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Influence of Gas-Solid Heat Transfer on Rapid PSA

SHIVAJI SIRCAR
Department of Chemical Engineering, Lehigh University, Bethlehem, Pa, 18015, USA
Shs3@Lehigh.edu; sircar@aol.com

Abstract. A simple analytical model of a Differential Pressure Swing Adsorption (DPSA) process on a single adsorbent particle was used to evaluate the effects of gas-solid heat transfer resistance on the cyclic working capacity of the particle. The commonly used assumption of instantaneous thermal equilibrium between the gas and the adsorbent inside an adsorber may not be valid when the gas flow rates are low, the adsorption kinetics is relatively fast, and the PSA cycle times are small.

Keywords: pressure swing adsorption, heat transfer, efficiency

Introduction

Realistic simulations of cyclic Pressure or Vacuum Swing Adsorption (PSA or VSA) processes for gas separation require simultaneous numerical solutions of coupled- partial differential equations describing the mass, the heat, and the momentum balances inside the adsorber (Hartzog et al., 1992; Gemmingen, 1993; Hartzog and Sircar, 1995). It is often assumed that the gas phase and the solid adsorbent are in thermal equilibrium with each other during the entire process in order to reduce the computation time. This paper theoretically examines the validity of the above-described assumption using a simple Differential Pressure Swing Adsorption (DPSA) cycle carried out on a single spherical adsorbent particle.

Practical Values of Gas-Solid Heat Transfer Coefficients

The gas-solid heat transfer coefficients in a packed bed adsorber depend on the gas flow rates through the adsorber. They can be different during different steps of a PSA/VSA cycle. They can also vary during the same step of a cycle. The column pressure drop often governs the acceptable gas flow rate through the adsorber.

Let us consider a simple VSA cycle for solvent vapor recovery. The feed gas (say N_2) containing a dilute amount of the solvent vapor is passed through an adsorber at a near atmospheric pressure to produce a clean product gas. The adsorbent is then back purged with a part of the clean gas under vacuum (=0.25 atm) for desorbing the adsorbed impurity. A new cycle is then started after pressurization with clean product gas. Table 1 shows acceptable values of gas (N_2) flow rates (G_o) based on empty cross section of the adsorption column and the corresponding pressure drops calculated by the well- known Ergun equation (Ergun, 1952).

The variables μ_g, k_g and C_g, are, respectively, the viscosity, the thermal conductivity and the heat capacity of the gas. The variable h is the gas-solid heat transfer coefficient. d_p(=0.2 cm) and ε (=0.4) are the adsorbent particle diameter and the column void fraction, respectively. The Nusselt number was calculated by using the Ranz equation (Ranz, 1952) or by the Kunii-Suzuki correlation (Kunii and Suzuki, 1967):

$$\text{Ranz: } \text{Nu} = 2.0 + 0.60[C_g\mu_g/k_g]^{0.33}[\text{Re}/\varepsilon]^{0.5}$$

$$\text{Kunii- Suzuki: } \text{Nu} = 0.032[\text{Pe}]^{1.5}$$

The second model yields a significantly lower value of h than the first in the low Peclet number region. However, its validity has been questioned by various authors (Gunn and De Souza, 1974; Dhingra et al., 1984). Nevertheless, Table 1 shows that a range 1 to 6 for the particle Nusselt number is very plausible

Table 1. Hydrodynamic and heat transfer properties.

Process steps	G_o lbmoles/ft^2 /hr	Pressure drop		Reynolds number (Re) (d_pG_o/μ_g)	Peclet number (Pe) $(d_pC_gG_o/k_g)$	Nusselt number (Nu) = (hd_p/k_g)	
		Psi/ft	Torr/ft			Ranz	Kunii & Suzuki
Adsorption at atmospheric pressure	10.0	0.102	5.2	42.5	30.7	7.5	5.4
Desorption by vacuum purge	1.0	0.024	1.3	4.25	3.1	3.7	0.2

for describing gas-solid heat transfer in packed bed adsorbers.

Differential PSA (DPSA) on a Single Adsorbent Particle

Consider a single spherical adsorbent particle (diameter d_p) which is in equilibrium with a gas phase consisting of an inert gas and a dilute adsorbate (partial pressure = P^o) at temperature T^o. The equilibrium specific adsorbate loading is n^o. The adsorbate partial pressure is instantaneously changed by a differential amount to $P^\infty(>P^o)$ at time $t = 0$ and held constant for a period of t_c causing a certain amount of the adsorbate to be adsorbed on the particle. The adsorbate partial pressure is then instantaneously reduced to P^o and held constant for a period of t_c causing a certain amount of the adsorbate to be desorbed from the particle. This process of cyclic ad(de)sorption is repeated until a steady state operation is achieved. The gas phase temperature stays constant at T^o during the entire process. The adsorbent temperature swings between T^s (the start of the adsoprtion step and the end of the desorption step) and T^f (the end of the adsorption step and the start of the desorption step). The corresponding cyclic steady state specific loadings of the adsorbate in the particle are given by, respectively, n^s and n^f.

Mathematical Model

The following mathematical model is formulated to describe the above- described DPSA cycle:

Equilibrium Relationship. The differential changes in the adsorbate partial pressure and the adsorbent temperature during the DPSA cycle permits linearization of the specific amount adsorbed at any time t $[n^*(t)]$, which is in equilibrium with the adsorbate partial pressure of $[P(t)]$ and adsorbent temperature of $[T(t)]$ at that time, with respect to changes in those variables. Thus,

$$[n^*(t) - n^o] = a[P(t) - P^o] + b[T(t) - T^o] \quad (1)$$

$$a = \{\partial n^*/\partial P\}_T,\ b = \{\partial n^*/\partial T\}_P = -aPq/RT^2 \quad (2)$$

where the variables a and b are equilibrium properties at P^o and T^o. The variable q is the isosteric heat of adsorption for the adsorbate at n^o and T^o, and R is the gas constant. The relationship between the variables a and b can be obtained using thermodynamics.

Under the operating conditions of the DPSA cycle, Eq. (1) simplifies to:

$$\text{Adsorption: } [n_a^*(t) - n^\infty] = b\theta_a(t); \quad P(t) = P^\infty \quad (3)$$

$$\text{Desorption: } [n_d^*(t) - n^o] = b\theta_d(t); \quad P(t) = P^o \quad (4)$$

where the variable $\theta[=\{T(t) - T^o\}]$ represents the differential change in the adsorbent temperature at time t. The subscripts a and d in Eqs. (3) and (4) represent the variables during the adsorption and the desorption steps of the DPSA cycle, respectively.

Mass Balance. It is assumed that the Linear Driving Force (LDF) model describes the kinetics of ad(de)sorption process. Thus,

$$[dn(t)/dt] = k[n^*(t) - n(t)] \quad (5)$$

where $n(t)$ is the specific amount of the adsorbate adsorbed at time t during the transient ad(de)sorption process of the cycle, and k is the over-all adsorbate mass transfer coefficient.

Heat Balance. It is assumed that the gas-solid film resistance controls the heat transfer to and from the adsorbent particle. Thus,

$$[d\theta/dt] = \alpha[dn/dt] - \beta\theta \tag{6}$$

$$\alpha = [q/c]; \quad \beta = [6.0/(d_p)^2][k_g/\rho c][hd_p/k_g] \tag{7}$$

where ρ and c are, respectively, the density and the specific heat capacity of the adsorbent particle.

Steady State Analytical Solution of the DPSA Model

Equations (1)–(7) can be solved simultaneously using the appropriate boundary conditions for the DPSA cycle to obtain the following analytical results:

$$\begin{aligned}(n^f - n^s)/(n^\infty - n^o) &= \varepsilon_{\text{non-isothermal}}\\ &= [(k + r_1)\{1 + \lambda_1\}\{1 - \lambda_2\} - (k + r_2)\{1 + \lambda_2\}\\ &\quad \times \{1 - \lambda_1\}]/[r_1 - -r_2][1 + \lambda_1 + \lambda_2 + \lambda_1\lambda_2]\end{aligned} \tag{8}$$

$$\begin{aligned}\theta^f = -\theta^s &= [(k + r_1)(k + r_2)(\lambda_1 - \lambda_2)]\\ &\quad \times \{n^o\Delta\}/[r_1 - r_2][1 + \lambda_1 + \lambda_2 + \lambda_1\lambda_2][bk]\end{aligned} \tag{9}$$

$$\begin{aligned}&\lambda_i = \exp\{r_i t_c\}; \quad r_i = -[k(1 - \alpha b) + \beta]\\ &\quad +/- \sqrt{\{[k(1 - \alpha b) + \beta]^2 - 4k\beta\}};\\ &\Delta = (n^\infty - n^o)/n^o\end{aligned} \tag{10}$$

where n^∞ is the specific equilibrium adsorbate loading at P^∞ and T^o.

The quantity $(n^f - n^s)$ is the steady-state, non-isothermal working capacity of the adsorbent particle for the adsorbate by the DPSA process. The quantity $(n^\infty - n^o) = [a(P^\infty - P^o)]$ represents the isothermal, equilibrium working capacity (maximum possible) for the adsorbate. Thus, $\varepsilon_{\text{non-isothermal}}$ is a relative measure of the efficiency of the DPSA process under non-isothermal, non-equilibrium operation. Equations (9) and (10) can be used to estimate the cyclic steady state adsorbent temperature changes.

Special Case Solutions

Equation (8) can be simplified for two extreme cases:

Isothermal Operation ($Nu \to \infty$, finite k).

$$\varepsilon_{\text{isothermal}} = [1 - \exp(-kt_c)]/[1 + \exp(-kt_c)] \tag{11}$$

Adiabatic Operation ($Nu \to 0$, finite k).

$$\begin{aligned}\varepsilon_{\text{adiabatic}} &= [1 - \exp\{-k(1 - \alpha b)t_c]/[(1 - \alpha b)]\\ &\quad \times [1 + \exp\{-k(1 - \alpha b)t_c\}]\end{aligned} \tag{12}$$

Relative Efficiency of the DPSA Process (€)

It is more appropriate to study the non-isothermal efficiency of the DPSA process relative to its isothermal efficiency. Thus,

$$\begin{aligned}\text{€}_{\text{non-isothermal}} &= \varepsilon_{\text{non-isothermal}}/\varepsilon_{\text{isothermal}} \quad \text{and}\\ \text{€}_{\text{adiabatic}} &= \varepsilon_{\text{adiabatic}}/\varepsilon_{\text{isothermal}}\end{aligned} \tag{13}$$

Examples of Relative Efficiencies of DPSA Process

Two different DPSA systems were evaluated for this work: (i) ad(de)sorption of 2.0% C_3H_8 from N_2 on BPL carbon, and (ii) ad(de)sorption of 2.0% C_2H_6 on 5A zeolite. Table 2 summarizes the physical and adsorptive properties of these two systems. The particle diameter was 0.2 cm.

These properties were obtained from the published literature (Valenzuela and Myers, 1989; Ruthven and Loughlin, 1971). The adsorption of C_3H_8 on the BPL carbon is relatively fast ($k = 0.4$ s^{-1}) (Sircar and Kumar, 1986), and that of C_2H_6 on the 5A zeolite is relatively slow ($k = 0.05$ s^{-1}) (Garg, 1972). These over-all mass transfer coefficients were experimentally measured for these systems.

Figure 1 shows the results of the model calculations for the C_3H_8 on BPL carbon system. The over-all

Table 2. Physical and adsorptive properties of the systems.

System	P^o (atm)	T^o (C)	n^o (mmole/g)	a (mmole/g/atm)	q (Kcal/mole)	ρ (g/cc)	c (cal/g/K)	k (s^{-1})
C_3H_8 on BPL Carbon	0.02	37.6	1.41	24.3	7.9	0.872	0.22	0.40
C_2H_6 on 5A Zeolite	0.02	26.9	0.329	12.6	8.8	1.20	0.22	0.05

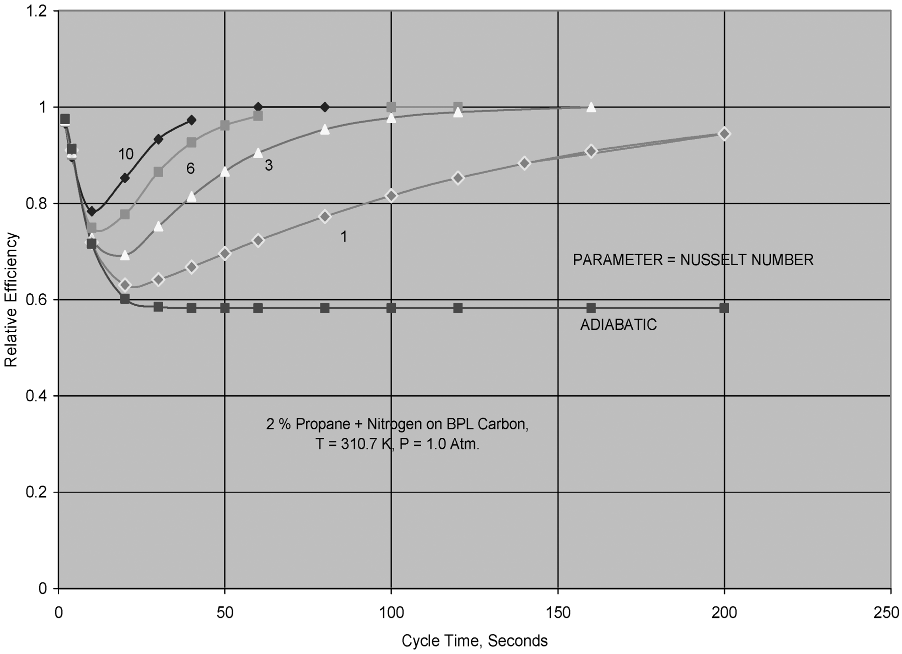

Figure 1. Model calculations for the C_3H_8 on BPL carbon system.

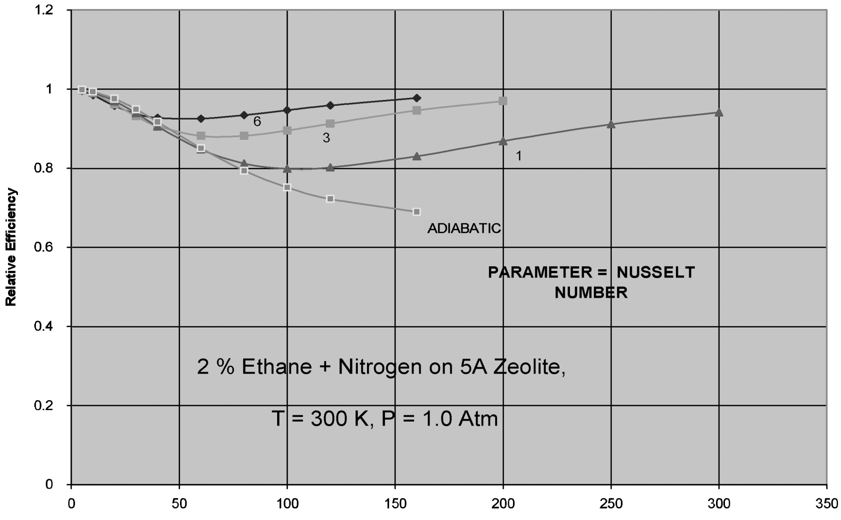

Figure 2. Model calculations for the C_2H_6 on 5A zeolite system.

efficiencies of the DPSA process ($\epsilon_{\text{non-isothermal}}$) are plotted against the total cycle times ($2t_c$) for different values of particle Nusselt numbers.

Figure 2 shows the results of the model calculations for C_2H_6 on 5A zeolite system. The behavior is qualitatively identical to that of Fig. 1 except that the decrease in the over-all efficiency is not as pronounced. The k value for this system is an order of magnitude lower than that of the previous case. Hence, the effect of the heat transfer resistance is less significant. Even then, it can not be ignored when the cycle times are small.

It may be seen that $\epsilon_{\text{non-isothermal}}$ approaches unity when the cycle time for the DPSA process approaches zero. The relative efficiency (<1) decreases as the cycle time increases. It goes through a minimum value (0.8 to 0.6) for finite values of Nusselt numbers (1–10), and then it increases again to approach unity at larger cycle times. The minimum relative efficiency decreases as the Nu number decreases and it occurs at lower cycle times as the Nu number increases. At very short cycle times (say < 10 s), the relative efficiency becomes insensitive to the values of the gas-solid heat transfer coefficients, and the DPSA process performance approaches that of the adiabatic operation. Thus, the effect of gas-solid heat transfer resistance can be significant on the performance of a PSA process when the Nusselt number is <6 (practically plausible values), particularly for short cycle times.

The maximum adsorbent temperature changes are very small for the above-described cases. For example, θ^f is equal to 0.094 C when $\mathrm{Nu} = 3$ and the relative efficiency is at its minimum (=0.69) (Fig. 1). The corresponding cycle time is 20 s. It can be shown that an artificial adsorbate mass transfer coefficient of $0.16\ \mathrm{s}^{-1}$ (actual value $= 0.40\ \mathrm{s}^{-1}$) will be required to match the $\varepsilon_{\text{non-isothermal}}$ and $\varepsilon_{\text{isothermal}}$ values at that minimum point.

This simple model analysis demonstrates that the assumption of instantaneous gas-solid thermal equilibrium inside an adsorbent column may not be valid for low gas flow rates, which may prevail in practical PSA columns during (i) an atmospheric adsorption step, (ii) an atmospheric or sub-atmospheric purge desorption step, and (iii) the tail ends of the depressurization, evacuation, and pressurization steps. Thermal equilibrium between gas and solid may not be attained irrespective of the value of the Nu when the PSA cycle times are relatively small (<20 s). Such is the case with most rapid PSA cycles (Sircar, 1996).

The influence of the gas-solid heat transfer coefficient on the PSA process will be more pronounced when the adsorbate mass transfer coefficient is large (say $> 0.2\ \mathrm{s}^{-1}$), and the Nu is small (<10). These conditions are often met by the practical adsorption systems.

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