Chemical Engineering Science 171 (2017) 100–116

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Upscaling multicomponent transport in porous media with a linear reversible heterogeneous reaction

Ting Qiu *, Qinglian Wang, Chen Yang

College of Chemical Engineering, Fuzhou University, Fuzhou 350116, Fujian, China

HIGHLIGHTS

- The upscaling process of mass transfer and reaction in porous media was carried out.
- A typical first-order reversible heterogeneous reaction was considered.
- The method of volume averaging was used to derive the macroscopic model.
- The influence of reaction rates on the effective parameters was investigated.
- A simple and practical empirical approach was proposed.

ARTICLE INFO

Article history:
Received 17 January 2017
Received in revised form 7 May 2017
Accepted 10 May 2017
Available online 15 May 2017

Keywords:
Porous media
Reversible reaction
Volume averaging
Effective parameters
Reaction rate

ABSTRACT

The upscaling process of multicomponent mass transfer and reaction in a rigid and homogeneous porous media was carried out using the method of volume averaging. The first-order reversible reaction which occurs at the solid-fluid interface was considered in this paper. The corresponding macroscopic governing equations were derived from the system dynamics at the pore scale. The effective coefficients were obtained by solving the associated closure problems. This study shows that if the backward reaction rate constant at the microscale is small enough, i.e. $k_{-} \rightarrow 0$, the obtained upscaled model is in accordance with the macroscopic model derived from the first-order irreversible heterogeneous reaction case which was extensively investigated in the literature. The influence of reaction rates on the effective parameters in the macroscopic equations was also investigated. It has been found that both forward and backward reaction rates have significant influence on the effective diffusivities and effective reaction rates in the macroscopic equations. The established equations were successfully verified by the comparison of the direct numerical calculations.

1. Introduction

Multicomponent transport with reaction in porous media is a common phenomenon, which may occur in many scientific and engineering disciplines, including chemical reaction engineering, petroleum engineering, groundwater hydrology, etc. Many researchers have taken great interest in the experimental studies of mass transfer and reaction in porous media. However, the experimental results only focused on some specific reactive system or some specific porous media structure (Gibilaro and Waldram, 1981; Baiker et al., 1982; Suzuki and Smith, 1972). In recent years, due to the advances in computational capabilities, numerical simulation has been applied to help researchers to elucidate the complex multicomponent transport with reaction process in porous media. The need for a precise mathematical model of reactive transport in porous media which is the basis for numerical simulation has been recognized.

The modeling of reaction-diffusion phenomena in porous media is a multiscale problem, which can be described either by pore-scale or by Darcy-scale models. At pore scale, despite current advances in computational capabilities, it is still impractical to model this complex process by the direct numerical simulations, since the pore-scale simulations require the detailed knowledge of pore geometry that is seldom available, especially for the complex porous system. Nevertheless, macroscopic model regards the porous medium as an averaged continuum system and can be obtained via suitable upscaling method, thus overcoming the difficulties at the pore scale. The upscaling techniques include the method of moment (Brenner, 1980), the method of volume averaging (Whitaker, 1999) and its modifications, pore-network

* Corresponding author.
E-mail address: tingqiu@fzu.edu.cn (T. Qiu).

http://dx.doi.org/10.1016/j.ces.2017.05.018
0009-2509/

Nomenclature

a_V	interfacial area per unit volume, 1/m
$A_{\gamma\kappa}$	solid-fluid interface within the averaging domain
$\mathbf{A}_j$	closure variable that maps $\nabla\langle C_A\rangle^\gamma$
AA_j	closure variable that maps $\langle C_A\rangle^\gamma$
C_i	concentration of species in the γ phase, mol · m^{-3}
$\mathbf{C}_j$	closure variable that maps $\nabla\langle C_C\rangle^\gamma$
$\langle C_i\rangle^\gamma$	intrinsic averaged concentration in the γ phase, mol · m^{-3}
$\langle C_i\rangle$	superficial averaged concentration in the γ phase, mol · m^{-3}
$\tilde{C}_i$	concentration spatial deviation in the γ phase, mol · m^{-3}
CC_j	closure variable that maps $\langle C_C\rangle^\gamma$
C_{AS}, C_{CS}	concentrations of species A and species C at the interface, mol · m^{-3}
d	particle diameter, m
D_i	molecular diffusion of species i, m · s^{-1}
$\mathbf{D}_{i,eff}$	effective diffusivity, m · s^{-1}
Da	Damköhler number (dimensionless)
k_+, k_-	forward and backward reaction rate constant, m · s^{-1}
$k_{+,eff}$, $k_{-,eff}$	effective forward and backward reaction rate constant, m · s^{-1}
k_{CA}, k_{CC}	external mass transfer coefficients, m · s^{-1}
l	characteristic length of pore scale medium structure, m
l_S	side length of unit cells, m
L	characteristic length-scale of the macroscopic domain, m
$\mathbf{n}_{\gamma\kappa}$	unit normal vector pointing from the γ-phase toward κ-phase
r_0	characteristic size of the averaging domain, m
Sh	Sherwood number
t	time, s^{-1}
$\mathbf{u}_{i,j}$	effective velocity-like coefficients
V_γ	domain occupied by the γ-phase
V_κ	domain occupied by the κ-phase

Greek letters

ε_γ	volume fraction occupied by the γ-phase
ϕ	Thiele modulus
Ω	macroscopic domain

Subscripts

γ	liquid phase
i	chemical component
in	inlet
out	outlet
$\gamma\kappa$	interface between the solid and fluid phase

models (Prat, 2002) and the method of homogenization (Ene and Poliševski, 1987), and so on.

Upscaling mass transfer and reaction processes in porous media has attracted considerable attentions from researchers in the literature. Most upscaled models are expressed in terms of effective coefficients that can be used to relate microscopic (pore-scale) characteristics to the macroscopic (Darcy-scale) counterparts. To quote some examples: Dykaar and Kitanidis (1996), Sharratt and Mann (1987), Valdés-Parada and Álvarez-Ramírez (2010) and Valdés-Parada et al. (2011) focused on the first-order irreversible reaction, and obtained the corresponding macroscopic models for the diffusion-reaction process in a porous medium. They found that the effective coefficients inside the upscaled models depend upon the nature and magnitude of the microscopic reaction rate as well as the essential geometrical structure of the solid matrix and the flow rate. Moreover, Wood et al. (2007) and Heße et al. (2009) considered a heterogeneous reaction with Michaelis-Menton type and Monod type kinetics, respectively. The kinetics equations are similar and can be given by $r = \frac{kC}{K+C}$. The macroscale transport equations for reactive chemical species were obtained. Dadvar and Sahimi (2007) used pore network and continuum models of porous media to estimate the effective diffusivities under reactive and nonreactive conditions, where the reactive conditions involved a second-order reaction and one governed by the Michaelis-Menten kinetics. The studied reaction kinetics equations were $r = kC^2$ and $r = \frac{k_1 C}{1+k_2 C}$, respectively. Porta et al. (2012) investigated reactive transport processes involving fast bimolecular homogeneous irreversible reaction $A + B \rightarrow C$ occurring within a porous medium based on the method of volume averaging. Guo et al. (2015) used the method of volume averaging to achieve the upscaled model for the mass transport in porous media with a heterogeneous reaction at the fluid-solid interface, typical of dissolution problems. The studied reaction kinetic equation was $r = v_S M_{Ca} k_S (1 - \frac{w_1}{w_{eq}})^n$. Lugo-Méndez et al. (2015) revisited the upscaling process of diffusive mass transfer of a solute undergoing a homogeneous reaction in porous media using the method of volume averaging. They explored a linearization approach for the purpose of solving the associated closure problem for the nonlinear reactions. Zhang et al. (2015) investigated the adsorption-diffusion process in the nanoporous media by means of homogenization theory. Santos-Sánchez et al. (2016) derived a mass equilibrium model to describe the diffusion and reaction processes in a cell cluster composed of different cell populations.

In the above-referenced works, several kinds of reactions were investigated, involving homogeneous and heterogeneous reactions. The involved reaction kinetic equations included $r = kC$, $r = \frac{kC}{K+C}$, $r = kC^2$, $r = \frac{k_1 C}{1+k_2 C}$, and $r = v_S M_{Ca} k_S \left(1 - \frac{w_1}{w_{eq}}\right)^n$ et al. However, in the chemical reaction engineering, there are two kinds of chemical reactions, namely irreversible and reversible reactions. Reversible reaction as a common reaction type was seldom investigated, except the work by Morales-Zárate et al. (2008), Battiato et al. (2009), Boso and Battiato (2013) and Battiato and Tartakovsky (2011). Morales-Zárate et al. (2008) presented a macroscopic model for diffusion and chemical reaction in double emulsion systems using the method of volume averaging. In this three-phase system, an irreversible reaction ($A + R \rightarrow P$) takes place in the drops phase while a reversible reaction ($A \Longleftrightarrow B$) occurs in the membrane phase. Furthermore, passive diffusion is considered in the continuous external phase. Battiato et al. (2009) and Boso and Battiato (2013) established macroscopic reaction-diffusion equations for the multicomponent reactive transport in porous media involving both homogeneous (bio-) chemical reactions between species dissolved in the fluid phase, $A + B \Longleftrightarrow C$ and heterogeneous reactions occurring at liquid-solid interface, $C \Longleftrightarrow S_{(S)}$. Battiato and Tartakovsky (2011) used the method of multiple-scale expansions to upscale a pore-scale advection-diffusion equation with a nonlinear heterogeneous reaction at the fluid-solid interface, $C \Longleftrightarrow S_{(S)}$.

Although these above-referenced works focused on the reversible reactions, the studied reaction types were different with the catalytic reaction which plays an important role in chemical engineering process. Firstly, many studies related to the reversible