Photo-electronic Measurement of Film Thickness for the Sulphonation of Methyl Esters in Falling Film Reactors

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ABSTRACT— ***An optical-electronic system was developed for the determination of film thicknesses in falling film reactors and applied to the analysis of methyl esters sulphonation. Calibration and experimental tests were performed to obtain a correlation between the film thickness (δ) and the measured Voltage (V) of the photo electronic cell. Voltage sensing and film thickness calculations were found to be highly dependent on the position of the sensing device from the reactor inlet and slightly dependant on the gas flow rate under the range of experimental values tested. This optical-electronic system allows a real-time quantitative description of the dynamic behavior of the undulations in the falling film.***

Keywords—Film thickness-- Falling film reactors-- optical sensors

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1.INTRODUCTION

Although falling film reactors (FFR) have been extensively studied for several years due to its application in different industrial processes, such as sulphonation, chlorination, and absorption columns, there are still several research gaps associated with the contribution of different hydrodynamic factors, which affect the transport phenomena within the reactor. A liquid film descending over a surface under the influence of gravity, either at low flows and at small Reynolds number values orin the presence or absence of a gas flow (parallel or countercurrent), does not completely develop a flat interface, featuring a random distribution of undulations on the interface. At higher flow rates an unstable transition stage exits just before the flow is fully developed, but as the flow descends the random formation of undulations in the film increases (Chu and Dukler, 1974, 1975; Killion and Garimella, 2001; Telles and Dukler, 1970).

In reactive systems, along with the reaction on the interface, heat and mass transfer phenomena on both gas and liquid phases take place. Such phenomena become substantially important at the gas-liquid interface. The driving forces for the transfer phenomena and the reaction may change as the process moves along the FFR, either by local changes in the fluids inertia, temperature, or concentration. Based on this, it would be possible to fully describe the reaction system using continuity, momentum, and thermodynamic equilibrium equations. However, the hydrodynamics within the reactor have a profound effect on its performance due to the redistribution effect on the local equilibrium conditions, species concentrations, and energy flows caused by the formation and evolution of undulations in the film's surface (Killion and Garimella, 2001). Several authors have attempted to study and predict the behavior of the film's undulations, their effect on the performance of the falling film systems, and how the undulations evolved as a function of Reynolds number in each of the phases (Karimi and Kawaji, 1999; Kil et al., 2001; Talens-Alesson, 2000). Experimental results have further confirmed that the appearance of small solitary undulations merge to form larger waves, which carry more matter transferring more energy and momentum (Zhang et al., 2000a; Zhang et al., 2000b). Some statistical methods have been used to describe the undulation behavior and several methods have been proposed to obtain a dynamic description of the undulations in the film [1-3].

In this paper, a non-invasive method to measure and evaluate the film thickness in a FFR system is described. Through this method a qualitative and quantitative description of the undulation phenomena in the liquid phase is obtained. Methyl esters (ME) sulphonation reaction was used as model reaction test due to its industrial importance in the synthesis of the active ingredient for detergent formulations. The results were analyzed by means of statistical description methods where the average film thickness is taken as the value of the mean of the data obtained.

2.EXPERIMENT

2.1 Materials and equipments

Film thickness distribution tests were performed in a falling film glass reactor of 1.27 cm inner diameter and 75 cm of length. A scheme of the sulphonation set up is presented in figure 1. The flow of air and methyl esters were selected based on the formation of a homogeneous film wetting the inner wall of the FFR (Diaz et al., 2013; Stein and Baumann, 1975). To measure film thickness, infrared (IR) optical sensors were used. The optical sensors consisted of infrared light-emitting diode (LED) and a photo sensor. The emitting LED and the photo transistor were coupled in a resistor network and a power supply connected in series circuit, ensuring that the LED maintains a constant light emitting and the photo transistor is operating in its linear region. The film reactor is fitted with three sets of optical sensors located at a distance of 10, 35 and 60 cm from the inlet of the ME into the reactor. In order to facilitate the description and analysis of the experiments and results, the photo sensor will be denominate as S1, S2 and S3 for the distances 10, 35 and 60 cm, respectively. The signals form the transistor receiver was digitized allowing data collection in real time, with 53 ms of average sampling. Signals from the digitizer were gather on a computer using MATLAB ^{TM}.

2.2 Experimental Procedure

Based on previous studies published elsewhere (Diaz et al., 2013), it was possible to establish the experimental ME and gas flow conditions where a proper thin film develops in the reactor wall. These conditions are summarized in Table 1. For the distribution of film thicknesses determination the reaction system was preheated to the adequate reaction temperature as reported by Torres (Torres, 2009) and Castaneda-Rivas (Castaneda and Rivas, 2004), 50 ^{o}C to 40 ^{o}C for the gas stream and the metal ester, respectively.

Table 1: Experimental conditions for ME sulphonation and hydrodynamic analysis [10].

Test	ME Flow (g/min)	Air Flow (L/min)
A	3.72	41.78
B	4.76	41.78
C	5.00	41.78
D	8.14	64.82
E	10.79	64.82
F	11.43	64.82

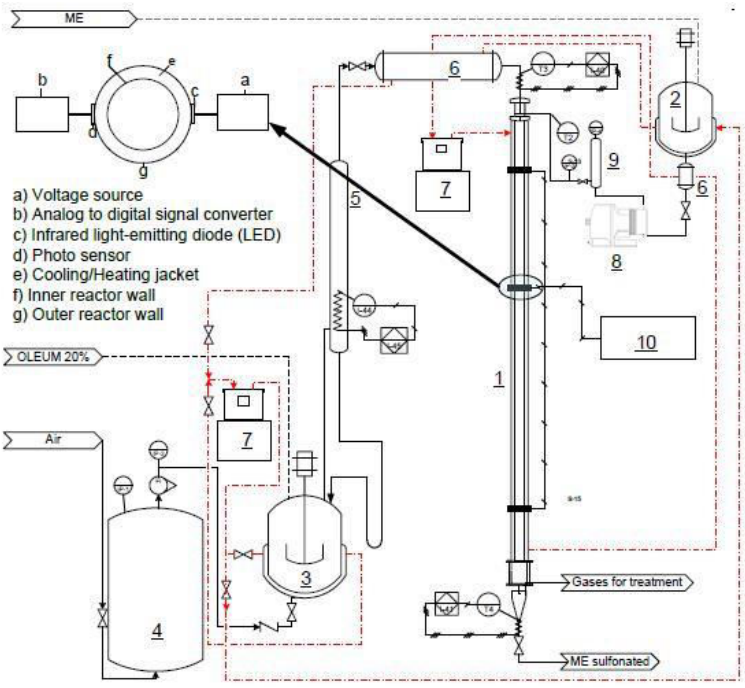

Figure 1: Sulphonation reaction system. 1) falling film reactor, 2) ME loading tank, 3) Oleum loading tank, 4) (H_2SO_4 concentrated) column, 5) demister, 6) heat exchangers, 7) thermostatic bath, 8) dosification pump, 9) Pulse impact reducer, 10) voltage source and analog to digital signal converter, process lines, (- -) heating and cooling lines.

The FFR was loaded with ME according to the values summarized in Table 1 and then to the gas flow was adjusted. To measure the film thickness, the voltage signal was collected, digitized, and transmitted to a computer using a serial port. A total of 200 data points were simultaneously taken by each sensor for all the experimental conditions presented in Table 1. The total sampling time for each sensor was 10.63 seconds, which provides an average measurement time of 53 milliseconds. This data collection time was defined based on those reported by Xu *et al.* (Xu et al., 2008), who reported that the shorter step time of a undulation is in the order of 60 ms.

2.3 Photo sensor calibration

In order to determinate the relationship between the film thickness and the voltage response in the photo sensors, a series of calibration experiments were performed. the calibration experiments were performed in 6 test cells of different deepness in which the liquid films presented in Table 2 can be created, each cell was place in between the LED emitter and the photo sensor system as shown in Figure 2. The photo-sensors were polarized by a power supply-resistance system that allowed the control of the input voltage. Hence, the photo sensor transistor receiver generates a voltage signal proportional to the amount of light collected, obtaining as a final result a voltage signal for each thickness measured. The data collected was used to obtain an equation that correlates the dependent variable (film thickness) as a function of the independent variable (voltage).

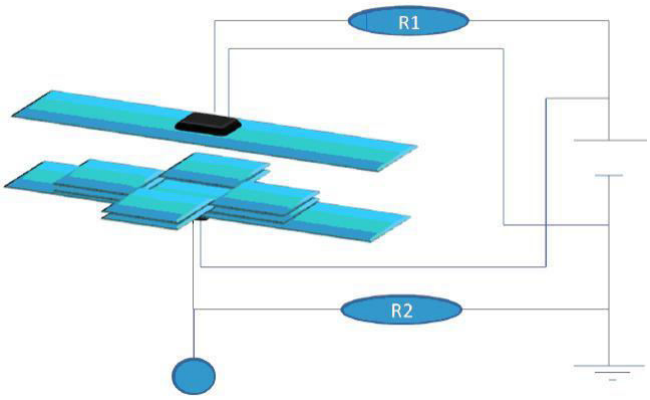

Figure 2: Photo sensor cell's calibration system representation.

Experimental conditions and results of the photo sensor calibration experiments are presented in Table 2

Table 2: Experimental conditions and results of the photo sensor calibration.

Induce potential	4.41 V		4.53 V		4.54 V		4.59 V	
Thickness (mm)	Empty	Full	Empty	Full	Empty	Full	Empty	Full
0	3.79	3.79	3.86	3.86	3.88	3.88	4.11	4.11
0.15	3.79	4.03	3.86	4.10	3.88	4.12	4.11	4.35
0.3	3.79	4.06	3.86	4.12	3.88	4.14	4.11	4.38
0.5	3.79	4.09	3.86	4.13	3.88	4.15	4.11	4.40
0.65	3.79	4.10	3.86	4.15	3.88	4.18	4.11	4.41
0.8	3.79	4.11	3.86	4.17	3.88	4.21	4.11	4.44
1	3.79	4.15	3.86	4.21	3.88	4.22	4.11	4.46

It can be observed, from Table 2, that as the induced voltage increases, the response value gets also higher. The experimental data presented in Table 2 were analyzed through the software STATGRAPHICS Centurion^{TM}, using the logistic regression model with maximum probability mapping, available for multivariable systems. Equation 1 shows the correlation obtained for the film thickness (δ) depending on the measured voltage (V) and the voltage of the empty cell (baseline, V_0) with a correlation coefficient R^2=0.94, where V_0 is the value of voltage obtained when there was not film created in the calibration cell.

$$\delta = \frac{e_{\eta}}{1 + e_{\eta}}$$

Where η is expressed by equation 2

$$[\eta = -172.573 + 42.2865 * V - 2.2884 * V_0]$$

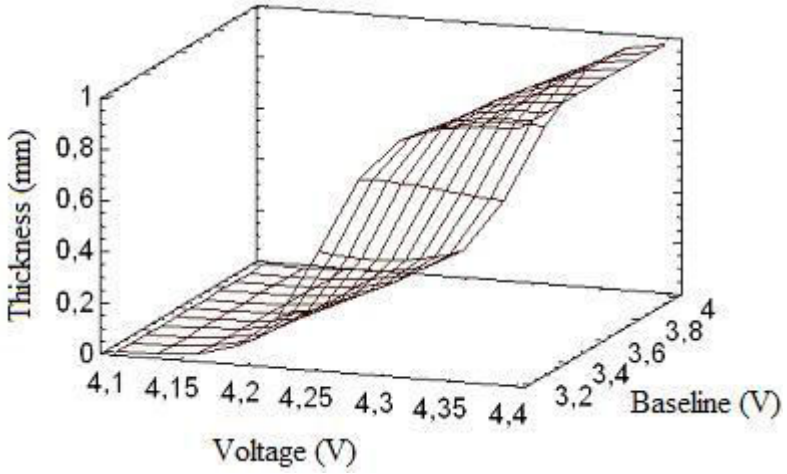

Figure 3: Surface response of δ as function of V and V_0.

A surface response generated using Equation 1 is presented in Figure 3. The experimental results showed that the voltage signal generated by the photo sensor increases with the film thickness, which may indicate that the presence of a small layer of liquid, between the glass plates, facilitates the passage of light through them and the photo sensors. On the other hand, it was observed for all the experimental measurements that the voltage signal never reached the value of the induced potential therefore providing an addecuate sensitivity and voltage range to perform the measurement of film thickness in the reactor.

3.RESULTS AND DISCUSSION

Before starting with the measurement of the liquid film thickness, , the voltage signal was a tested in the absence of liquid flow and only gas was fed into the reactor. These tests were done with the purpose of simulate the situation in which no liquid film has formed (zero thickness). The voltage signal measured for these tests did not present significant changes in the experimental values or in the statistical parameters neither in presence nor in gas flow absence. The result obtained from the experiments, with film thickness equal zero (no ME flow), are reported in Table 3. It is important to highlight that from these results was possible to establish that the voltage measurements are not affected by the gas flow in the reactor therefore providing a single base line for each sensor.

Table 3: Zero film thickness experiments data

	Sensor 1 (S1)	Sensor 2 (S2)	Sensor 3 (S3)
Position (cm)	10	35	60
Minimum voltage (V)	3.0231	4.1137	4.2901
Maximum voltage (V)	3.0642	4.1536	4.3583
Average voltage (V)	3.0437	4.1336	4.331
Standard deviation	0.01186	0.01152	0.01278
Variance coefficient	0.00239	0.00279	0.00295
SNR	256.4	35.4	338.9

Once the photo sensors were calibrated and the zero thickness film measurements were performed, the experimental measurements were followed by the determination of the film thickness on a FFR, operating under the conditions summarized in Table 1. Hence, it was assumed that the film, formed during the experiments, is homogeneous in the radial direction. Therefore along the perimeter of the reactor at any length, the film thickness will be the same.

Representative results of the film thickness, obtained from the voltage signals, measured in the photo sensors (S1, S2 and S3) as function of time are presented in Figure 4 and Figure 5 for experiments A and F, respectively. The film thickness measured for experiments A, B, C, D, E, and F are summarized in Table 4.

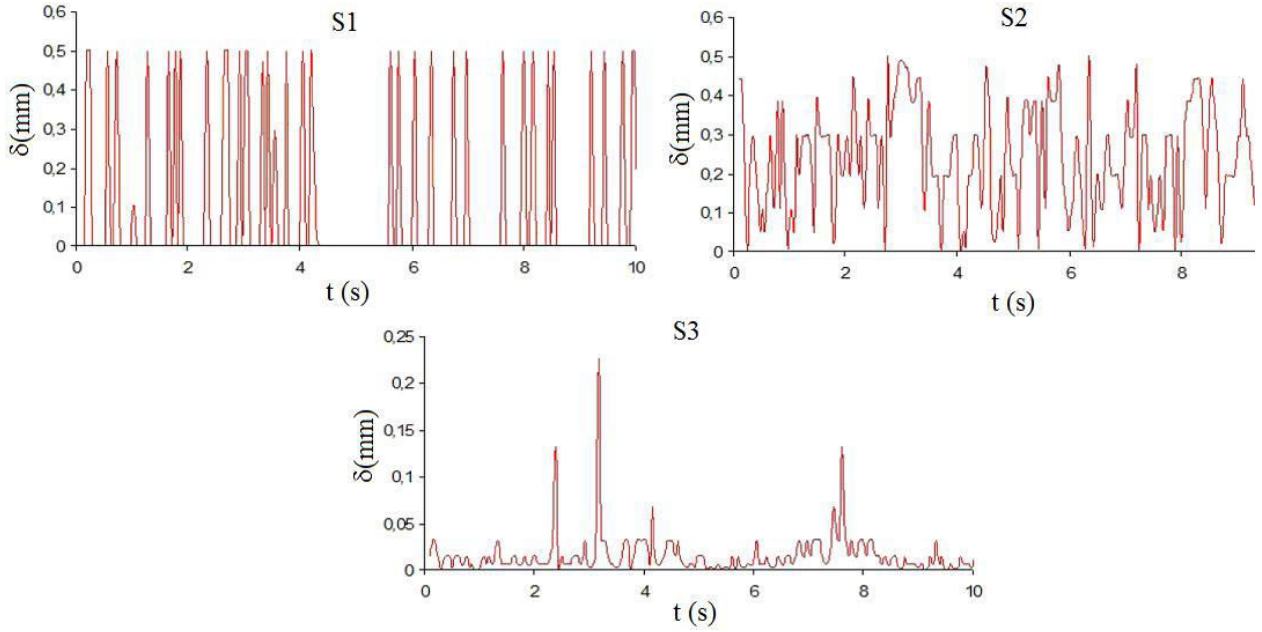

Figure 4: Film thickness measured at S1, S2 and S3 for test A.

The film thickness profiles on Figures 4 and 5 show the effect of the gas entering the reactor, which is reflected in wider oscillation in the voltage values measured by the photo sensor S1 located closer to the gas inlet. It can also be observed the evolution of the film thickness as well as the reduction of voltage oscillation through the reactor length. This behavior turns out to be characteristic of the system studied, where the inlet of gas to the reactor occurs through a sudden expansion close to the position of the sensor S1. Therefore, the measured voltage reported by S1 reflects the high hydrodynamic instability in the development of the gas flow. On the other hand, a more stable thickness is observed from the data obtained by the sensor S3, which lies away from the gas inlet section. It can be considered that at this point the hydrodynamic of both gas flow and liquid flow have been completely developed, implying that a more reliable measurement of the thickness value will be located at S3 position.

The results presented in Table 4 indicate higher variability of the film thickness with the position of the sensors from the reactor inlet than the gas flow rate. Average film thicknesses, lower than 0.5 mm, were measured for the different flows conditions, which featured Reynolds numbers lower than 300 in the liquid phase

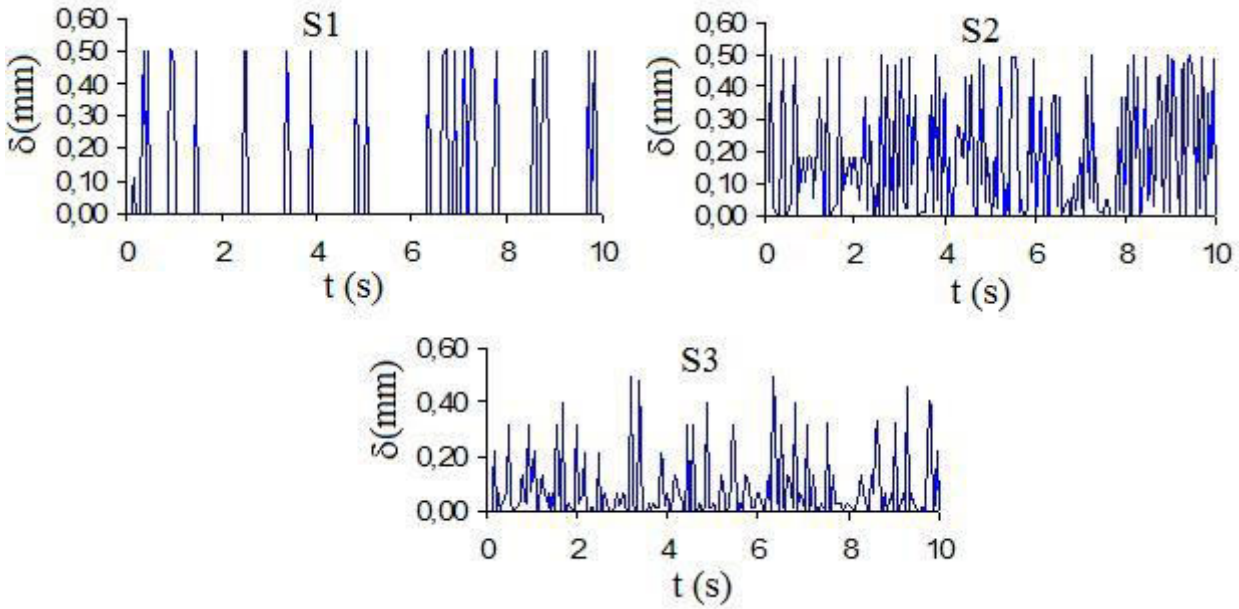

Figure 5: Film thickness measured at S1, S2 and S3 for test F.

The experimental film thickness values were compared against the predicted values obtained by means of a mathematical model proposed by Gutierrez *et al.* (Gutierrez et al., 1988) for alkyl benzenes sulphonation in a FFR. The mean error between the mean experimental film thickness and predicted value oscillates in the range from 9 to 54%, depending in the reaction condition used in the mathematical model.

Table 4: Summary of film thickness.

Test A (3.72 g/min ME; 41.78 L/min air)			
	Sensor 1 (S1)	Sensor 2 (S2)	Sensor 3 (S3)
Position (cm)	10	35	60
Average thickness (mm)	0.094	0.023	0.015
Maximum thickness (mm)	0.5	0.5	0.23
Minimum thickness (mm)	0	0	0
Test B (4.76 g/min ME; 41.78 L/min air)			
Position (cm)	10	35	60
Average thickness (mm)	0.066	0.048	0.045
Maximum thickness (mm)	0.5	0.083	0.12
Minimum thickness (mm)	0	0.01	0
Test C (5.00 g/min ME; 41.78 L/min air)			
Position (cm)	10	35	60
Average thickness (mm)	0.12	0.079	0.050
Maximum thickness (mm)	0.5	0.17	0.12
Minimum thickness (mm)	0	0.02	0
Test D (8.14 g/min ME; 64.82 L/min air)			
Position (cm)	10	35	60
Average thickness (mm)	0.05	0.069	0.024
Maximum thickness (mm)	0.5	0.5	0.3
Minimum thickness (mm)	0	0	0
Test E (10.79 g/min ME; 64.82 L/min air)			
Position (cm)	10	35	60
Average thickness (mm)	0.15	0.13	0.048
Maximum thickness (mm)	0.5	0.44	0.21
Minimum thickness (mm)	0	0.011	0
Test F (11.43 g/min ME; 64.82 L/min air)			
Position (cm)	10	35	60
Average thickness (mm)	0.063	0.17	0.077
Maximum thickness (mm)	0.5	0.5	0.5
Minimum thickness (mm)	0	0	0

CONCLUSIONS

Experimental determination of film thickness in falling film reactor was performed using a LED emitter photo sensor system. Calibration and reaction tests were performed and correlated to obtain a statistical correlation between the film thickness (δ), measured voltage (V) and the voltage of the empty cell (baseline, V_0). Voltage sensing and film thickness calculations were highly dependant on the position of the sensing device respect to the gas feeding point and slightly dependant of the gas flow, under the range of experimental values tested. This optical-electronic system allows a real-time quantitative description of the dynamic behavior of the undulations in the film.

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