid phase become significant, and an increase in the film thickness take place due to the higher viscosity of the sulphonate matter. While in the gas phase the mass transfer is affected by the lower SO_3 concentration. However, this model has been widely discussed since the numerical solution of the differential equations involved an arbitrarily defined uneven partition of the domain of the liquid phase and because this model is fitted with several parameters, which made this model only useful for the original conditions [1, 11-13].

In 1996 Dabir et al. [1] suggested a new model that includes the effects of film waves in the transfer phenomena near the interface including eddy diffusivities to calculate an effective diffusivity in laminar flow. This approach was also considered by Gutierrez et al. [9], but in their model Dabir et al. included the interfacial drag effects in the mass transfer coefficients. This model was verified with the experimental measures made by Gutierrez et al., and can predict: conversions, interface temperature profiles and the film thickness along the reactor [12].

One of the most recent mathematical model for LABs sulphonation was developed by Talens in 1999 [12], based on the Gutierrez's model. In this model Talens tried to consider all kind of elements which had not been considered in previous models avoiding the Johnson and Crynes modification to the Gilliland-Sherwood equation (Equation 1), in order to obtain an accurate representation of experimental data.

To date, the sulphonation of methyl esters, which is a renewable alternative for the active ingredient of detergent formulations, has been treated from the kinetic point of view but a full understanding of the process and the different variables involved in the scale up of the process are still to be studied [13, 14, 15, 16]. In this paper, sulphonation of methyl esters from palm stearin have been performed at the sulphonation bench scale plant of the Universidad Nacional de Colombia (Bogota campus). The performance of the sulphonation process was analyzed controlling both kinetic parameters like the SO_3/ME molar ratio and hydrodynamic parameters such as mean residence time of the liquid phase and flow regimes in both phases.

2. MATERIALS AND METHODS.

2.1. Methyl esters.

Methyl esters (ME) were obtained from transesterification of hydrogenated palm stearin with methanol in the way described in [17], table 1 shows the main characteristics of this methyl ester [13].

Table 1. Methyl ester characteristics

Free fatty acids (% oleic)	0.0
Iodine value	0.61
Wet (%)	0.008
Fusion point ($^{\circ}\text{C}$)	30
(mg KOH/g sample)	187.6
Acid value (mg KOH/g ME)	0.228
C_p (75 – 78 $^{\circ}\text{C}$) (J/g $^{\circ}\text{C}$)	2.18
Average molar weight (gr/mol)	281.97

Transport properties such as density and viscosity for the ME of palm stearin at different temperatures were measured and published in [13].

2.2. Sulphonation agent

The sulphonation agent used was SO_3 , which was obtained by bubbling dry air in oleum 20 % at 80°C . The air was dried by passing it through a column filled with concentrated H_2SO_4 , and the flow was measured and controlled before being fed to the oleum tank with a DwyerTM flow meter. The air flow was calibrated measuring the pressure at the flow meter outlet. The air stream with the dragged SO_3 were bubbled in a diluted H_2SO_4 solution (0.053 M), where the SO_3 was trapped as H_2SO_4 and measured with a mettler toledo titrator DL53®.

A complete description of the system and methods used to quantify the content of SO_3 are presented in [14, 18].

2.3. Falling film reactor

The experiments were carried out in a falling film glass reactor of 1.27 cm diameter and 75 cm of length. A scheme of the sulphonation set up is presented in figure 1. The flow of nitrogen, and methyl esters were selected based on the formation of a homogeneous film wetting the inner wall of the FFR. The two different nitrogen flows with their respective SO_3 compositions, which were used for the tests, are listed in table 2. It was observed that higher gas pressures allow the formation of a homogeneous liquid film for a wider range of ME flows. Whereas, low gas pressures require a minimum amount of ME flow [18]. This leads to operation with SO_3/ME molar ratios below the minimum required for a proper sulphonation (SO_3/ME molar ratio > 1) [19].

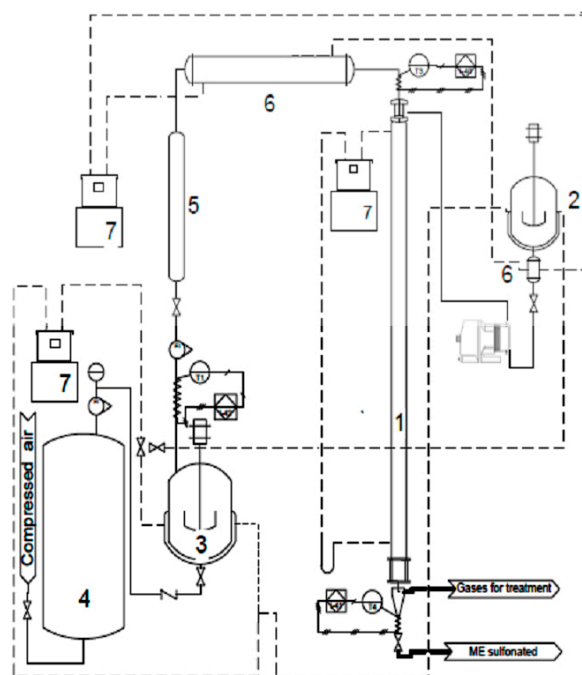


Figure 1. Sulphonation bench scale set up. 1) falling film reactor, 2) ME loading tank, 3) Oleum loading tank, 4) (H_2SO_4 concentrated) column, 5) demister, 6) heat exchangers, 7) thermostated baths. Solid lines represent process lines, and dashed lines represent heating and cooling lines.

Table 2 presents the experimental matrix conditions where the operation temperatures for the FFR were set as based on those reported in [13] (40°C for the ME and FFR wall, and 50°C for the gas stream). The properties of the gas

mixtures at the working pressures and temperatures were calculated using the corresponding states methods [20]. Whereas, the liquid properties were assumed as those of the ME which are presented in [18]. Active matter percentage (% AM) in the sulphonated ME was measured with a volumetric method titrating with Hyamine 1622 using disulfine blue as an indicator [13, 18].

Table 2. Experimental conditions (EC) for ME sulphonation and hydrodynamic analysis.

EC	Air flow L/min	SO ₃ flow mol/min	ME flow mol/min	Molar ratio SO ₃ /ME
A	41.8	1.99E-02	1.32E-02	1.5
B	41.8	1.99E-02	1.69E-02	1.2
C	41.8	1.99E-02	1.77E-02	1.1
D	64.8	4.57E-02	2.89E-02	1.6
E	64.8	4.57E-02	3.83E-02	1.2
F	64.8	4.57E-02	4.05E-02	1.1

2.4. Residence time distributions RTD

Residence time distribution in the liquid phase was measured for the conditions listed in table 2 in absence of SO₃. A step experiment was performed using Prussian red as a tracer. Once both gas and ME flows were stabilized, the ME feed was suddenly changed for a ME solution with the tracer using a three way valve. Ten samples were collected at the FFR outlet for each test condition. The samples were collected at intervals once the feed stream was switched and the collection time for each sample varied depending on the ME flow conditions from 30 to 120 s in order to guarantee enough sample volume for analysis.

The concentration of tracer in the liquid stream at the FFR exit was measured with a Milton Roy Spectronic20™ at 460 nm.

3. RESULTS AND DISCUSSIONS.

Figure 2 shows the cumulative RTD functions obtained experimentally for each one of the experimental conditions listed in table 2 in absence of SO₃. The experimental data was observed to be well described by the dispersion model presented in equation 3 with a correlation coefficient of at least $R^2 \geq 0.8$.

$$F(t) = 2 \left[1 - \operatorname{erf} \left[\frac{1}{2} \sqrt{Pe} \left[\frac{1 - \frac{1}{\tau}}{\sqrt{1 + \tau}} \right] \right] \right] \quad (3)$$

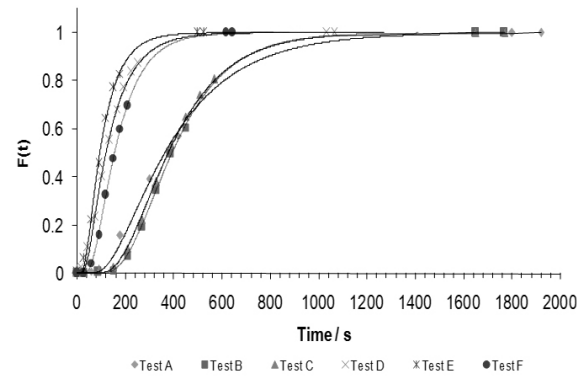


Figure 2. Cumulative RTD curves for the experimental conditions. The discrete points represent the experimental samples while the solid lines were obtained with the dispersion model (Equation 3), for each EC

Table 3 shows the calculated values for the mean residence time τ and the Peclet number Pe . Although, the system would be expected to show a behavior closer to a laminar flow reactor, the experimental shape of the cumulative RTDs discard that the behavior of the liquid phase can be described in this way [21]. The values calculated for the Peclet number show that the hydrodynamic behavior of the liquid phase in the reactor cannot be described neither as a stirred tank reactor ($Pe < 0.005$) nor a plug flow reactor ($Pe > 40$) [22]. The results obtained can be explained from the effect of the co-current gas and the waves formed in the film, which affect the velocity profiles in the liquid phase.

Average axial velocities and effective diffusivities were calculated from the mean residence time Peclet values. Hence, the Reynolds numbers in the liquid phase Re_L were calculated using the properties of the ME at the operating temperatures [13]. These values are listed in table 3.

To calculate the Reynolds numbers of the gas phase an iterative calculation was performed using equations 4 to 8. The conceptual development to calculate the shear stress and the friction factor for a wavy interface is well described in [9-11, 23]. An iterative calculation was required to calculate Re_L and Re_G , since the thickness of the liquid film will affect the flow area of the gas in the reactor. In this way an average value of the film thickness δ , was also calculated and reported in table 3 along with Re_G for each experiment.

$$Re_L = \frac{4\rho_L \Gamma}{\mu_L} \quad (4)$$

$$\Gamma = \frac{\rho_L g \delta^3}{3\mu_L} - \frac{\tau_G \delta^2}{2\mu_L} \quad (5)$$

$$\text{Re}_G = \frac{d_i W_G}{A_i \mu_G} \quad (6)$$

$$\tau_G = f \rho_G U_G^2 \quad (7)$$

$$f = \text{Re}_G^{-1/4} \quad (8)$$

The results presented in table 3 are supplemented with the values of the percentage of the active matter obtained at the studied conditions. The results show that along with the SO_3/ME molar ratio, the hydrodynamic conditions highly affect the performance of the reactor. This can be observed directly with the amount of active matter obtained in the product at the end of the reactor. The results suggest that higher residence time of the liquid phase enhance the sulphonation reaction even when the SO_3/ME molar ratio is kept constant.

The effect of the gas phase regime with the reactor performance is plotted in figure 3, as a ratio of the

Reynolds numbers of the gas phase to the liquid phase. The results indicate that enhancing turbulence in the gas phase not only favors the formation of a homogeneous film, but together with a low Reynolds number in the liquid phase tend to increase the advance of the reaction in the FFR; a phenomena also seen in highly exothermic reactions in plug flow reactors [24].

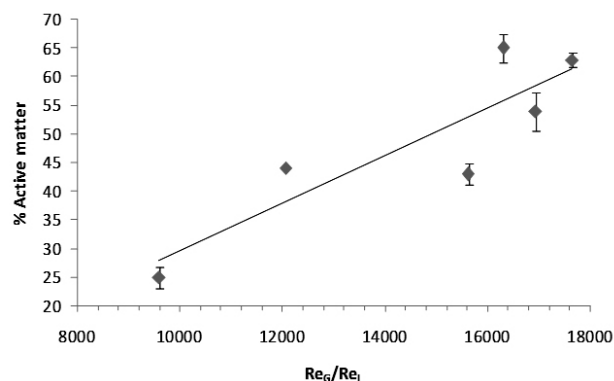


Figure 3. Relationship of the phase regimes with the degree of sulphonation reached in the FFR. The results suggest that high turbulence in the gas phase and low Reynolds numbers in the liquid phase enhances the advance of the reaction

Table 3. Experimental results from the sulphonation of ME in a FFR.

Test	Molar ratio SO_3/ME	Active Matter % \pm SD	Mean residence time τ s	Pe (LU_L/D_L) number	Average axial velocity (liquid)		Average film thickness δ mm	
					U_L m/s	Re_L		
A	1.5	65 \pm 2.5	363	3.72	2.07E-03	43.7	711810.66	6.25E-03
B	1.2	63 \pm 1.2	393	4.76	1.91E-03	40.3	711756.23	6.01E-03
C	1.1	54 \pm 3.3	377	5	1.99E-03	42.1	711784.45	6.13E-03
D	1.6	44 \pm 0.1	120	8.14	6.25E-03	132.1	1593208.65	5.66E-03
E	1.2	25 \pm 1.9	96	10.79	7.85E-03	166.0	1593551.55	6.34E-03
F	1.1	43 \pm 1.9	156	6.18	3.71E-03	102.0	1592863.97	4.97E-03

4. CONCLUSIONS.

The sulphonation of methyl esters from palm stearin was successfully tested reaching a percentage of active matter (sulphonated matter) above 60 % in a reactor 0.75 m long.

The sulphonation of methyl ester from palm stearin was found to be highly affected by the hydrodynamics of the process. The fact that the film thickness is a relevant factor in the percentage of active matter indicates that under the working conditions, the controlling step in the reaction is the mass transfer of reactants and products in

the liquid phase. Under similar conditions of SO_3/ME molar ratios, a greater residence time of the liquid phase allows the development of hydrodynamic conditions that enhances the diffusion over the convection in the liquid phase, as reflected in the values of the Pe number. The overall effect of this increase in the diffusional movement is a better mixing of the reactants at the molecular level enhancing the advance of the reaction.

Although, it was not feasible to operate the reactor over a wider range of flows for liquid and gas phase due to operative limitations, it was feasible to get an insight of the importance of the hydrodynamics and its effects in the performance of the sulphonation in a FFR.

5. ACKNOWLEDGMENTS

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6. NOTATION

A_t = Cross sectional area. m^2

d_t = Equivalent diameter. m

f = Friction factor

g = Acceleration of gravity. m/s^2

Pr = Prandtl number

Re_G = Gas Reynolds number.

Re_L = Liquid Reynolds number.

Sc = Schmidt number

Sh = Sherwood number

Nu = Nusselt number

U_G = Gas flow velocity. m/s

W_G = Gas mass flow. Kg/s

Greek symbols

δ = Film thickness. mm

μ = Viscosity. $Kg/m.s$

ρ = Density. Kg/m^3

Γ = Volumetric flow rate of the liquid per unit wetted perimeter. m^2/s

τ_r = Shear stress at the gas-liquid interface

Subscripts

G = Gas phase

L = Liquid phase

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