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Theoretical investigation of thermal effects in non-isothermal non-equilibrium reactive liquid chromatography

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ABSTRACT

A mathematical model is formulated and numerically approximated to simulate reaction and separation occurring jointly in a chromatographic column. To cover realistic problems, the reversibility of the reactions and the occurrence of temperature gradients are considered. The model is formed by a system of convection–diffusion–reaction partial differential equations coupled with differential and algebraic equations. The presence of nonlinear transport dominated terms in mass and energy balance equations and stiffness of the reaction terms are the main sources of instabilities if simple numerical schemes are applied. In this work a high resolution finite volume scheme is applied to accurately solve the model equations. The numerical case studies, treating two stoichiometrically different reactions, demonstrate the degree of coupling concentration and thermal fronts. The impact of several key parameters on process performance is illustrated. The results obtained are seen as very useful to understand the velocities and shapes of concentration and thermal fronts in chromatographic reactors. They reveal potential for improving reactor performance exploiting the unavoidable non-isothermal operation.

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1. Introduction

Fixed-bed absorbers or desorbers have high demand in various process industries where traditional separation operations like distillation, solvent extraction, crystallization and evaporation are not applicable due to physicochemical limitations. In chromatographic reactors, chemical or biochemical reactions and chromatographic separations take place simultaneously. The setup provides an integrated process in a single unit that enhances the conversion of reactants and product purity. In contrast to the sequentially connected conventional reactors and separators, chromatographic reactors effectively reduces the number of units and improves the conversion, yield and separation capacity. During the elution of reactants

pulses through a chromatographic reactor, heats are generated or consumed continuously due to enthalpies of adsorption, chemical reaction, and mixing. Additionally, thermal effects can also originate from viscous heat dissipation, particularly in HPLC columns packed with fine particles, see [Brandt et al. \(1997\)](#). Such phenomena should be taken into account in scale-up of the reactor concept because increasing the column diameter eventually renders the system nearly adiabatic.

The concept of a fixed-bed chromatographic reactor can be better explained by considering a single chromatographic column in which a reversible reaction of the type $A \rightleftharpoons B + C$ takes place. In this model process, rectangular pulses of reactant A are periodically injected into an inert carrier stream that elutes through the column packed with the stationary phase.

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During the elution, the reactant A reacts to form the products B and C due to the catalytic effects of the solid phase. Because of different affinities of the components B and C, they move at different velocities in the chromatographic reactor. Resultantly, both components are separated and their backward reaction is suppressed, leading to high conversion at the column outlet. The situation is highly favorable, when the reactant A elutes between the products B and C. A complete conversion of the reactant is possible when the residence time of the sample in the reactor is long enough. For further details about the principles and applications of chromatographic reactors see [Villiermaux \(1981\)](#), [Ganetsos and Barker \(1993\)](#), [Sardin et al. \(1993\)](#), [Borren and Fricke \(2005\)](#), and [Fricke et al. \(2005\)](#).

Temperature distributions are typically neglected in the analysis of liquid chromatography and chromatographic reactors by assuming that the effects caused by heats of adsorption and reaction are negligible. For that reason most of the available literature is limited to the isothermal conditions. Only a few contributions considering non-isothermal conditions are available in the literature, see e.g. [Sainio \(2005\)](#), [Sainio et al. \(2007, 2011\)](#), [Tien and Seidel-Morgenstern \(2011\)](#), [Graça et al. \(2012a,b\)](#), and [Javeed et al. \(2012\)](#). On the other hand, thermal effects have been widely discussed in the case of gas phase reactions in solid packings, see e.g. [Kruglov \(1994\)](#), [Yongsunthon and Alpay \(1999\)](#), [Xiu et al. \(2002\)](#), [Glöckler et al. \(2006\)](#), and [Eigenberger et al. \(2007\)](#).

Mathematical modeling is an essential part of the chromatographic theory for describing its dynamical process. It provides a procedure for predicting the dynamical behavior of solute in the column without extensive experiments. Due to different considerations of simplifications, several types of models have been established and applied to illustrate the behavior of chromatographic columns. These include the general rate model, the lumped kinetic model, the linear driving force model, the linear model, and the equilibrium dispersive model, see e.g. [Ruthven \(1984\)](#), [Carta \(1988\)](#), [Guiochon \(2002\)](#), [Guiochon and Lin \(2003\)](#), and [Guiochon et al. \(2006\)](#). All these models need an important input information regarding the thermodynamic equilibrium of the distribution of the components between the mobile and stationary phases. These models are categorized as non-equilibrium and equilibrium transport models. In the equilibrium models sorption is presumed to be instantaneous, while sorption in the non-equilibrium models is thought to be governed by first-order kinetics, see [Ruthven \(1984\)](#), [Guiochon \(2002\)](#), and [Guiochon et al. \(2006\)](#).

The purpose of this contribution is to quantify how temperature influences conversion and separation in non-isothermal and non-equilibrium liquid phase chromatographic reactors. When the heat of reaction and enthalpy of adsorption are sufficiently high, the system may deviate significantly from isothermal behavior. In such a scenario, it is necessary to include a partial differential equation (PDE) for the energy balance in the existing model equations of isothermal chromatographic reactor. A high resolution finite volume scheme is proposed to solve the model equations. Several case studies of three and four-component reactions are presented to illustrate the interactions of concentration and thermal fronts and to identify the key parameters that influence the reactor performance. The results demonstrate that the reactor performance considerably improves under non-isothermal operation as compared to isothermal operation, i.e. both conversion of reactants and the amount products are increased.

This article is arranged as follows. In Section 2, a non-equilibrium mathematical model for non-isothermal liquid chromatographic reactor is formulated. In Section 3, a high resolution flux-limiting finite volume scheme is derived and implemented for solving the model equations. Section 4 introduces a procedure for some tests to check the consistency of results. In Section 5, numerical case studies are carried out. Finally, Section 6 gives conclusions and remarks.

2. The mathematical model

This section presents a mathematical model for describing the non-equilibrium transport of reactants and products in a single-column adiabatic chromatographic reactor. Mathematically, the non-isothermal single-column chromatographic reactor is analogous to a more frequently studied non-isothermal unsteady-state fixed-bed reactor, see e.g. [Rhee et al. \(1989\)](#) and [Sainio et al. \(2007\)](#).

In this work, the nonlinear reactive lumped kinetic model (RLKM) is used to describe the non-equilibrium and non-isothermal transport of reactants and products in an adiabatic chromatographic reactor. The model incorporates the rate of variation of the local concentration of solute in the stationary phase and back-mixing in the column due to dispersion. It lumps hereby the contribution of internal and external mass transport resistances into a mass transfer coefficient denoted by k . It is assumed that a single reaction takes place exclusively in the solid phase. There are no radial concentration and temperature gradients in the column and sample migrates in the z -direction by advection and axial-dispersion. Thus, only axial-dispersions cause band broadening denoted by $D_{z,i}$ and λ_z in the mass and energy balances, respectively. Compressibility of the mobile phase is assumed to be negligible. No interactions take place between the solvent (carrier) and the solid phase. Moreover, there is no heat added or removed from the system except via the inlet and outlet streams, i.e. reactor is operated under adiabatic condition.

Based on the above assumptions, the mass equations of a one-dimensional RLKM for a fixed-bed chromatographic reactor can be expressed as (e.g. [Zhong and Meunier, 1994](#); [Guiochon et al., 2006](#))

$$\frac{\partial c_i}{\partial t} = -u \frac{\partial c_i}{\partial z} + D_{z,i} \frac{\partial^2 c_i}{\partial z^2} - F k_i (q_i^* - q_i), \quad i = 1, 2, \dots, N_c, \quad (1)$$

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i) + \nu_i r^{\text{het}}. \quad (2)$$

Here, c_i is the concentration of the i th component in the fluid phase, q_i is the solid phase equilibrium concentration of the i th component, u represents the constant interstitial velocity of the mobile phase, $D_{z,i}$ denotes the axial-dispersion coefficient of i th component, t is the time, and z is the axial-coordinate along the column. Moreover, $F = (1 - \epsilon)/\epsilon$ is the phase ratio based on the porosity $\epsilon \in (0, 1)$, r^{het} is the heterogeneous reaction rate, ν_i is the corresponding stoichiometric coefficient of i th component, and N_c represents the total number of components. Note that, the stoichiometric coefficient ν_i is negative for reactants and positive for products. For large values of the mass transfer coefficients k_i , i.e. for $k_i \rightarrow \infty$, the current non-equilibrium RLKM reduces to the reactive equilibrium dispersive model (REDM) studies by [Javeed et al. \(2012\)](#).

If the enthalpy of mixing is neglected, the non-equilibrium energy balances for a differential volume element in an

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