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Falling film reactors modelling

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1. Introduction

Anionic surfactants are the key component in a detergent formulation. These molecules are composed of a lipophilic "tail" (typically C12-C14) and a hydrophilic "head" (i.e. SO_3^-). Organic molecules obtained from renewable sources, such as vegetable oils, are currently used as raw materials. The synthesis is normally performed in continuous falling-film reactors where SO3 is dissolved in a thin film of organic compound, following the mechanism reported in Eq. 1 [1].

$$\mathrm{ROH} + 2\mathrm{SO_3} \xrightarrow[\text{fast}]{} \mathrm{ROSO_2OSO_3H}$$
$$\mathrm{ROSO_2OSO_3H} + \mathrm{ROH} \longrightarrow 2\mathrm{ROSO_3H} \qquad (1)$$

The reaction is characterized by high exothermic tenor (ΔH=-150kJ/mol), thus a critical aspect deals with the heat exchange system. For this reason, the reaction is typically performed in multi-tubular systems, characterized by very efficient heat exchange. Modelling such a reactor is a hard topic to be faced, because a rigorous model should consider both the heat and mass-transfer phenomena in both gas and liquid phases. By considering that normally the liquid film flows under laminar regime, fact due to the high residence time necessary to achieve high conversion, the system increases in complexity, because it is necessary to implement the mass diffusion and heat transfer contributes also in the radial coordinate of the reactor. In the present work, a detailed mathematical model is proposed and dodecyl benzene sulfonation has been chosen as a case study [2].

The developed model can be considered an advancement respect to the recent efforts published in the literature [1-3]. The breakthrough idea is to develop a model where no rate-determining-step is considered, writing the opportune mass and heat balance equations on both the gas and liquid phases.

2. Methods

The model was implemented in gPROMS ModelBuilder v.4 software, by solving the axial and particle radial partial derivatives with respectively backwards and centered finite difference method with respectively 100 and 50 discretization points.

3. Results and discussion

The mass balance equations related to SO_3 in gas and liquid phase and the organic compound are respectively reported in Eqs. 2-3, while the heat balance equations related to the gas, liquid phase and reactor jacket in Eq.s 4-5.

$$\frac{u_G}{L}\frac{\partial c_{SO_3,G}}{\partial \zeta} = -k_G a_G \left(c_{SO_3,G} - m c_{SO_3,L}\Big|_{y=0}\right) \tag{2}$$

$$\frac{u_L}{L}\frac{\partial c_{i,L}}{\partial \zeta} = \frac{1}{\delta_L}\frac{\partial}{\partial y}\left(\frac{D_i + D_T}{\delta_L}\frac{\partial c_{i,L}}{\partial y}\right) - rxn,\ i = SO_3, A \tag{3}$$

$$\frac{u_G}{L}\frac{\partial \rho_G c_{p,G} T_G}{\partial \zeta} = 0,\ \frac{u_L}{L}\frac{\partial \rho_L c_{p,L} T_L}{\partial \zeta} = -\frac{1}{\delta_L}\frac{\partial}{\partial y}\left(\frac{-k_L}{\delta_L}\frac{\partial T_L}{\partial y}\right) + \Delta H_{rxn} rxn + \Delta H_{sol} J_L \tag{4}$$

$$\frac{u_J}{L}\frac{\partial \rho_J c_{p,J} T_J}{\partial \zeta} = -UA_J\left(T_L\Big|_{y=1} - T_J\right) \tag{5}$$

A parametric study was performed by fixing the experimental conditions adopted in the literature (L=2m, $F_{SO3,feed}$=2.2·10^{-3}mol/s, $SO_{3,feed}$=4%,SO_3/A=1.1mol/mol, T_{feed}=320K) [3] and the kinetic rate laws with related parameters [3]. As an example, the result of the substrate conversion is reported in Figure 1A, while the liquid temperature in Figure 1B.

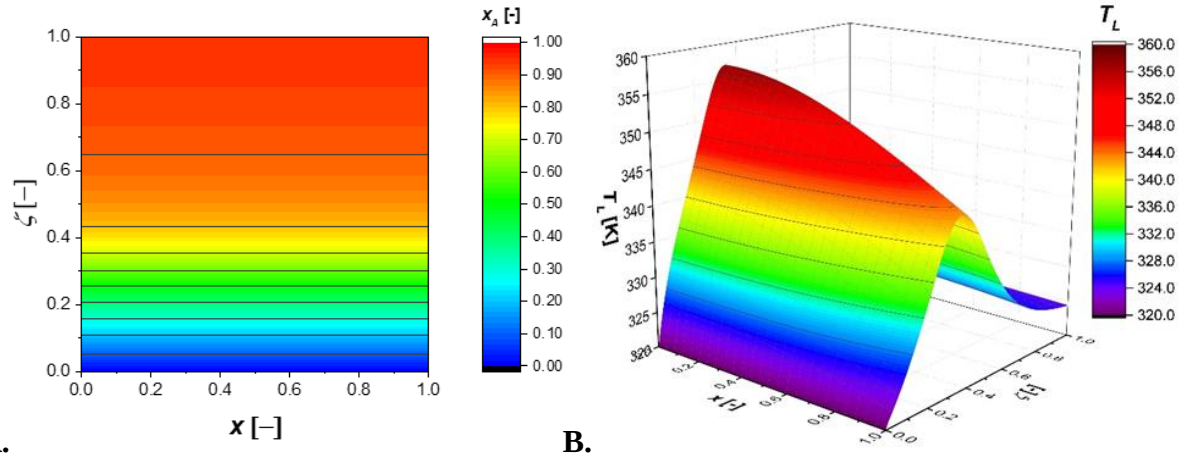

Figure 1. A. Conversion of the organic substrate as a function of the axial dimensionless coordinate (ζ) and parametric with the radial dimensionless coordinate (y). B. Dimensionless liquid temperature variation with the axial dimensionless coordinate (ζ) and the radial dimensionless coordinate (y).

The trends are reliable, and the conversion shows a profile in the liquid film radial coordinate. The film thickness decreases with the conversion degree, fact that strictly depends on the physical properties of the substance to be sulfonated.

4. Conclusions

A detailed gas-liquid falling-film reactor for sulfonation reaction was developed. Both heat and mass transfer equations have been implemented and the model predictions are reliable. The model can be used in designing large-scale reactors, because all the involved physical and chemical phenomena are implemented.

References

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