MODELLING AND SIMULATION OF PESSURE SWING ADSORPTION

[1] B.B.PATEL, [2]Prof. C.G.BHAGCHANDANI
[1] M.E. (Computer aided process design), Department Of Chemical Engineering, L.D.College of Engg. Ahmedabad, Gujarat
[2]ASSOCIATE PROFESSOR, Department Of Chemical Engineering, L.D.College of Engg. Ahmedabad, Gujarat

bhumikach@yahoo.com, cgbhagchandani@rediffmail.com

ABSTRACT *PSA is an adsorption-based separation process in which separation is achieved when an adsorbent preferentially adsorbs one or more components from a feed mixture. A brief back ground on the principles of adsorption and different kinds of cyclic adsorption processes are discussed. The first task in the design of PSA is to select the adsorbent thus adsorbent properties (capacity, selectivity, regenerability) also discussed. As an alternative to the Pressure Swing Adsorption (PSA) based on the Skarstrom cycle or its variants, a novel two-bed PSA – called duplex PSA has been proposed by Hirose and independently by Leavitt to get both products of high purities and a modified duplex PSA has been presented to enhance the product purities for and productivities.*

Keywords: *adsorption, PSA, gas separation,*

I INTRODUCTION:

1.1 PSA overview

Pressure swing adsorption (PSA) has become a subject of interest in gas separations because of its low energy requirement and cost. The cryogenic separation of air involves liquefaction followed by distillation. Because of the complexity of the process, a very large production scale required for it to be economical.

Separation of gases accounts for a major fraction of the production cost in chemical, petrochemical, and related industries. There has been a growing demand for economical and energy efficient gas separation processes. The new generation of more selective adsorbents developed in recent years has enabled adsorption-based technologies to compete successfully with traditional gas separation techniques, such as cryogenic distillation and absorption. The last few decades have seen a considerable increase in the applications of adsorptive gas separation technologies, such as pressure swing adsorption (PSA). Pressure swing adsorption is a versatile technology for separation and purification of gas mixtures. While initial applications of PSA included gas drying and purification of dilute mixtures, current industrial applications include solvent vapor recovery, air fractionation, production of hydrogen from steam-methane reformer (SMR) and petroleum refinery off gases, separation of hydrocarbons such as carbon monoxide-hydrogen, carbon dioxide-methane, and n-parafins separation, and alcohol dehydration.

Advent of commercial PSA operations started with the early patents on this subject granted to Skarstrom and Guerin de Montgareuil and Domine. Since then, PSA has become the state-of-the-art separation technology for applications like air fractionation and hydrogen production. Many of these processes are described in published books and review articles on this subject. Moreover, Sircar has given an extensive list of publications on PSA which highlights growth in the research and development of PSA technology.

PSA processes involve selectively adsorbing certain components of a gas mixture on a microporous-mesoporous solid adsorbent at a relatively high pressure, via gas-solid contact in a packed column, in order to produce a gas stream enriched in less strongly adsorbed Components of the feed gas. The adsorbed components are then desorbed from the solid by lowering their gas-phase partial pressures inside the column to enable adsorbent re-usability. Desorbed gases, as a result, are enriched in the more strongly adsorbed components of the feed gas. No external heat is generally used for desorption. The selectivity in a PSA process comes from differences in either adsorption equilibrium or adsorption kinetics between the components to be separated. While a PSA process carries out adsorption at superambient pressure and desorption at near-ambient pressure level, a vacuum swing adsorption (VSA) process undergoes Adsorption at near-ambient pressure, while desorption is achieved under vacuum. Practical PSA/VSA processes are substantially sophisticated with multiple adsorber columns executing a wide variety of non-steady-state operating steps in a non-trivial sequence. Besides adsorption and desorption, such a sequence also involves a multitude of complementary operating steps essential to control product gas purity and recovery, and optimize overall separation efficiency. Each bed undergoes this sequence of steps repeatedly, and thus

the entire PSA system operates in a cyclic manner. Some of the advantages of PSA systems and key reasons for recent growth of this technology are as below:

- PSA and VSA processes operate at ambient temperatures and do not require any solvent for product recovery or adsorbent regeneration. As a result, their capital expenditure is quite less

compared to cryogenic technologies. Primary operating cost for these processes comes from the energy requirements for compression and vacuum generation. Hence, PSA processes are cost-effective compared to traditional technologies, and are especially desirable when lower production rates or lower product purities are required.

- Pressure manipulation serves as an extra degree of thermodynamic freedom, thus introducing significant flexibility in process design as compared with conventional technologies such as distillation, extraction or absorption.

- Numerous microporous-mesoporous adsorbents are available which are specifically tailored and engineered for a particular application, thus exhibiting high selectivity and adsorption capacity which leads to extremely high purity and recovery separation.

2. Pressure swing adsorption

Pressure swing adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. To understand the design and operation of PSA processes, knowledge of adsorption principles and dynamic behavior of an adsorption column is vital.

2.1 Adsorption Phenomena and Processes

The essential requirement of all adsorption separation processes is an adsorbent which preferentially adsorbs one component (or one family of related components) from a mixed feed. The selectivity of the adsorbent may depend on a difference in adsorption equilibrium or on a difference in sorption rates (kinetic selectivity). All adsorption separation processes involve two principal steps: adsorption, during which the preferentially adsorbed species are picked up from the feed; regeneration or desorption, during which the adsorbed species are removed from the adsorbent, thus "regenerating" the adsorbent for use in the next cycle. The adsorption can be affected by changing either the pressure or the temperature, i.e. the degree of adsorption increases with pressure and decreases with temperature.

Gas adsorbers are used for removing trace components from gas mixtures. The commonest example is the drying of gases in order to prevent corrosion, condensation or an unwanted side reaction. Any potential application of adsorption has to be considered along with alternatives such as distillation, absorption and liquid extraction. Each separation process exploits a difference between properties of the components to be separated. In distillation, it is volatility. In absorption, it is solubility. In extraction, it is a distribution coefficient.

2.2 Adsorbent properties
Capacity:

Capacity (or loading) is the most important characteristic of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid-phase concentration, the temperature, and other condition (especially the initial condition of the adsorbent). Typically, adsorption capacity data are gathered at affixed temperature and various adsorbate concentration (or partial pressures for a vapor or gas), and the data are plotted as an isotherm (loading versus concentration at constant temperature). Adsorption capacity is of paramount importance to the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels.

Selectivity:

The simplest is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration drops towards zero. The closest analogy is to relative volatility (e.g. in distillation) in that the smallest the value, the larger the required equipment. An ideal situation occurs when the major component is not adsorbed much (so it can be thought of as an inert "carrier"), which leads to a very large selectivity.

Regenerability:

All cyclic adsorption applications rely on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component (adsorptive or adsorbate) must be relatively weakly adsorbed. The heat of adsorption, which is mentioned later, provides a measure of the energy required for regeneration, and in that regard low values are desirable. Regeneration might be accomplished by a thermal swing, pressure swing, chemical (e.g. by displacement, elution, or supercritical extraction), or sometimes by combination of those. In some cases, regeneration takes place by contacting the adsorbent with a fluid in another phase than is used during loading. The regenerability of an adsorbent affects the fraction of the original capacity that is retained (sometimes called the working capacity), and the, time, energy, etc. required for regeneration.

2.3 PSA Operation

A pressure-swing adsorption (PSA) process cycle is one in which desorption takes place at a pressure much lower than adsorption. Reduction of pressure is used to shift the adsorption equilibrium and affect regeneration of the adsorbent.

Pressure-swing cycles are classified as:

(1) PSA, which, although used broadly, usually swings between a high super atmospheric and a low super atmospheric pressure;

(2) VSA (vacuum-swing adsorption), which swings from a super atmospheric pressure to a sub atmospheric pressure; and

(3) PSPP (pressure-swing parametric pumping) and RPSA (rapid pressure-swing adsorption), which operate at very fast

cycle times such that significant pressure gradients develop in the adsorbent bed (see the subsection on parametric pumping).

Otherwise, the broad principles remain the same. Low pressure is not as effective in totally reversing adsorption as is temperature elevation unless very high feed to purge pressure ratios are applied (e.g., deep vacuum). Therefore, most PSA cycles are characterized by high residual loadings and thus low operating loadings. These low capacities at high concentrations require that cycle times be short for reasonably sized beds (seconds to minutes). These short cycle times are attainable because particles of adsorbent respond quickly to changes in pressure.

3 Description of original and modified duplex PSA

Fig. 1 shows the half cycle of original duplex PSA. In Step-1, feed is introduced into Bed-1, which is at high pressure (P_H), at an intermediate point along its length. The raffinate drawn from the bottom of Bed-1 is collected into surge tank-2. A part is drawn as raffinate product and the rest is recycled to Bed-2 which is at low pressure (P_L). The extract drawn from the outlet of Bed-2 is collected into surge tank-1. A part of it is drawn as extract product and the rest is recycled to the top of Bed-1. In Step-2, pressure in Bed-1 is set to P_L and in Bed-2 to P_H by transfer of the gas as shown Fig. 1. Step-1 and Step-2 need not be of the same duration. Step-3 and Step-4 of the cycle (not shown) are the mirror images of the Step-1 and Step-2, with the roles of the beds reversed

Fig. 2 shows six steps of the modified duplex PSA cycle. There is a minor difference between the original and modified duplex PSA. In the latter the extract product is drawn from Bed-1 in Step-3 while Bed-2 is idle and from Bed-2 in Step-6 while Bed-1 is idle.

4 Mathematical modeling

In mathematical modeling the following assumptions are made:

(a) The gas obeys the ideal-gas law,
(b) The process is isothermal,
(c) The gas mixing in the bed is represented by a
   Dispersed-plug flow model,
(d) The contents in each of the surge tanks are well
   Mixed,
(e) The interphase mass transfer is represented by the
   Linear driving force (LDF) model,
(f) The adsorption equilibria can be represented by
   the extended Langmuir isotherm model,
(g) The pressure drop across bed can be estimated by
   Blake–Kozney equation, and
(h) The Blake–Kozney equation is applicable to
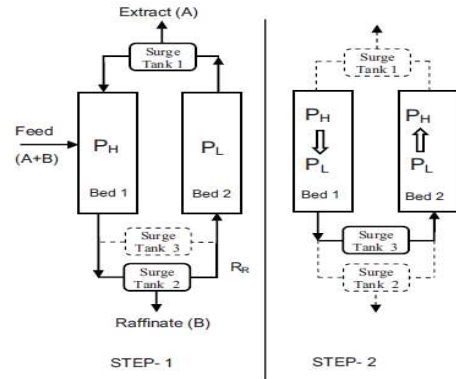   unsteady flow in blow down and pressurization.

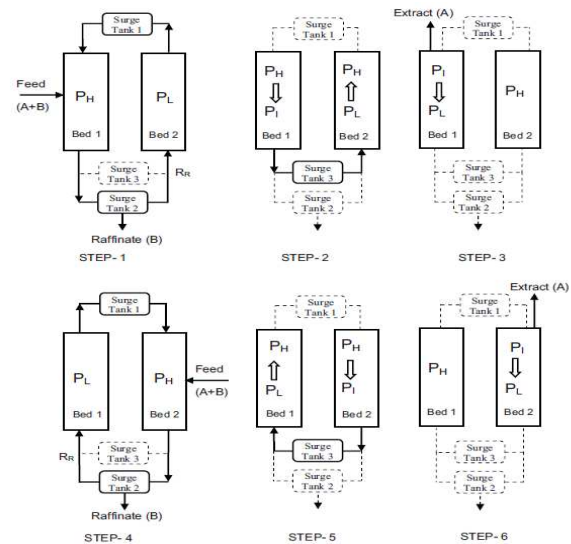Fig. 1. Schematic of half-cycle of original duplex PSA.

Fig. 2. Schematic of modified duplex PSA.

Fig. 3 depicts different fluxes crossing the boundaries of a differential element of adsorbent bed. Refer to notation for the definitions of symbols. The mass balance of species 'i' over the differential element (Δz) in the gas phase can be
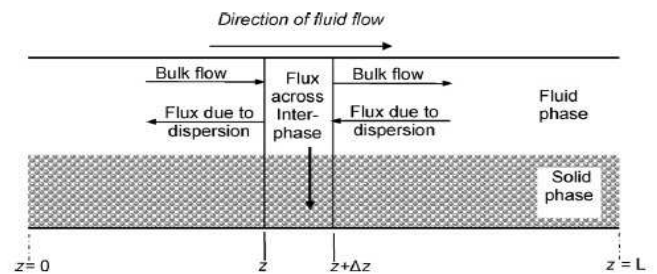

Fig. 3. Schematic diagram of the bed.

given as

$$\varepsilon_B A \left\{ -D_L \frac{\partial c_i}{\partial z} \Big|_z \right\} + \varepsilon_B A (vc_i|_z) = \varepsilon_B A \left\{ -D_L \frac{\partial c_i}{\partial z} \Big|_{z+\Delta z} \right\} +$$

$$\varepsilon_B A (vc_i|_{z+\Delta z}) + \varepsilon_B A \, \Delta z \frac{\partial c_i}{\partial t} + A \, \Delta z (1-\varepsilon_B) \frac{\partial q_i}{\partial t} \qquad (1)$$

Eq. (1) can be rendered into the form

$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \left(\frac{\partial v c_i}{\partial z}\right) + \frac{\partial c_i}{\partial t} + \frac{(1-\varepsilon_B)}{\varepsilon_B}\frac{\partial q_i}{\partial t} \tag{2}$$

here c_i, molar concentration, can be expressed for an ideal gas mixture as

$$c_i = \frac{P x_i}{RT} \tag{3}$$

The pressure effect on axial dispersion can be expressed as (Huang & Chou, 1997)

$$D_L = \frac{D_{r,m}}{P} \tag{4}$$

The interstitial fluid velocity given by the Blake–Kozney equation is

$$v = -\frac{d_p^2 \varepsilon_B^2}{150\mu((1-\varepsilon_B)^2}\frac{\partial P}{\partial z} \tag{5}$$

which can be written as

$$v = -K \frac{\partial P}{\partial z} \tag{6}$$

where $K = (-d_p^2 \varepsilon_B^3)(150\mu(1-\varepsilon_B)^2)$

On substituting Eqs. (3), (4) and (6) into Eq. (2) we get

$$\frac{\partial x_i}{\partial t} = \frac{D_{i,0}}{P}\frac{\partial^2 x_i}{\partial z^2} + K\left(x_i\frac{\partial^2 P}{\partial z^2} + \frac{x_i}{p}\left(\frac{\partial P}{\partial z}\right)^2 + \frac{\partial P}{\partial z}\frac{\partial x_i}{\partial z}\right) - \frac{x_i}{p}\frac{\partial P}{\partial t}$$
$$- \frac{(1-\varepsilon_B)}{\varepsilon_B}\frac{RT}{p}\frac{\partial q_i}{\partial t} \tag{7}$$

On summing up Eq. (7) for both components, we get the equation for total pressure for binary mixture as

$$\frac{\partial P}{\partial t} = KP\frac{\partial^2 p}{\partial z^2} + K\left(\frac{\partial P}{\partial z}\right)^2 - \frac{(1-\varepsilon_B)}{\varepsilon_B}RT\sum_{i=1}^{2}\frac{\partial q_i}{\partial t}\frac{\partial q_i}{\partial t} \tag{8}$$

On substituting Eq. (8) in Eq. (7) reduces to

$$\frac{\partial x_i}{\partial t} = \frac{D_{i,0}}{P}\frac{\partial^2 x_i}{\partial z^2} + K\left(\frac{\partial p}{\partial z}\right)\left(\frac{\partial x_i}{\partial z}\right)$$
$$+ \frac{(1-\varepsilon_B)}{\varepsilon_B}\frac{RT}{p}\left(x_i\frac{\partial q_i}{\partial t} - \frac{\partial q_i}{\partial t}\right) \tag{9}$$

and the mass-transfer rate for the ith species between the gas and solid phase is

$$\frac{\partial q_i}{\partial t} = k_i(q_i^s - q_i) \tag{10}$$

Eqs. (8)–(10) can be solved with appropriate initial and boundary conditions to obtain $x_i(z,t)$, $v(z,t)$, $P(z,t)$ and $q(z,t)$.

The initial and boundary conditions for the each step of the above mentioned two cycles are given below: The end where gas stream enters into the bed is set as z = 0, and the end where gas stream leaves the bed as z = L.

- Blowdown step: At the start of the blow down step the bed is assumed to be saturated with feed at pressure P_H. Thus for the first cycle,

I.C. : $x(z,0) = x_f$; $q_i(z,0) = q_{if}^*$; $P(z,0) = P_H$ for all z (11)

And for rest of cycles,

I.C.: at $t = t_{b-}$: $x(z, t_{b-}) = x(z, t_{f+})$;

$Q(z, t_{b-}) = q(z, t_{b-}) = P(z, t_{f+})$ (12)

B.C.: at z = 0 $\left.\frac{\partial P}{\partial z}\right|_{z=0} = 0, \left.\frac{\partial P}{\partial z}\right|_{z=0} = 0$ (13)

B.C.: at z = L $\left.\frac{\partial x}{\partial z}\right|_{z=L} = 0, v = -K\left.\frac{\partial P}{\partial z}\right|_{z=L}$ (14)

- Purge: The profile at the end of blowdown step is set as the initial profile for the purge step and the pressure is assumed to be constant throughout the step.

I.C. : at $t = t_{pu-}$: $x(z, t_{pu-}) = x(z, t_{b+})$;

$q(z, t_{pu-}) = q(z, t_{b+})$; $P(z, t_{pu-}) = P(z, t_{b+})$ (15)

B.C.: at z = 0 $\left.\frac{\partial x}{\partial z}\right|_{z=0} = -\frac{v}{D_L}(x_R - x|_{z=0}), v = -K\left.\frac{\partial P}{\partial z}\right|_{z=0}$ (16)

B.C.: at z = L $\left.\frac{\partial P}{\partial t}\right|_{z=L} = 0, \left.\frac{\partial x}{\partial z}\right|_{z=L} = 0$ (17)

- Pressurization step: The profile at the end of purge step is set as the initial profile for pressurization step.

I.C. : at $t = t_{pr-}$: $x(z, t_{pr-}) = x(z, t_{pu+})$;

$q(z, t_{pr-}) = q(z, t_{pu+})$; $P(z, t_{pr-}) = P(z, t_{pu+})$ (18)

B.C.: at z = 0 $\left.\frac{\partial x}{\partial z}\right|_{z=0} = -\frac{v}{D_L}(x'_R - x|_{z=0})$,

$v = -K\left.\frac{\partial P}{\partial z}\right|_{z=0}$ (19)

B.C.: at z = L $\left.\frac{\partial x}{\partial z}\right|_{z=L} = 0, \left.\frac{\partial p}{\partial z}\right|_{z=L} = 0$ (20)

- Feed: The profile at the end of the pressurization step is set as initial profile for feed step. Fig. 4 depicts the boundary condition around feed inlet position in the bed.

I.C. : at $t = t_{f-}$: $x(z, t_{f-}) = x(z, t_{pr+})$;

$q(z, t_{f-}) = q(z, t_{pr+})$; $P(z, t_{f-}) = P(z, t_{pr+})$ (21)

B.C.: at $z = 0$ $\left.\frac{\partial x}{\partial z}\right|_{z=0} = -\frac{v}{D_L}(x_{RE} - x|_{z=0})$,

$$v = -K \left.\frac{\partial P}{\partial z}\right|_{z=0} \tag{22}$$

B.C.: at $z = L$ $\left.\frac{\partial P}{\partial t}\right|_{z=L} = 0$, $\left.\frac{\partial x}{\partial z}\right|_{z=L} = 0$ $\qquad$ (23)

z^-_F and z^+_F represents position just before and after the feed inlet point respectively.

B.C.: at $z = z^-_F$ $\left.\frac{\partial P}{\partial t}\right|_{z=z^-_F} = 0$, $\left.\frac{\partial x}{\partial z}\right|_{z=z^-_F} = 0$ $\qquad$ (24)

B.C.: at $z = z^+_F$ $\left.\frac{\partial x}{\partial z}\right|_{z=z^+_F} = -\frac{v}{D_L}(x^I_f - x|_{z=z^+_F})$,

$$v = -K \left.\frac{\partial P}{\partial z}\right|_{z=0} \tag{25}$$

The parameters used in the model are estimated as follows:

The equilibrium solid-phase concentration is obtained from the extended Langmuir equation

$$q^f_i = \frac{q_{s,i} b_i c_i}{1 + \sum_{i=1}^{N} b_i c_i} \tag{26}$$

The axial dispersion coefficient has been estimated from the correlation (Huang & Chou, 1997)

$$D_{LO} = 0.75 D_M + \frac{0.5 d_p v}{1 + 9.5 D_M (d_p v)} \tag{27}$$

The velocities in the blowdown and pressurization steps were adjusted using the valve equation (based on a simple pipe flow and equivalent length of a valve) as

$$\frac{\Delta p}{\rho_g} = \frac{4 f l_e v^2}{2 d_{pipe} g_c} \tag{28}$$

On operating, we get

$$v = -kC \Delta P^{0.5} \tag{29}$$

where, C is proportionality constant and k accounts for fractional opening of valve. The theoretical energy required for a change of pressure from P1 to P2 of a stream is calculated from

$$W = \frac{n \gamma RT}{\gamma - 1} \left[\left(\frac{P_2}{P_1}\right)^{((\gamma - 1)/\gamma)} - 1 \right] \tag{30}$$

Where n is the total number of moles. If the pressure is varying during the step, the work done is calculated by numerical integration over time.

5. FUTURE SCOPE:

A modified duplex PSA has been presented, to enhance the product purities and productivities. Simulation studies will be carried out to explore the attainable product purities and possible process intensification for CO_2 capture with the original and modified duplex PSA.

6. REFERENCES:

1. N.O. Lemcoff and A.I. LaCava. Effect of regeneration pressure level in kinetically controlled pressure swing adsorption* Gas Separation Et Purification 1992 Vol 6 No 1
2. R.T. Yang Gas Separation by Adsorption Processes Butterworths, Boston, 1987
3. Don W. Green, Robert H. Perry: Perry's Chemical Engineer's Handbook, McGraw-Hill, Seventh edition
4. Kent S. Knaebel. Adsorbent selection. Adsorption Research, Inc. Dublin, Ohio 4301
5. J. F. Richardson et al. Particle Technology and Separation Processes Coulson and Richardson's Chemical Engineering, 5th edition, Volume 2
6. numero.cheme.cmu.edu/uploads/anshul_thesis.pdf
7. en.wikipedia.org/wiki/pressure swing adsorption
8. R.S. Thakur et al. Process intensification in duplex pressure swing adsorption Computers and Chemical Engineering 35 (2011) 973–983