Computers and Chemical Engineering 94 (2016) 18–27

Contents lists available at ScienceDirect

Computers and Chemical Engineering

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

Development of an equilibrium theory solver applied to pressure swing adsorption cycles used in carbon capture processes

Gabriel Oreggioni, Daniel Friedrich, Mauro Luberti, Hyungwoong Ahn, Stefano Brandani*

Scottish Carbon Capture and Storage, School of Engineering, The University of Edinburgh, The King's Buildings, Edinburgh EH9 3FB, UK

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form 30 June 2016
Accepted 18 July 2016
Available online 21 July 2016

Keywords:
Adsorption dynamics
Equilibrium theory
Hyperbolic systems
Godunov method
Carbon capture
Pressure swing adsorption

ABSTRACT

An equilibrium theory simulator (Esim) for the simulation of cyclic adsorption processes is presented. The equations are solved with a Godunov upwind flux scheme that does not require either the evaluation of characteristics or shock equations or the imposition of a numerical entropy condition to track shocks. Esim is able to simulate non-trace and non-isothermal adsorption systems with any adsorption isotherm. Esim has been validated against gPROMS based simulations that use the full set of governing equations (including mass and heat transfer resistances and axial dispersion) carried out under conditions close to the limits where equilibrium theory is valid. Esim enables the establishment of bounds for the optimal performance of an equilibrium driven separation and requires only the measurement of adsorption isotherms.

1. Introduction

Pressure Swing Adsorption (PSA) cycles are widely used as gas separation unit operations; examples of industrial applications include hydrogen purification and air separation for the production of both nitrogen and oxygen (Ruthven, 1984; Ruthven et al., 1994). In the case of hydrogen purification and oxygen production the separation is based on equilibrium selectivity. The more strongly adsorbed components are held by the solid and a high purity product is obtained. Production of nitrogen is achieved via a kinetic selectivity because oxygen has a slightly smaller critical diameter and diffuses more rapidly in solids that have critically sized micropores (Ruthven et al., 1994). Clearly in this case the separation is operated far from equilibrium conditions, which would either favour nitrogen due to the larger quadrupole moment or would yield a small equilibrium selectivity if van der Waals forces prevail (Ruthven, 1984). CO_2 post-combustion capture from coal fired power plants using PSA can be achieved using adsorbents that show high equilibrium selectivity (see for example Kikkinides et al., 1993; Krishnamurthy et al., 2014; Webley, 2014), but in this case more complex process configurations are needed because carbon dioxide is the more strongly adsorbed component (see for example Ebner and Ritter, 2002; Luberti et al., 2013; Wang et al., 2013). For these systems, the materials are designed to reduce mass transfer resistances, which are primarily in the macropores (Hu et al., 2014).

The design and optimisation of PSA processes are complex because the system is intrinsically dynamic, depends on a large number of parameters and the simulations have to be carried out until the adsorption columns reach cyclic steady state (CSS) (Cheng et al., 1998; Friedrich et al., 2013 and Simo et al., 2008). For equilibrium driven separations any mass transfer resistance or other terms that lead to dispersion of the separation front will reduce the efficiency of the separation. For this reason, simulations which neglect any effects that lead to dispersion of the separation front can establish optimal bounds on the performance of equilibrium driven separations (Ruthven, 1984; Ruthven et al., 1994). To achieve this, these simulations assume instantaneous mass and heat transfer between the gas and solid phase and negligible axial dispersion. Thus equilibrium theory assumes that the adsorbed phase is in equilibrium with the gas phase: the adsorbed phase concentration is calculated directly from the adsorption isotherm and the gas phase concentration. This simplification reduces the number of differential equations since only the mass and the energy balances in the gas phase have to be solved without mass and heat transfer resistances and axial dispersion terms (Ruthven, 1984). Thus equilibrium theory simulations can establish the range of optimal conditions of the full process from a limited number of experimental equilibrium measurements or molecular simulations (see for example Banu et al., 2013).

---

* Corresponding author.
E-mail address: s.brandani@ed.ac.uk (S. Brandani).

http://dx.doi.org/10.1016/j.compchemeng.2016.07.020
0098-1354/

Nomenclature

Notation

α	Coefficient defined in Eqs. (10) and (11) (s^{-1})
b^0	Pre-exponential Arrhenius coefficient for Langmuir isotherm linear constant (bar^{-1})
C	Total fluid phase concentration (mol/m^3)
$\bar{c}$	Vector of fluid phase concentrations (mol/m^3)
c_i	Concentration of component i in the fluid phase (mol/m^3)
c_i^f	Feed concentration for component i (mol/m^3)
c_i^0	Initial concentration in the bed for component i (mol/m^3)
Cp	Molar heat capacity (gas phase) (J/mol K)
cp_s	Mass solid heat capacity at constant pressure (J/kg K)
D	Axial diffusion coefficient (m^2/s)
D_c	Column diameter (m)
ε	Bed porosity
f	Conservative flux
f_i	Conservative flux for component balance equation (mol/m^2s)
$F^n_{j-\frac{1}{2}}$	Numerical flux on the left boundary of the cell.
$F^n_{j+\frac{1}{2}}$	Numerical flux on the right boundary of the cell.
h_f	Volumetric enthalpy (J/m^3)
ΔH_i	Enthalpy of adsorption for component i (J/mol)
h_{molar}	Molar enthalpy (J/mol)
h_{refi}	Reference enthalpy for component i (J/mol)
k_{LDF}	Linear Driving Force constant (m/s)
k_{TE}	Thermal axial dispersion (W/m K)
L	Column length (m)
N_C	Number of components.
P_{feed}	Feed pressure (bar)
P_{vacuum}	Vacuum Pressure (bar)
q_i	Concentration of the adsorbed phase (mol/m^3)
qi^*	Concentration of the adsorbed phase calculated using isotherm function (mol/m^3)
$\tilde{q}_i$	Average concentration of adsorbed phase (mol/m^3)
q_s	Adsorbent saturation capacity (mol/m^3)
ρ_s	Solid density (kg/m^3)
s	Characteristic speed (m/s)
Δt	Time step size (s)
t_{ads}	Adsorption step time (s)
t_{blow}	Blowdown step time (s)
t_{press}	Pressurisation step time (s)
t_{purge}	Purge step time (s)
T	Temperature (K)
T^f	Feed temperature (K)
T^0	Initial temperature in the bed (K)
U_g	Volumetric internal energy (gas phase) (J/m^3)
U_s	Volumetric internal energy (adsorbent) (J/m^3)
v	Interstitial velocity (m/s)
v^f	Interstitial velocity at feed conditions (m/s)
W	Generic variable of interest.
$\tilde{W}$	Spatial average value for the variable of interest
Δx	Grid size (m)
y_i^f	Component feed mole fraction.

Traditional PSA cycle solvers (see for example Ruthven et al., 1994; Kumar et al., 1994; Nilchan and Pantelides, 1998; Sun et al., 1996; Da Silva et al., 1999; Reynolds et al., 2006; Haghpanah et al., 2013) can be used to mimic the limiting ET case by including very fast mass transfer kinetics and reducing axial dispersion. This method does not take full advantage of the ET simplification but requires the solution of the complete, larger set of equations for both gas and solid phases and furthermore being based on the solution of parabolic PDEs may become unstable, ie some dispersion in the shocks is necessary to stabilise the numerical solution.

Equilibrium theory has been employed by several authors to solve adsorption dynamics and the main results are well summarised by Ruthven (1984) and Ruthven et al. (1994). The importance of equilibrium theory in understanding adsorption dynamics starts from the pioneering work of Glueckauf (1949). Subsequent major contributions can be found in the papers published by Helffreich (1967), Rhee et al. (1970, 1971), Klein (1984) and Basmadjian and Coroyannakis (1987) and in the monograph by Rhee et al. (1989). In most of these articles, simplifying assumptions such as trace adsorption separation and linear or Langmuir equilibrium based systems were considered in order to allow the solution of the system of equations using the method of characteristics. The development of a characteristic based ET solver requires a check for the condition of shock formation, a detailed analysis is needed when using different adsorption isotherms (see for example Mazzotti, 2006). The use of equilibrium theory to PSA was developed mainly by Knaebel and Hill (1985), Kayser and Knaebel (1989) and Pigorini and Le Van (1997a,b) who published analytical solutions for isothermal trace PSA systems. Ebner and Ritter (2002) modified the analytical solution presented by Kayser and Knaebel (1989) to simulate PSA cycles aimed at the concentration/production of the strongest adsorbing species with linear equilibrium isotherms.

For the solution of the ET models under non-linear conditions, the typical approach is the use of the method of characteristics (Ruthven, 1984). The difficulties in the application of the method of characteristics for the hyperbolic problem lie in the need to derive specific expressions for the analysis of the condition of the formation of shocks. In the case of multi-component and non-isothermal adsorption systems efficient schemes are needed for the numerical solution of the system under study, which do not require this analysis and are applicable to any adsorption isotherm. Several authors such as Guinot (2003), Leveque (2002) and Toro (2009) have developed the use of finite volume based approximate Riemann schemes in the solution of hyperbolic equations arising from the modelling of different engineering problems particularly in the field of wave propagation in fluid dynamics. The Godunov scheme (Godunov, 1962) is the simplest of these approaches since it assumes that the variables of interest are constant along the finite volume (cell) and during each simulation time step thus it is a first order in space and time scheme; higher order schemes have also been developed (see for example Beam and Warming, 1976 and Lax and Wendroff, 1960). However, for higher order methods oscillations are observed when tracking shocks (Leveque, 2002).

In this contribution we focus on the development of a numerical Godunov type scheme for the solution of the pure hyperbolic equation arising from the mass and energy balance in PSA cycles using the equilibrium theory. The novel tool is capable of simulating multi-component, non-isothermal and non-trace adsorptive separation units. This approach has been previously used in the works published by Loureiro and Rodrigues (1991), Lim et al. (2001) and Leveque (2002) for dilute single component isothermal systems which show a single transition. In this particular case, the gas velocity remains constant and the application of the Godunov type scheme is straightforward. Bourdarias et al. (2006) employed a wave propagation form of the Godunov method to simulate non trace binary ET adsorption systems but the extension to multiple transitions (multicomponent non-isothermal systems) and arbitrary adsorption isotherms is missing. PSA processes include velocity gradients in the adsorption and desorption steps due to