

Progress in Pressure Swing Adsorption Models During the Recent 30 Years*

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Abstract The pressure swing adsorption (PSA) models discussed here are divided into three categories: partial differential equation model, electrical analogue model and neural network model. The partial differential equation model, including equilibrium and kinetic models, has provided an elementary viewpoint for PSA processes. Using the simplest equilibrium models, some influential factors, such as pressurization with product, incomplete purge, beds with dead volume and heat effects, are discussed respectively. With several approximate assumptions *i.e.*, concentration profile in adsorbent, “frozen” column, symmetry and heat effects of bed wall, the more complex kinetic models can be simplified to a certain degree at the expense of a limited application. It has also been found that the electrical analogue model has great flexibility to handle more realistic PSA processes without any additional hypothesis.

Keywords gas separation, pressure swing adsorption, mathematical model

1 INTRODUCTION

Pressure swing adsorption (PSA) is an important separation technology for gas mixtures and has been commercialized successfully for air drying, separation of oxygen and nitrogen in air, hydrogen purification, solvent vapor recovery and various separations in which it is difficult to separate by other common techniques, such as distillation and extraction. Gas separation can be carried out by PSA through periodic pressure variation, in which adsorption and desorption take place in turn. PSA is attractive since the adsorbent can be desorbed easily and quickly only by pressure declining. Moreover, it can provide high purity products in a very short cycle period, which is due to the more rapid response of a gas-solid system to pressure changes than to temperature changes.

Despite its wide commercial application, it is difficult to depict the inherent nature of PSA numerically since it is a complicated dynamic process involving all transfer phenomena (mass, heat, and momentum transfer). Furthermore, the performance of a PSA system is controlled by various coupled process variables, as well as the basic equilibrium and kinetic relationship for a gas-solid adsorption system.

After its invention^[1], a great deal of theoretical and experimental researches have been focused on PSA modeling in order to gain a deep insight into the PSA essence and then to provide principled instructions for process design and optimization. During the last thirty years, a wide variety of mathematical models were proposed based on theories extending from

simple to complex. Coupled with various approximations, a complex PSA process can be simulated in a relatively simple way. It is obvious that the less constraints the model has, the wider applicability the model will have. In a word, the development of PSA models follows the trend of progressive increase in the complexity by eliminating the simplifying restrictions step by step, at the expense of more computation time in a complete operation period. However, because of its complicated essence, a reliable mathematical simulation, which provides a perfect representation of a general and real PSA process, is still required.

2 CLASSICAL PSA CYCLE

PSA plants differ by the distinct bed numbers varying from one to tens. The most typical PSA process is the two-bed, four-step Skarstrom cycle^[2], which is basic to design and optimization of more complicated PSA processes. A schematic diagram of the PSA cycle is shown in Fig.1 for two identical beds packed with adsorbent. A minute description of such operation steps is as follows^[3].

In the first step, high-pressure feed mixture is continuously supplied to Bed 1, and sorbable components are taken up by adsorbents. A portion of the purified effluent of Bed 1, still with high pressure, is taken off as product. The remainder is throttled down to a low pressure and is fed to Bed 2 to purge previously adsorbed species. In the second step, Bed 2 is pressurized by the feed and Bed 1 is depressurized or blowdown to the purge pressure for desorption. The

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feed gas passes in and the exhaust gas goes out, both through the feed end. The third and fourth steps are the same as the first two except that the points of gas introduction and removal are reversed with respect to Steps 1 and 2.

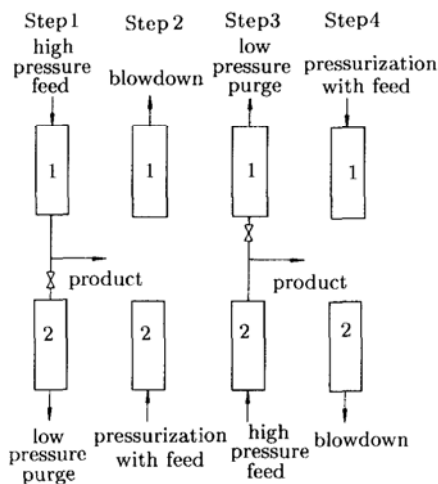


Figure 1 Steps of the Skarstrom cycle^[3]

3 OVERALL APPROXIMATIONS

Almost all PSA models have exploited a few basic approximations to reflect real PSA systems, ignoring certain insignificant factors for the overall performance of PSA processes. The following general approximations are introduced:

- (1) Gas behaviors ideally;
- (2) The flow pattern is described by the plug flow model;
- (3) Adsorbent particles are spherical;
- (4) Pressure gradient inside adsorbent is negligible;
- (5) The radial concentration and temperature in the adsorption bed are constant;
- (6) For nonisothermal models, except adsorption equilibrium, transport (heat and mass transfer diffusivity, viscosity, *etc.*) and thermodynamic (heat capacity, heat of adsorption, *etc.*) properties are independent of temperature.

Based on these approximations, to a certain extent, a convenient way can be employed for further detailed research. Some influence of the above approximations has been considered in a few mathematical models^[4-7]. In fact, for the majority of the PSA systems investigated, especially the cases in an experimental scale, the above-listed approximations are reasonable.

4 PARTIAL DIFFERENTIAL EQUATION MODEL

In the early two decades of the PSA development, attention was focused to disclose the innate charac-

ter of PSA system by means of a large number of scientific experiments. On the basis of the fundamental equilibrium and dynamic separation principles, the equilibrium-based theory and kinetic-based theory can be fully developed and used to guide further practice. The mass conservation equation of adsorbent beds^[8]

$$D_a \frac{\partial^2 c}{\partial Z^2} = \frac{\partial(uc)}{\partial Z} + \frac{\partial c}{\partial t} + \frac{1-\epsilon}{\epsilon} \frac{\partial q}{\partial t}$$

was derived from the packed bed continuity assumption. All the partial differential equation models are developed to solve the equation simultaneously with the relation of the interstitial velocity u and pressure or momentum conservation equation if momentum transfer is significant, and adsorption rate expression for $\partial q/\partial t$, and heat conservation equation if thermal effect is significant under the corresponding boundary conditions during pressure swing.

4.1 Equilibrium models

The simplest PSA mathematical models, so-called local equilibrium models, have been derived with the assumptions that no mass and heat transfer resistance exist between gas phase and solid adsorbent, or q be related to c with instantaneous adsorption equilibrium. Axial dispersion and heat effect are also neglected to further simplify the calculation. Featuring its simplicity, avoiding CPU-time-consuming numerical solution and cycling iteration for the steady operating conditions, the equilibrium models have been widely used to give initial research to PSA processes. Despite the extreme assumptions, simulation results given by equilibrium models can fit with the experimental data for some special PSA systems to an acceptable extent.

4.1.1 Progress of equilibrium models

Early models were limited to the purification of binary mixtures in which the preferentially adsorbed component was at a trace level^[3,9]. Fernandez and Kenney^[10] expanded the theory to the separation of a binary mixture with arbitrary feed composition with required numerical integration of some of the relevant equations^[11]. An analytical solution was obtained to the equations governing PSA processes with linear uncoupled isotherms for both components of arbitrary composition^[12]. Later, the binary linear isotherm (BLI) theory was developed with the assumption of constant pressure during feed and purge steps^[13]. The close correspondence between the BLI theory and experimental results suggests that the theory might be applicable to the design of some type of commercial-scale PSA processes. The isotherms in almost all of the above models are linear. However, the assumption is somewhat deficient for many practical systems even at very low partial pressure of adsorbate.

Then the continued studies were engaged in examining the effect of nonlinear isotherms. The equilibrium-based theories for PSA with nonlinear isotherms were reported^[10,14,15]. In each case the governing equations were integrated numerically. After that, an analytical solution was presented to the continuity equation applied to a specific PSA cycle for the case of a binary mixture having simple uncoupled nonlinear isotherms^[11], still with the assumption of constant pressure during feed and purge steps. Besides, other researches were carried out to evaluate the effects of particular nonlinear isotherm forms (*i.e.*, Langmuir-Freundlich isotherm and extended Langmuir isotherm) to the overall PSA performance^[16,17]. Most nonlinear isotherms employed ignored the effect of competitive adsorption, which may play an important role for multicomponent adsorption in some PSA processes.

Actually, it is difficult to describe a multicomponent adsorption equilibrium because of the complicated interactions of adsorbates and the energetic heterogeneity of adsorption sites. The simplest linear isotherms are rather crude for bulk PSA separation, even in narrow operation limits. Only for some special cases with quite homogeneous adsorbents can multicomponent Langmuir isotherms be used accurately. Ideal adsorbed solution theory (IAST)^[18] works very well for quite a number of cases, and recently the theory are combined with micropore size distribution to give more accurate predictions^[19], but it needs thermodynamically sound equations to fit the scattered data. The scattered data in multidimension are usually fitted by extended Langmuir isotherms^[17,20–24] and loading ratio correlation equations^[14,25], through the “black box”, which is not universal for most systems. Thus balance should be obtained between the computing complication and the simulating errors permitted.

Another approach to develop the basic equilibrium theory was provided by considering axial pressure drop in the adsorption beds with Darcy's law^[26] to predict proportional dependence of the pressure drop on flow rate^[26–28]. In these researches, average bed permeability was introduced additionally, though the permeability of the packed adsorption column may vary with the cyclic pressure changes. It has been demonstrated that the importance of the effect of pressure drop along the column increases with the decrease in cycling time. A possible explanation of small discrepancies between calculating results and experimental data is the assumption of instantaneous equilibrium, which is more difficult to attain at higher feed pressure and higher gas flow rate.

4.1.2 Cycle analysis

(1) Pressurization with product

By contrast to Skarstrom PSA cycle, pure product, the light component (the less strongly adsorbed component of the binary mixture), is used to pressurize the beds to the high feed pressure instead of the feed mixture^[11,13,17,25,29,30]. It seems reverse intuitively that the recovery of the light component which can be obtained by pressurization with product is generally superior to that attainable by pressurization with feed^[8]. The primary underlying principle is that, when the adsorbent is pressurized with feed, the adsorbent near the feed end contacts the heavy component (the more strongly adsorbed component) with high concentration at low pressure. The adsorption capacity of beds in the case is relatively low. This leads the concentration wave of the heavy component to penetrate further into the bed. As a result, the adsorbent bed is less than fully utilized. In addition, an actual pressurization may make the flow deviate from the plug flow.

(2) Incomplete purge

Roušar and Ditl^[31] analyzed the effect of an incomplete purge by numerical integration of the local equilibrium model and suggested an optimization strategy. Matz and Knaebel^[29] found an increase in light-product recovery for difficult separations (*i.e.*, low separation factor and/or high heavy-component concentration in feed) by the method of incomplete purge. Recently, Roušar and Ditl^[32] solved the same equilibrium-based equations analytically for bulk separation with a low separation factor to determine the optimum purge amount. It has been found that, for bulk separation, the recovery at the optimum point is several times higher than that by total purge. Conversely, little improvement can be yielded over incomplete purge for purifying a trace heavy component. Generally, reducing the amount of purge always results in increased recovery, but beyond some limits, only impure product can be obtained.

(3) Beds with dead volume

A local equilibrium model of well-stirred cell involving dead volume at each end of the adsorption column was proposed by Cheng and Hill^[33]. Although the process is a three-step one-column process without purge step, the basic viewpoint of dead volume effects is quite the same. There are several disadvantages to dead volume assumption with few advantages^[8]. Introduction of dead volume at the feed end leads to lower the separation performance. The only positive aspect of the product-end dead volume is that it can hold a little amount of gas enriched with the light component to partially purge the bed during blowdown.

The detailed effects of dead volume on each step of Skarstrom cycle are presented by Ruthven *et al.*^[8].

(4) Heat effects

In real PSA processes, temperatures are going up and down, at any given point in the bed, accompanying adsorption and desorption steps, and the temperature variations have influence on the separation quality. Overwhelming majority of the equilibrium models, however, neglect the heat effects even for bulk separations. However, two efficient approaches have been provided to reduce the excursion of temperature in a cyclic period^[25]. The first one is by allowing heat exchange between the adsorbers, for example, by using a shell-and-tube type heat exchanger, in which the shell and the tube are the separating beds. In the second process, an inert material with a high heat capacity is added into the adsorbent bed. The inert additive serves to store the heat during adsorption and release it during desorption, so as to eliminate the heat effects.

4.2 Kinetic models

Although the local equilibrium model is widely used to gain insight into PSA processes due to its simplicity, it cannot provide exact predictions to the cases based on kinetic separation. In many cases, mass transfer resistance must be considered because of the finite mass transport because of relatively high fluid velocity, particular in rapid PSA separations. Including the effects of axial mixing and mass transfer resistance, the kinetic models are, therefore, more realistic and sufficiently general to be applied for detailed optimization studies^[8]. However, unlike the equilibrium-based approach, kinetic models essentially require numerical integration of the governing equations for transient simulation. Even so, it has the advantages of flexibility and great accuracy at the expense of increasing computation.

It is just because of the interconnected micropore structure that the porous adsorbents exhibit tremendous adsorption power. When fluid contacts with the porous medium the adsorbate molecules must cross the external fluid film and penetrate into the porous structure during adsorption, and travel the same path in the opposite direction during desorption^[8]. Both external film resistance and internal pore diffusion resistance exist in mass transfer processes, in which the overall mass transfer rate depends on the structure of adsorbent and operation conditions.

4.2.1 Pore diffusion model

Pore diffusion models have been presented by Yang and Doong^[14,21,30], and Raghavan *et al.*^[34]. The former developed pore diffusion models to predict PSA bulk separations by neglecting axial dispersion and

pressure gradient in the bed, while the latter dealt with macropore diffusion in an isothermal trace system including axial dispersion. The mass conservation equation in particles involves in the whole set of governing equations with the relevant pore diffusivity determined by prior experiment. In order to simplify nonisothermal simulations, thermal equilibrium is assumed between the fluid and adsorbent particles, though this assumption possibly gives rise to the premature arrival of the thermal wave front^[21]. Nonetheless, the close agreement between numerical results and experimental data has corroborated the reliability of such mathematical model.

4.2.2 Linear driving force model

Although a pore diffusion model provides more realistic representation of the adsorption kinetic mechanism, the linear driving force (LDF) model can correctly predict the trends of the experimentally observed behavior^[24]. It has been extensively employed with great success for dynamic separations, regardless of the actual nature of the mass transfer resistance, since it offers much more faster computation (at least ten times faster than the pore model solution on the same machine).

In the LDF model the adsorption rate equation is presented as follows^[8]

$$\frac{\partial q_i}{\partial t} = k_i(q_i^* - q_i)$$

where

$$k_i = \Omega_i \frac{\varepsilon_p D_p}{R_p^2} \frac{c_0}{q_0} \quad \text{macropore diffusion control}$$

$$k_i = \Omega_i \frac{D_c}{r_c^2} \quad \text{micropore diffusion control}$$

The problem, how to adopt a suitable value of Ω for the linear rate expression, has caused much attention soon after the initial introduction of the LDF model. In most cases, the value of Ω is commonly taken as 15. However, reports have shown that it may depend on the (dimensionless) cycle time^[34,35]. In the studies using the LDF model, the match between theory and experiment was achieved by arbitrarily adjusting Ω values^[36,37]. On the other hand, detailed researches of diffusion in micropore adsorbents reveal that the micropore diffusivity varies strongly with sorbate concentration^[38,39]. The extension of the diffusion model to allow for concentration dependence of diffusivities, however, increases the numerical calculations considerably. Despite the limitations of the LDF model discussed above, the LDF model approach is adequate in almost all the dynamic separations.

4.2.3 Approximate assumption

- (1) Concentration profile in adsorbent

The mathematical complexity of the pore diffusion equations is reduced by assuming a parabolic concentration profile within each adsorbent particle^[14,21,30,40,41]. This approximation for solid-phase diffusion previously used by Liaw *et al.*^[40] has been proved to be indeed a good one for long contact time of fluid and adsorbents^[41]. However, it is less accurate at short cycle time because some uncertainty in its validity becomes marked in a rapid PSA system.

(2) "Frozen" column

Most equilibrium models assume that the column pressure remains constant during the high-pressure adsorption and low-pressure purge steps. In the kinetic models, it is assumed that no mass transport between fluid and adsorbent occurs in the short periods during pressurization and blowdown stages^[20,22,34,42-48]. Under this approximation, the adsorbed phase is considered as frozen, which leads to constant molar fractions in the gas phase during blowdown, while at the end of the pressurization, the profile of the residual gas compressed by the feed extends only a fractional distance p_L/p_H of the entire length of the column to the product end. This approximation is acceptable for purification processes and has been used for many bulk separations based on dynamic principle. However, it is not reasonable since the change of pressure cannot be instantaneous. Therefore, in a more rigorous mathematical model mass transfer between fluid and solid phases during pressurization and blowdown should be allowed, especially for the equilibrium-controlled processes.

(3) Symmetry

All the multi-bed PSA processes mentioned so far have an implicit fundamental: PSA plants are operated in an absolutely symmetrical manner. With this constraint, a solution for only one adsorber needs to be obtained because of the same operation procedure for each bed. Asymmetrical operation (*i.e.*, asymmetrical flow between two columns), however, is inevitably encountered in actual processes, especially for industrial applications, because the packed condition in each bed and the resistance of valves to different flow directions cannot be completely the same. For a large-scale PSA unit the asymmetrical operation can cause drastically different temperature profiles in different adsorbers. Simulation results from a two-bed system with asymmetrical flow in either the purge or equalization step show that a significant drop in the product purity can occur when there is more than 10% difference of flows (by artificial controlling) between the two beds in both cases^[49].

(4) Heat effects of bed wall

Two simplifications, constant temperature (equal

to that of the feed mixture) or adiabatic condition are employed for the heat balance of the column wall in the heat transfer equations^[23,30,42]. The reality should be between the two extremes, near to the isothermal state. Researches have further revealed that the adiabatic condition, which can be closed for a large commercial PSA plant, generally results in the worst separation. For small-scale laboratory units with low heat of adsorption and high heat transfer coefficient between packings and bed wall, the constant temperature assumption of the bed wall is quite reasonable.

5 ELECTRICAL ANALOGUE MODEL

Starting from the basic equilibrium and kinetic mathematical models, several new models have been introduced in the last ten years with the recent rapid development of numerical calculation and computer science. Great flexibility can be achieved with the aid of these new tactics, even for handling complicated PSA processes. Furthermore, it provides a theoretical fundamental to open up new paths for the application of PSA technology.

The electrical analogue was introduced to simulate the heat transfer in a packed bed and the elution curves of a chromatograph^[50,51]. In the study of chromatograph, an electrical circuit to represent the linear chromatograph was constructed, in which resistors are equivalent to fluid and transfer resistances, and capacitors are equivalent to accumulation in voidage of column and adsorption in adsorbent, and then the elution curves were determined fast and conveniently by measuring electrical voltage with an oscilloscope.

The electrical analogue model is a particular and effective measure for PSA simulation^[5,52-55]. It successfully converts the whole PSA flow scheme into an electrical circuit by introducing equivalent electrical elements, such as resistor, capacitor and inductor. By this analogy method, mass, heat and momentum transfer processes can be discussed indirectly by analyzing the electricity acting on its elements. In this way, the complicated boundary conditions in the partial differential equation model has been evaded ingeniously, and some of the above approximate assumptions, such as dead volume in bed, frozen column and symmetry, can be eliminated by adding capacitors/resistors to the electrical circuit. Compared with the experiments in rapid PSA pressurization and depressurization, quite consistent results obtained by this method have testified its validity. Comparing to the more rigorous kinetic models of the partial differential equation model, the electrical analogue model is promising because it needs shorter computing time to complete a cyclic simulation with equivalent accuracy.

The electrical analogue was used to predict PSA ethanol drying process with 3A molecular sieve as the adsorbent^[5]. It is shown that the anisotropic valve, mounted to connect the adsorption column with product tank, and vacuum desorption may both improve the operation to obtain higher purity products.

6 NEURAL NETWORK MODEL

Neural networks have been applied to describe the behavior of PSA processes in the recent work^[56,57]. The neural network model has the advantage of being easy to use, and the computing time in the design and optimization of a PSA process is shorter compared to the calculation based on the mechanism models. Although quite a good prediction can be obtained from the neural model, it cannot be extrapolated, *i.e.*, it covers only the variable space where the experimental data is available. Therefore, by combining the predictions of the essential mechanism model with those from the neural network, a complete neural network model can be built with a much faster and accurate response.

7 PROSPECTIVE

It has been demonstrated that simulations of multicomponent PSA process are rather complex to be handled, which mainly depends on the development of the equilibrium and kinetic theories on multicomponent adsorption. A kind of universal equations to fit the discrete data from experiments or the multicomponent adsorption theory, such as IAST and its modification, is also necessary for saving CPU time of solving the governing equations of the model. For a real application, it should be better to select a mathematical model in which the hypotheses are the closest to the realistic system to provide a more reliable simulation.

The iteration procedure of solving the equations requires models running fast and the corresponding steady algorithm, especially in the optimization and optimal control of a PSA process. One of the methods is combining the governing equations with other computing technique, such as neural network. The optimal control might act out of the character of the time schedule control in present PSA processes to give PSA a good performance and new concepts: unsteady feed, asymmetrical/aperiodic operation.

Heat effect is significant in a large-scale PSA unit, but so far few researches published simulate the radial distribution of temperature and velocity in a PSA bed.

PSA models will be developed to meet the needs of new PSA technology. Solvent vapor recovery^[46,47,58,59] and hybrid separations, such as

adsorption-reaction^[60,61] and PSA-membrane^[62-64], have drawn much attention recently. In other way, the PSA modeling may be used to explore new processes of adsorption.

8 CONCLUSIONS

The progress of PSA models is accompanied with the introduction of reasonable assumptions. The equilibrium models are attractive for their simplicity and have been used to analyze some phenomena, such as pressurization with products, incomplete purge, beds with dead volume, heat effect, *etc.*, to get closer to an actual PSA process. More complicated kinetic models are simplified with the assumption of parabolic distribution of concentration in adsorbent, linear driving force expression, frozen column and succinct heat effect. The connection of the essential pieces of PSA with the electrical elements in the electrical analogue model looks like what is done in an actual PSA equipment, so that some assumptions in the partial differential equation models are eliminated naturally in the electrical analogue. The combination of the neural network and the mechanism models may be a good way to have both less calculation and the rigorous derivation of the mechanism models at the same time.

NOMENCLATURE

c	gas-phase concentration mol·m ⁻³
D_a	axial dispersion coefficient, m ² ·s ⁻¹
D_c	micropore diffusivity, m ² ·s ⁻¹
D_p	macropore diffusivity, m ² ·s ⁻¹
k	LDF mass transfer coefficient, s ⁻¹
p_H	high pressure, N·m ⁻²
p_L	low pressure, N·m ⁻²
q	quantity of gas adsorbed, mol·kg ⁻¹
R_p	macroparticle radius, m
r_c	microparticle radius, m
t	time, s
u	interstitial fluid velocity, m·s ⁻¹
Z	position in the bed, m
ε	bed porosity
ε_p	porosity of adsorbent particle
Ω	parameter defined by LDF model

Superscripts

* equilibrium

Subscripts

i adsorbed component i
 0 reference value usually the feed state

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