International Journal of Heat and Mass Transfer 73 (2014) 600–615

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

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

Reduced-order modeling of carbon dioxide absorption and desorption with potassium carbonate promoted by piperazine

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ARTICLE INFO

Article history:
Received 25 November 2013
Received in revised form 13 February 2014
Accepted 13 February 2014
Available online 15 March 2014

Keywords:
CO_2 absorption
Multiscale modeling
Karhunen–Loève Galerkin method

ABSTRACT

Carbon dioxide emitted from the power plants may be removed in an absorber-stripper unit, where CO_2 mass transfer enhanced by chemical reactions occurs. The mass transfer enhancement factor can be found accurately once we find the CO_2 profile in the liquid film around a packing material. However, it costs a tremendous amount of computer time to solve governing diffusion–reaction equations for the relevant chemical species at each grid point of the packed bed to determine the enhancement factor accurately. Therefore, in the traditional models of packed bed, one adopts an approximate enhancement factor found from a simple model. In the present work, we employ the Karhunen–Loève Galerkin (KLG) method for the solution of the diffusion–reaction equations describing the CO_2 absorption with potassium carbonate promoted by piperazine in the liquid film. With the KLG method, the computational time for the diffusion–reaction equations is reduced drastically and the rigorous model for the enhancement factor can be adopted in the industrial packed beds. The resulting reduced order model is found to predict the concentration profiles of chemical species accurately. It shall be adopted in the multiscale model for a packed bed, where the macro scale describes the overall geometry of the packed bed and the micro scale describes the transport and reaction in the thin liquid film around a packing at an arbitrary macro location in the bed.

1. Introduction

Absorption with simultaneous chemical reactions may be used to remove carbon dioxide from combustion gases of fossil fuel-fired power plants. The chemical reaction can significantly increase the solubility of CO_2 and reduce the required solvent flow rate for a given removal specification. Chemical reaction also increases the rate of absorption and liquid-phase mass transfer coefficient, resulting in the size reduction of the absorption or desorption column. Usually for the absorption of carbon dioxide, various amines such as monoethanolamine (MEA) and diethanolamine (DEA) have been adopted due to their fast reaction rates. The desirable absorbers should have lower heat of regeneration to save energy cost and fast reaction rate to reduce columm size. Although potassium carbonate has a lower heat of regeneration, its reaction rate is slower compared to amines. Several researchers [1] have investigated the effects of blending of various amines or amine and potassium carbonate, and found that they accelerated the absorption process. Cullinane and Rochelle [2] investigated the promoted potassium carbonate (K_2CO_3) using piperazine (PZ) as a promoter. Piperazine has a cyclic diamine structure and helps the rapid formation of the carbamates. The promoted potassium carbonate also retains its low energy of regeneration. Cullinane and Rochelle [2,3] investigated and presented the thermodynamic and kinetic data for the aqueous potassium carbonate systems promoted with piperazine, using a wetted wall column. Employing these data, they modelled the system of mass transfer with chemical reactions and found that absorption rates comparable to those seen in 7 m MEA were achieved in a 20 wt% K_2CO_3 solution promoted with 0.6 m piperazine. Their model also predicted that the apparent rate constant of piperazine in 20 wt% K_2CO_3 was approximately five times faster than in water.

Chemical reactions in the liquid film make steep the concentration profile of CO_2 near the gas–liquid interface, resulting in the enhanced mass transfer rate of CO_2. Using the thermodynamic and kinetic model of Cullinane and Rochelle [2,3], one can find the concentration gradients of all species across the liquid film and thus the enhancement factor for CO_2 absorption [4]. In this way, a packed bed models [5] may be able to make more accurate predictions with detailed chemical kinetics in the liquid film than when it adopts the empirically determined formula for the enhancement

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http://dx.doi.org/10.1016/j.ijheatmasstransfer.2014.02.044
0017-9310/

factor [4]. For this purpose of better predictions, one has to solve, at each grid point of the numerical model of absorption or desorption bed, a set of differential equations that describes the mass transfer with chemical reaction of carbon dioxide in aqueous potassium carbonate promoted by piperazine. Since the implementation of the kinetic model of Cullinane and Rochelle [2,3] in the industrial CO_2 absorption bed would require a tremendous amount of computer time and memory, it is imperative to devise an efficient computational technique to make this scheme feasible.

In the present work, we exploit the Karhunen–Loève Galerkin (KLG) method [6,7] for the solution of the diffusion–reaction equations that describes the CO_2 absorption with potassium carbonate promoted by piperazine in the liquid film. Employing the KLG method, the computational time for the diffusion–reaction equations is reduced drastically and the rigorous model for the enhancement factor can be adopted in the industrial absorption beds. The KLG method is a Galerkin method employing the empirical eigenfunctions of the Karhunen–Loève decomposition as basis functions [6]. With the empirical eigenfunctions, one can a priori limit the function space considered to the smallest linear subspace that is sufficient to describe the observed phenomena. This allows the reduction of governing differential equations to a minimal set, resulting in a drastic reduction of computational time without loss of accuracy. The KLG method has been applied to convection-diffusion problems [6], incompressible fluid flows [8], compressible fluid flows [9], various inverse problems involving conduction and natural convection [10], control [11,12], radiative transfer [13] and the Fokker–Planck equations [14]. Recently, the applicability of the KLG method has been expanded significantly with the introduction of auxiliary variables such that it can be adopted for systems with exponential nonlinearities and non-solenoidal flows [15].

In the present work, the KLG method is employed to convert the diffusion–reaction equations in the liquid film to a reduced-order model which predicts the enhancement factor of CO_2 transfer rigorously. The resulting reduced-order model shall be adopted in the multiscale model for a packed bed, where the macro scale describes the overall geometry of the packed bed and the micro scale describes the transport and reaction in the thin liquid film around packings at an arbitrary macro location in the bed [16].

2. Transport and reaction in a liquid film

There have been many mass transfer theories considered in chemical engineering; film theory [17], penetration theory [18], surface renewal theory [19] and eddy diffusivity theory [20]. Glasscock and Rochelle [21] showed that the steady-state eddy diffusivity theory is an excellent approximation to the unsteady-state surface renewal theory, concluding that it is unnecessary to solve unsteady equations for mass transfer with chemical reactions in a turbulent liquid film. Thus we adopt the steady-state eddy diffusivity model in the present work. In this model the general material balance equation for a chemical species ϕ in a turbulent liquid film may be represented as:

$$\nabla[(D_\phi + \epsilon_0 + \epsilon x^2)\nabla\phi] = -R_\phi \tag{1}$$

where R_ϕ is the overall rate of the reaction of species ϕ, D_ϕ is the laminar diffusivity of species ϕ and $\epsilon_0 + \epsilon x^2$ is the turbulent eddy diffusivity. As x, the distance from the gas–liquid interface, increases, the effect of eddies becomes more dominant. The constant ϵ_0 is introduced to take into consideration the turbulence at the interface. In the present work, we adopt the formula for ϵ suggested by Prasher and Fricke [22]. A description of all species and reactions considered for the absorption and desorption of carbon dioxide in the aqueous solution of potassium carbonate promoted by piperazine may be summarized as follows [2].

$$CO_2(aq) + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \tag{2}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \tag{3}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \tag{4}$$

$$PZH^+ + H_2O \rightleftharpoons PZ(\ell) + H_3O^+ \tag{5}$$

$$PZ(\ell) + CO_2(aq) + H_2O \rightleftharpoons PZCOO^- + H_3O^+ \tag{6}$$

$$H^+PZCOO^- + H_2O \rightleftharpoons PZCOO^- + H_3O^+ \tag{7}$$

$$PZCOO^- + CO_2(aq) + H_2O \rightleftharpoons PZ(COO^-)_2 + H_3O^+ \tag{8}$$

Table 2
Chemical reaction rate constants complied by Cullinane and Rochelle [3].

	$m^6 kmol^2 s$
$k^0_{PZ-H_2O}$	0.6×10^3
$k^0_{PZ-PZCOO^-}$	48.9×10^3
k^0_{PZ-PZ}	70.1×10^3
$k^0_{PZ-CO_3^{2-}}$	145.1×10^3
$k^0_{PZ-OH^-}$	1857×10^3
$k^0_{PZCOO^- -H_2O}$	0.4×10^3
$k^0_{PZCOO^- -PZCOO^-}$	66.3×10^3
$k^0_{PZCOO^- -PZ}$	95.1×10^3
$k^0_{PZCOO^- -CO_3^{2-}}$	96.7×10^3

Table 1
Equilibrium constants complied by Cullinane and Rochelle [2].

Equation number	Definition of equilibrium constant	Slow or fast	$\ln K_i = A_i + \frac{B_i}{T} + C_i \ln T$		
			Ai	Bi	Ci
(2)	$K_{HCO_3^-} = \frac{x_{HCO_3} - x_{H_3O^+}}{x_{CO_2} x^2_{H_2O}}$	Slow	231.4	−12092	−36.78
(3)	$K_{CO_3^{2-}} = \frac{x_{H_3O^+} x_{CO_3^{2-}}}{x_{HCO_3^-} x_{H_2O}}$	Fast	216.0	−12432	−35.48
(4)	$K_w = \frac{x_{H_3O^+} x_{OH^-}}{x^2_{H_2O}}$	Fast	132.9	−13446	−22.48
(5)	$K_{PZCOO^-} = \frac{x_{PZCOO^-} x_{H_3O^+}}{x_{PZ} x_{CO_2} x_{H_2O}}$	Slow	−29.31	5615	0.0
(6)	$K_{PZH^+} = \frac{x_{PZ} x_{H_3O^+}}{x_{PZH^+} x_{H_2O}}$	Fast	−11.91	−4351	0.0
(7)	$K_{PZ(COO^-)_2} = \frac{x_{PZ(COO^-)_2} x_{H_3O^+}}{x_{PZCOO^-} x_{CO_2} x_{H_2O}}$	Slow	−30.78	5615	0.0
(8)	$K_{H^+PZCOO^-} = \frac{x_{PZCOO^-} x_{H_3O^+}}{x_{H^+PZCOO^-} x_{H_2O}}$	Fast	−8.21	−5286	0.0