

Chromatographic reactor modelling

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1. Introduction

Reactive chromatography is a very actual topic for chemical reaction engineering. The concept implies the combination of reaction and chromatographic separation in the same unit [1], allowing the intensification of chemical processes. The chromatographic reactor concept offers several advantages: (i) enhancement of conversion surmounting equilibrium limitations, (ii) possibility of full separation of pure products, (iii) potential to influence the selectivity of complex reaction networks [2].

Modelling of chromatographic reactors is still an open issue, as the efforts published in open literature are simplified, thus characterized by a low predictive power [3, 4]. In this century, more advanced models has been published in literature, including heat transfer aspects, but simplifying the fluid dynamics to plug flow [5]. In the present work, a new Dynamic Adsorptive Chromatographic Reactor model (DACR) is presented. The model is based on the description of the underlying chemistry and physics in detail, focusing the attention on all the possible mass transfer steps appearing in the chromatographic column reactor. Axial dispersion was measured with dedicated experiments; external mass transfer resistance was evaluated from existing correlations; intraparticle diffusivity was considered to comprise the sum of two contributions: (i) pore diffusivity; (ii) surface diffusivity. The model was tested on literature data for the methyl acetate hydrolysis and it was used to predict the behaviour of the chromatographic reactor performance in a sensitivity study.

2. Methods

A chromatographic reactor equipment was designed and tested to determine the axial dispersion coefficients. The partial differential equation (PDE) system describing the chromatographic reactor was solved with the method of lines already implemented in gPROMS Model Builder v. 4.0. The reaction occurs in a liquid-solid system; hence it is necessary to write mass balance equations related to both phases. The model was written in a time-dependent form, to simulate the evolution of the concentration profiles along the reactor bed. The fluid dynamics was described by considering both axial dispersion and liquid film mass transfer:

$$\frac{\partial C_{i,B}}{\partial t} = -u_z \frac{\partial C_{i,B}}{\partial z} + D_z \frac{\partial^2 C_{i,B}}{\partial z^2} - \frac{k_m a_{sp}}{\epsilon'} (C_{i,B} - C_{i,L}|_{p=R_p}) \quad (1)$$

while the intraparticle mass balance equation was adopted as in Eq. 2.

$$\begin{aligned}
 [(1-b_i)\varepsilon_p + b_i] \frac{\partial C_{i,L}}{\partial t} &= (1-\varepsilon_p)\nu_i r + \varepsilon_p D_{i,P} \frac{1}{r_p^2} \frac{\partial}{\partial r_p} \left(r_p^s \frac{\partial C_{i,L}}{\partial r_p} \right) \\
 &+ (1-\varepsilon_p) D_{i,S} \frac{1}{r_p^2} \frac{\partial}{\partial r_p} \left(r_p^s b_i \frac{\partial C_{i,L}}{\partial r_p} \right) \\
 C_{i,S} &= b_i C_{i,L}
 \end{aligned}
 \tag{2}$$

3. Results and discussion

The experiments were conducted at different temperatures (from 298 to 328K), analysing continuously the output stream. The experimental data were interpreted by measuring the axial dispersion coefficients by residence time distribution (RTD) measurements, estimating the fluid-solid mass transfer coefficient with an existing correlation and fitting the surface diffusivity for each temperature. The results are reported in Figure 1A, showing in any case a good agreement.

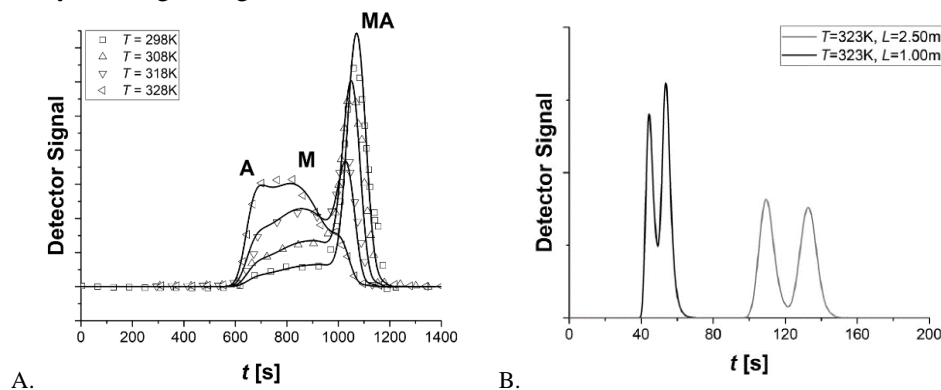


Figure 1. A. Methyl acetate hydrolysis experiments performed in a chromatographic reactor loaded with Dowex 50W-X8. A: acetic acid, M: methanol, MA: methyl acetate. B. Simulation of a full-conversion, complete separation system.

The Péclet number ranged between 800 and 2000 depending on the volumetric flow rate and resulted to be independent with temperature. Surface diffusivity values at different temperatures allowed to calculate surface adsorption activation energy of 83, 97 and 123kJ/mol for respectively acetic acid, methanol, methyl acetate, values in agreement with the chemical nature of the components and their interaction with the solid catalyst.

A sensitivity study was conducted to investigate the best operation conditions to achieve full reactant conversion and complete product separation. Using a reactor length of 1m and working at 303K with a flowrate of 0.75mL/min we scored the best result (Figure 1B).

4. Conclusions

A novel chromatographic reactor model was developed (DACR). The modelling approach consists of the simultaneous solution of both liquid bulk and intraparticle mass balance equations. No rate-determining steps were assumed, and the fluid dynamics of the reactor bed was described in terms of the axial dispersion model. Axial dispersion coefficients were determined with dedicated experiments collected from the chromatographic reactor equipment. The model showed a high flexibility in interpreting the experimental data and a good prediction power that will allow the design of a continuous equipment intensifying esterification and hydrolysis processes.

References

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