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 SO$_3$. The results show that along with the SO$_3$/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)

1. INTRODUCCIÓN

Falling film devices 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 SO$_3$. The results show that along with the SO$_3$/ME ratio the hydrodynamic of both phases (gas and liquid) present in the reactor have a strong influence over the sulphonation efficiency.
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 alquil 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].

\[
\begin{align*}
Sh_G &= 0.046 \left( Re_G \right)^{0.83} \left( Sc_G \right)^{0.44} \\
Nu_G &= 0.046 \left( Re_G \right)^{0.8} \left( Pr_G \right)^{0.35}
\end{align*}
\]  

(1)  

(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 \( \text{SO}_3/\text{ME} \) 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>
<thead>
<tr>
<th>Table 1. Methyl ester characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Free fatty acids (% oleic)</td>
<td>0.0</td>
</tr>
<tr>
<td>Iodine value</td>
<td>0.61</td>
</tr>
<tr>
<td>Wet (%)</td>
<td>0.008</td>
</tr>
<tr>
<td>Fusion point (°C)</td>
<td>30</td>
</tr>
<tr>
<td>Acid value (mg KOH/g ME)</td>
<td>187.6</td>
</tr>
<tr>
<td>( C_P ) (75 – 78 °C) (J·g°C)</td>
<td>2.18</td>
</tr>
<tr>
<td>Average molar weight (g/mol)</td>
<td>281.97</td>
</tr>
</tbody>
</table>

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 \( \text{SO}_3 \), 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 \( \text{H}_2\text{SO}_4 \), and the flow was measured and controlled before being fed to the oleum tank with a Dwyer™ flow meter. The air flow was calibrated measuring the pressure at the flow meter outlet. The air stream with the dragged \( \text{SO}_3 \) were bubbled in a diluted \( \text{H}_2\text{SO}_4 \) solution (0.053 M), where the \( \text{SO}_3 \) was trapped as \( \text{H}_2\text{SO}_4 \) and measured with a mettler toledo titrator DL53®.

A complete description of the system and methods used to quantify the content of \( \text{SO}_3 \) 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 \( \text{SO}_3 \) 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 \( \text{SO}_3/\text{ME} \) molar ratios below the minimum required for a proper sulphonation (\( \text{SO}_3/\text{ME} \) molar ratio > 1) [19].

![Figure 1. Sulphonation bench scale set up. 1) falling film reactor, 2) ME loading tank, 3) Oleum loading tank, 4) (\( \text{H}_2\text{SO}_4 \) concentrated) column, 5) demister, 6) heat exchangers, 7) thermostated baths. Solid lines represent process lines, and dashed lines represent heating and cooling lines.](image)
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 Hymamine 1622 using disulfine blue as an indicator [13, 18].

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

<table>
<thead>
<tr>
<th>EC</th>
<th>Air flow L/min</th>
<th>SO$_3$ flow mol/min</th>
<th>ME flow mol/min</th>
<th>Molar ratio SO$_3$/ME</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>41.8</td>
<td>1.99E-02</td>
<td>1.32E-02</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>41.8</td>
<td>1.99E-02</td>
<td>1.69E-02</td>
<td>1.2</td>
</tr>
<tr>
<td>C</td>
<td>41.8</td>
<td>1.99E-02</td>
<td>1.77E-02</td>
<td>1.1</td>
</tr>
<tr>
<td>D</td>
<td>64.8</td>
<td>4.57E-02</td>
<td>2.89E-02</td>
<td>1.6</td>
</tr>
<tr>
<td>E</td>
<td>64.8</td>
<td>4.57E-02</td>
<td>3.83E-02</td>
<td>1.2</td>
</tr>
<tr>
<td>F</td>
<td>64.8</td>
<td>4.57E-02</td>
<td>4.05E-02</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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 SO$_3$. 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$^\text{TM}$ 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 SO$_3$. The experimental data was observed to be well described by the dispersion model presented in equation 3 with a correlation coefficient of at least $R^2 \geq 0.8$.

$$F(t) = 2 \left[ 1 - \text{erf} \left( \frac{1}{2} \sqrt{\frac{Pe}{1+\rho}} \right) \right]$$

(3)

Table 3 shows the calculated values for the mean residence time $\tau$ 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 $\delta$, was also calculated and reported in table 3 along with $Re_G$ for each experiment.

$$Re_L = \frac{4 \rho_L \Gamma}{\mu_L}$$

(4)
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 SO₃/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 SO₃/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.](image)

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>
<thead>
<tr>
<th>Test</th>
<th>Molar ratio SO₃/ME</th>
<th>Active Matter % ± SD</th>
<th>Mean residence time t s</th>
<th>Pe (LU₀/Dₓ) number</th>
<th>Average axial velocity (liquid) U₀ m/s</th>
<th>Pe</th>
<th>Average film thickness δ mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5 65 ± 2.5</td>
<td>363</td>
<td>3.72</td>
<td>2.07E-03</td>
<td>43.7</td>
<td>711810.66</td>
<td>6.25E-03</td>
</tr>
<tr>
<td>B</td>
<td>1.2 63 ± 1.2</td>
<td>393</td>
<td>4.76</td>
<td>1.91E-03</td>
<td>40.3</td>
<td>711756.23</td>
<td>6.01E-03</td>
</tr>
<tr>
<td>C</td>
<td>1.1 54 ± 3.3</td>
<td>377</td>
<td>5</td>
<td>1.99E-03</td>
<td>42.1</td>
<td>711784.45</td>
<td>6.13E-03</td>
</tr>
<tr>
<td>D</td>
<td>1.6 44 ± 0.1</td>
<td>120</td>
<td>8.14</td>
<td>6.25E-03</td>
<td>132.1</td>
<td>1593208.65</td>
<td>5.66E-03</td>
</tr>
<tr>
<td>E</td>
<td>1.2 25 ± 1.9</td>
<td>96</td>
<td>10.79</td>
<td>7.85E-03</td>
<td>166.0</td>
<td>1593551.55</td>
<td>6.34E-03</td>
</tr>
<tr>
<td>F</td>
<td>1.1 43 ± 1.9</td>
<td>156</td>
<td>6.18</td>
<td>3.71E-03</td>
<td>102.0</td>
<td>1592863.97</td>
<td>4.97E-03</td>
</tr>
</tbody>
</table>

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 SO₃/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

The authors express their gratitude to Universidad Nacional de Colombia for the financial support through the DIB project number 8830

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

\( \text{Re}_G \) = Gas Reynolds number.

\( \text{Re}_L \) = Liquid Reynolds number.

\( \text{Sc} \) = Schmidt number

\( \text{Sh} \) = Sherwood number

\( \text{Nu} \) = Nusselt number

\( U_G \) = Gas flow velocity. m/s

\( W_G \) = Gas mass flow. Kg/s

Greek symbols

\( \delta \) = Film thickness. mm

\( \mu \) = Viscosity. Kg/m.s

\( \rho \) = Density. Kg/m\(^3\)

\( \tau \) = Volumetric flow rate of the liquid per unit wetted perimeter. m\(^2\)/s

\( \tau \) = Shear stress at the gas-liquid interface

Subscripts

\( G \) = Gas phase

\( L \) = Liquid phase

REFERENCES


