

## HYDROGEN PURIFICATION BY PERIODIC ADSORPTION

**Christian Barg** – cbarg@enq.ufrgs.br

**Argimiro R. Secchi** – arge@enq.ufrgs.br

**Jorge O. Trierweiler** – jorge@enq.ufrgs.br

Departamento de Engenharia Química, Universidade Federal do Rio Grande do Sul,  
Rua Sarmento Leite, 288/24, CEP 90050-170 - Porto Alegre, RS – Brazil

**José Maria P. Ferreira** – jferreira@copesul.com.br

COPEL Sul Petroquímica S.A., Triunfo, RS – Brazil

***Abstract.** The periodic adsorption processes have been widely used for industrial applications, mainly because it spends less energy than the usual gas separation processes, like the cryogenic distillation. The largest commercial application of periodic adsorption processes is the pressure swing adsorption (PSA) applied to hydrogen purification. Although its wide use in the chemical and petrochemical industry, there are no reports in the open literature about complete modeling studies of a complex commercial unit, with multiple adsorbents and multiple beds and several feed components. This study has as objective the modeling, optimization and dynamical analysis of an industrial PSA unit for hydrogen purification.*

***Keywords:** PSA, Gas purification, Periodic adsorption, Control*

### 1. INTRODUCTION

In order to attend the necessity of understanding these new processes, several works had been done in the literature. The main problem in simulating such units is the computational time, and most published works are related to experimental units, which are simpler than commercial plants, in order to study some specific aspect and avoid the influence of other disturbances. Some studies on the optimization of such processes were made.

In this work, the modeling and simulation of an industrial hydrogen purification unit are carried out. The unit has six beds and operates twelve steps, one step to purify the hydrogen by adsorption, and eleven steps to regenerate the bed and make it ready to start adsorption again. The unit can produce hydrogen with 99.99% purity, 90% recovery, from a feed with about 95% hydrogen, 5% methane, and traces of carbon monoxide. There are six identical vessels with three kinds of adsorbents. The first layer is an alumina guard bed, to prevent eventual contamination with benzene or water, followed by two layers of activated carbon and zeolite. The time elapsed by each step is defined by two parameters, the  $(T1 + T2)$  and the  $(T1/T2)$ , where  $T1$  and  $T2$  are the steps times. In a recent work (Barg et al., 1999) showed that in this system the  $T1/T2$  ratio has no effect on the product purity or on the hydrogen

recovery. Then the cycle time represented by the  $T1 + T2$  parameter is optimized, and the effect of feed flow rate and adsorption pressure on the optimal cycle time is studied. The system non-linearity is studied by means of a proportional gain analysis.

## 2. PROCESS DESCRIPTION

The unit operates the following twelve different steps: provide pressure equalization 1 (PE1), hold (HD), provide pressure equalization 2 (PE2), provide pressure equalization 3 (PE3), provide purge (PP), blowdown (BD), purge (P), receive pressure equalization 3 (RE3), receive pressure equalization 2 (RE2), receive pressure equalization 1 (RE1), repressurization (REP), and adsorption (ADS). Figure 1 shows a diagram of the process, describing the different steps of a complete PSA cycle. For example, at beginning of a cycle, bed 1 is connected with bed 3, and bed 4 is connected with bed 6 undergoing pressure equalization, while bed 2 is in adsorption step and bed 5 is blowing down.

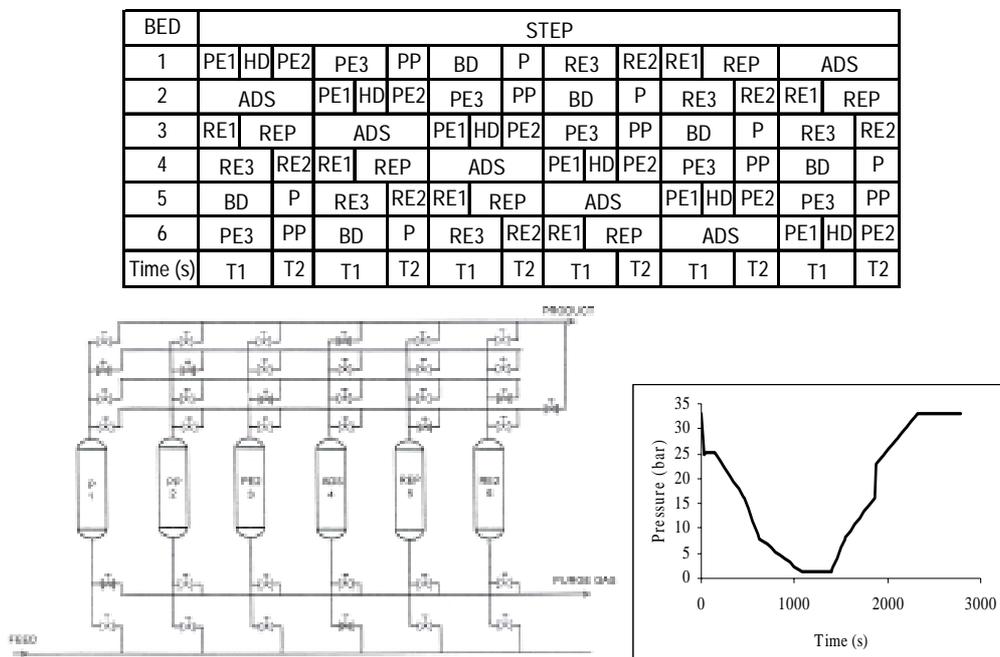


Figure 1 - Sequence of steps and pressure variation of a bed on a complete PSA cycle.

The equalization steps are used to improve recovery, utilizing the gas living a bed that is reducing the pressure to increase the pressure of another one. This practice reduces the amount of product gas necessary to repressurize the bed. The purge is the step where the bed is regenerated, when another bed (in the provide purge step) provides gas to purge the bed at low pressure, promoting the desorption of the adsorbed material. Due to the synchronism, there is a period of time when the bed should wait (hold step) until the other beds are ready to change the step. After the provide purge step, there is an inversion of the flow direction. The blowdown is done in countercurrent direction, in order to increase the concentration of the strongly adsorbed component at the bed entrance, just before the countercurrent purge step. Figure 1 also shows a typical pressure variation curve of a bed in a complete cycle. This profile is related to the bed 1 in the shown sequence.

The difference between the adsorption strength of each component is the driving force for the separation, and the regeneration of the bed is based on the desorption capacity of the more strongly adsorbed component at the purge pressure. If a component interacts strongly with the

adsorbent, it will poison the bed. The alumina layer was added to the system due to its weak adsorption capacity, enabling desorption of substances that would be irreversibly adsorbed on the activated carbon or on the zeolite.

### **3. MATHEMATICAL MODEL**

As distributed systems, the PSA processes should be modeled by a set of partial differential and algebraic equations. It is also an inherently dynamic and periodic process, which can achieve a cyclic steady state (CSS) after a certain number of cycles.

#### **3.1 Model assumptions**

The assumptions adopted are those commonly used in the literature, and can be summarized below:

- The alumina layer is not considered, assuming there is no water or benzene in the feed, and the adsorption of the others components on the alumina surface is negligible;
- A plug-flow model with axial dispersion represents the flow;
- The system is non-isothermal, with local thermal equilibrium assumed between the gas phase and the adsorbent particles. The thermal axial dispersion is considered;
- The system is a bulk separation process, then the change of velocity due to adsorption (or desorption) is taken into account by the overall mass balance;
- The multicomponent adsorption equilibrium is computed adopting the extended Langmuir model. The isotherm constants are taken from literature (Park et al., 1998), and have been checked from experiments with a single component. No consideration was made concerning interaction between different molecules, either on the different kinds of active sites;
- The adsorption of hydrogen is considered negligible;
- A linear driving force model is adopted to compute the mass transfer dynamics, with constant overall mass transfer coefficient;
- Darcy's equation is used to compute the pressure drop across the bed;
- The ideal gas law is assumed;
- The linear time dependence of the pressure in the pressure equalization, provide purge, and repressurisation steps is known from plant data, assuming perfect pressure control;
- All transport parameters, as well as physical properties of gas and solid phases are taken from classical literature;
- Heat transfer to the surroundings is negligible.

The different layers follow the same balance equations, but with different sets of physical properties and equilibrium parameters. Thus a balance equation must be done for each adsorbent layer.

#### **3.2 Balance equations**

With the preceding assumptions, the balance equations to model the system are given. The overall mass balance applied to the gas phase is written below, where the latest term on the right side of the equation takes into account the adsorbed quantity.

$$\frac{\partial \rho}{\partial t} = -\frac{\partial(v\rho)}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \sum_{i=1}^{n-1} \frac{\partial q_i}{\partial t} \quad (1)$$

where  $\rho$  is the gas density,  $v$  is the gas interstitial velocity,  $\varepsilon$  is the bed porosity,  $q_i$  is the amount of component  $i$  adsorbed,  $z$  is the axial dimension, and  $t$  is the time. The component mass balance, for the gas phase is given by:

$$\frac{\partial C_i}{\partial t} = D_z \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial(v \cdot C_i)}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\partial q_i}{\partial t} \quad i = 1, \dots, n-1 \quad (2)$$

where  $n$  is the number of components,  $D_z$  is the axial dispersion coefficient, and  $C_i$  is the molar concentration of component  $i$  in the gas phase. The energy balance gives:

$$\left( Cp_g + \frac{1-\varepsilon}{\varepsilon} \cdot Cp_s \right) \frac{\partial T}{\partial t} = K_z \cdot \frac{\partial^2 T}{\partial z^2} - v \cdot Cp_g \cdot \frac{\partial T}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \cdot \sum_{i=1}^{n-1} \Delta H_{ads,i} \cdot \frac{\partial q_i}{\partial t} \quad (3)$$

where  $Cp_g$  is the mean heat capacity of the gas,  $Cp_s$  is the heat capacity of the adsorbent,  $K_z$  is the thermal axial dispersion coefficient,  $T$  is the temperature, and  $\Delta H_{ads,i}$  is the heat of adsorption of component  $i$ .

The extended Langmuir isotherm for adsorbed components can be written as:

$$q_{i,eq} = \frac{q_{i,sat} \cdot b_i \cdot P_i}{1 + \sum_{j=1}^n b_j \cdot P_j} \quad (4a)$$

$$q_{i,sat} = a_{1,i} + \frac{a_{2,i}}{T} \quad \text{and} \quad b_i = b_{0,i} \cdot \exp\left(\frac{b_{1,i}}{T}\right) \quad (4b)$$

where  $a_{1,i}$ ,  $a_{2,i}$ ,  $b_{0,i}$ ,  $b_{1,i}$  are the isotherm parameters for the component  $i$  in each adsorbent material,  $P_i$  is the partial pressure of component  $i$  in the gas phase, and  $q_{i,eq}$  is the amount of  $i$  adsorbed in equilibrium with the gas phase partial pressure of  $i$  at system temperature in that point.

The linear driven force equation, to model the mass transport between gas and solid is:

$$\frac{\partial q_i}{\partial t} = k_i \cdot (q_{i,eq} - q_i) \quad (5)$$

where  $k_i$  is the overall mass transfer coefficient for the component  $i$  in each adsorbent material. The Darcy's equation to model the pressure drop across the bed is given by:

$$\frac{\partial P}{\partial z} = -\frac{180\mu v}{dp^2} \frac{(1-\varepsilon)^2}{\varepsilon^2} \quad (6)$$

where  $P$  is the pressure,  $\mu$  is the viscosity, and  $dp$  is the mean particle diameter.

### 3.3 Boundary conditions

The solution of the previous equations needs some initial conditions to solve the equations with temporal derivatives. The bed is considered initially clean, filled up only with hydrogen, and the pressure is equal to the initial pressure of the first step of the bed. The temperature is assumed to be equal to the feed temperature.

The same balance equations are used to all the steps of the process. The differences from one step to another are accounted by the boundary conditions. On pressure variable steps, the pressure changes are assumed to have a linear dependency with time, here represented by  $P(t)$ . The boundary conditions used in the model are the following. For fluid entering a bed:

$$X_i = X_{i,in} \quad \text{and} \quad T = T_{in} \quad (7)$$

where  $X_i$  is the molar fraction of component  $i$  in the gas phase,  $X_{i,in}$  is the molar fraction of component  $i$  and  $T_{in}$  is the temperature in the stream that is entering the bed. For fluid leaving a bed and for a closed end:

$$\frac{\partial C_i}{\partial z} = 0 \quad \text{and} \quad \frac{\partial T}{\partial z} = 0 \quad (8)$$

Table 1. Boundary conditions for pressure and velocity.

Steps	ADS	PE, REP, PP	BD	P
$z = 0$	$v = v_f$	$v = 0$	$P = P(t)$	$P = P_D$
$z = L$	$P = P_{ads}$	$P = P(t)$	$v = 0$	$v P(z) = -v_{out} P_{out}$

Table 1 shows the boundary conditions for pressure and velocity, where  $v_f$  is the interstitial velocity at feed entrance,  $P_{ads}$  is the adsorption pressure,  $P_D$  is the purge pressure,  $P_{out}$  is the pressure and  $v_{out}$  is the interstitial velocity in the exit of the bed which is providing purge gas.

The intersection of the layers is modeled with a set of continuity equations on the variables (pressure, velocity, temperature, and concentrations) and their axial derivatives.

### 3.4 Optimization strategy

There are some options to be used in optimization of periodic adsorption processes. An example is the work of Nilchan (1997), who uses the time domain discretization, plus the addition of appropriated time boundary conditions, to achieve the optimal cycle time for a given operational condition. That method could not be used in this case, because of the number of discrete variables that it creates. Usual personal computers do not have enough memory to do this actually.

The objective of this work is to study the optimal cycle time as a function of the feed flow rate and the adsorption pressure of the unit. Several different cases were simulated, covering a wide operational range. In this case, the product must have hydrogen purity at least equal to 99.9%. The optimal cycle time was defined as the cycle time that achieves that product purity with the specified operational conditions. The cycle time that provides optimal recovery is referred as the *optimal cycle time*.

As can be seen in the works of Barg et al. (1999) and Barg (2000), the product purity varies with changes in feed conditions (flow rate, temperature, pressure and composition). As industrial units present those variations, mainly in the feed flow rate and feed pressure, an automatic correction should be used to avoid operating the unit out of the optimal point.

#### 4. RESULTS AND DISCUSSION

Several combinations of different feed flow rates and adsorption pressures were used, covering a wide operational range. The product purity and the hydrogen recovery obtained for each simulation are presented in Table 2. The optimal cycle time for each condition was obtained from these results.

In this specific example, the product specification was supposed to be equal to 99.9% hydrogen purity. The particle properties were measured in laboratory, and the adsorption isotherms were taken from literature. The model was solved using the orthogonal collocation on finite elements method.

Table 2. Purity and recovery for different conditions.

Inlet conditions		$P_{ads} = 30.7 \text{ bar}$		$P_{ads} = 32.7 \text{ bar}$		$P_{ads} = 34.7 \text{ bar}$	
Cycle time (s)	Inlet (kg/h)	Purity	Recovery	Purity	Recovery	Purity	Recovery
2400	1020	99.9762	95.09	99.9926	93.46	99.9992	91.81
3300	780	99.9627	95.33	99.9801	93.81	99.9978	92.17
3300	1020	99.7874	96.52	99.8588	95.35	99.9108	94.12
4200	540	99.9924	94.65	99.9976	92.86	99.9997	91.14
4200	780	99.8146	96.41	99.8806	95.20	99.9283	93.95
4200	1020	99.5195	97.31	99.6361	96.41	99.7319	95.47
5100	540	99.9350	95.65	99.9679	94.23	99.9898	92.72
5100	780	99.6203	97.10	99.7114	96.11	99.7937	95.07
6000	540	99.8272	96.36	99.8897	95.14	99.9358	93.86

From the Table 2 can be observed the variation of purity and recovery with cycle time for each case. The industrial units usually use the cycle time as manipulated variable to control the product purity. The control action assumes that, in case of variation in the feed flow rate, the change in the cycle time must be inversely proportional to the inlet feed variation. This work shows that this is a reasonable assumption to bring the system close to the optimal operating point.

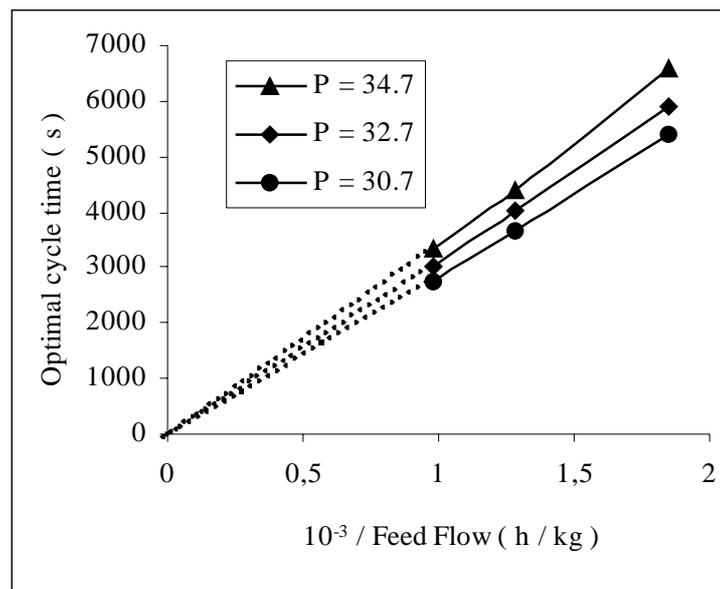


Figure 2. Optimal cycle time for different adsorption pressures (P, in bar).

In Figure 2 can be seen the variation of the optimal cycle time with the reciprocal of feed flow rate for different adsorption pressures, where it is observed the linear dependency. With this result it is possible to adjust the correct proportionality constant (gain) to tune the control system.

On industrial units the cycle time is linearly corrected for variations in the adsorption pressure. Again, the results showed in Figures 3 confirm that assumption to maximize product recovery, with a small deviation for low feed flow rates.

Actually in the industrial units, this feedforward control system is not enough to maintain the process at the optimal operation point. It is necessary an automatic feedback control to adjust the measured purity based on the cycle time, which is usually done manually by the operators.

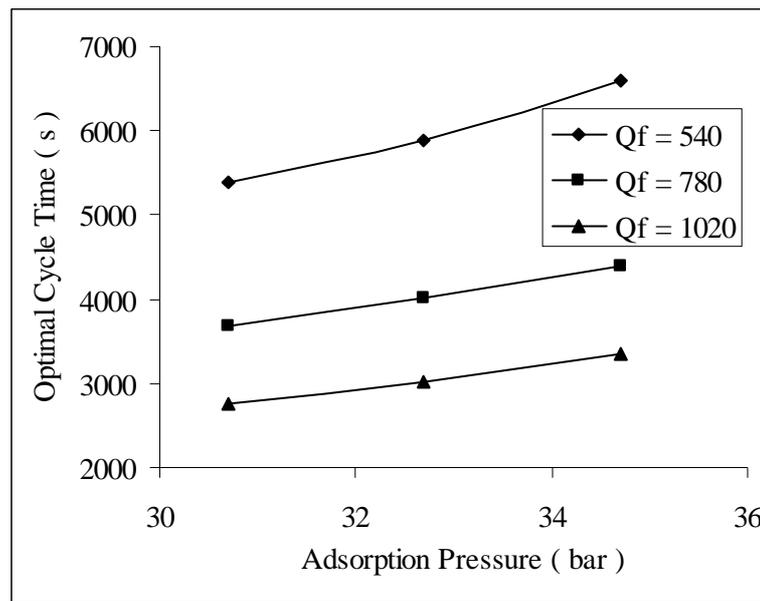


Figure 3. Optimal cycle time for different feed flow rates ( $Q_f$ , in kg/h).

The proportional gain of the cycle time relative to the product purity was calculated. The results are presented in Table 3. The proportional gain was defined as the ratio of the proportional variation on the purity obtained from a given proportional variation on the cycle time. Thus, if the gain is equal to  $-0.1$  means that an increase of 10% on the cycle time would result on a reduction (note the minus signal) of 1% on the product purity.

Table 3. Proportional gain for different adsorption pressures.

P = 32.7 bar		P = 30.7 bar		P = 34.7 bar	
Gain ( $10^{-3}$ )	Purity	Gain ( $10^{-3}$ )	Purity	Gain ( $10^{-3}$ )	Purity
-1.7	99.968	-3.3	99.935	-0.6	99.990
-5.2	99.890	-7.2	99.827	-3.6	99.936
-4.7	99.881	-6.9	99.815	-3.2	99.928
-4.9	99.859	-6.9	99.787	-3.2	99.911
-9.6	99.711	-11.1	99.620	-7.6	99.794
-10.4	99.636	-12.6	99.519	-8.4	99.732

A linear system has constant proportional gain for different operating points. If the gain differences are large from one point to another (characterizing a nonlinear system), the controller would need an adaptive mechanism to account for the different control actions that should be taken.

In this system is observed that the proportional gain presents strong variations for different operating points. Because these variations, it is difficult to foresee the proportional gain that would be observed at different conditions. An important result from this work is the observation that the proportional gain varies only when the purity varies, for different adsorption pressures or for different feed rates. If the purity is maintained constant, the gain will be also almost constant.

In Figure 4 is presented the variation of the proportional gain with product purity for different adsorption pressures. The gain presented only little variations with the adsorption pressure, and its behavior with product purity apparently can be well represented by a linear fit.

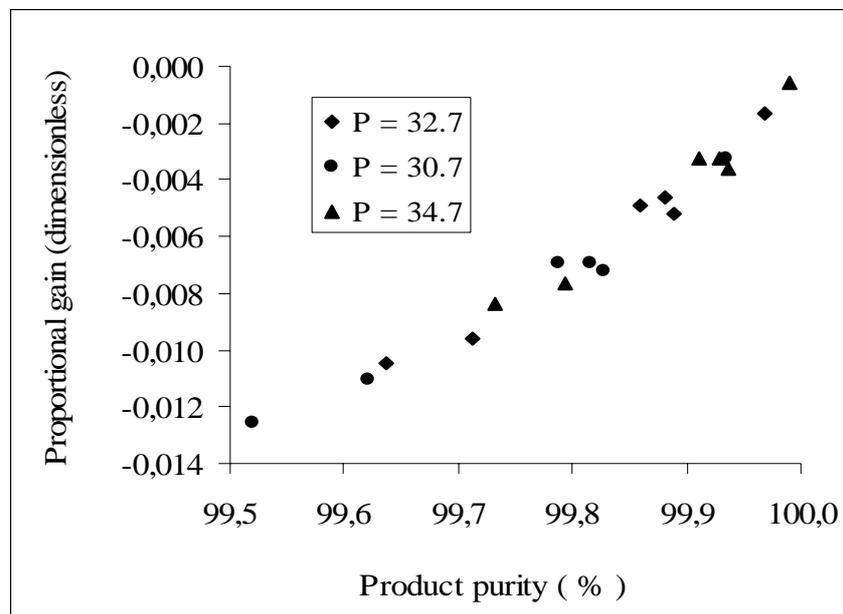


Figure 4. Proportional gain *versus* product purity.

## 5. CONCLUSIONS

A PSA system was simulated and optimized. The optimal cycle time was identified for different adsorption pressures and feed flow rates. The dependency of the optimal cycle time with these parameters was studied, showing that it is possible to design an optimal controller, to maintain the system at maximum recovery while keeping the product at the specification. The use of linear approximations in feedforward control strategies, commonly used in industrial PSA applications, brings the system close to the optimal operating point, but need a tuning strategy to adjust the gains, which can be obtained by the present work.

The dynamics of the PSA system was studied. The proportional gain of product purity for cycle time variations was calculated. The gain was showed to be very dependent on the operating point, typical of non-linear systems. It is was showed a linear relation between the gain and product purity.

## REFERENCES

- Barg, C., Ferreira, J.M.P., Trierweiler, J.O. and Secchi, A.R., 1999, Simulation and Optimization of an Industrial PSA Unit, Proceedings of the ENPROMER'99, Florianópolis, Brazil.
- Barg C., "Simulação e Otimização de Unidades Industriais PSA para Purificação de Hidrogênio", *M.Sc. Thesis*, UFRGS, 2000.
- Pantelides, C.C., 1996, An Advanced Tool for Process Modeling, Simulation and Optimization, Presented at CHEMPUTERS EUROPE III, Frankfurt.
- Nilchan, S., 1997, The Optimization of Periodic Adsorption Processes, Ph.D. Thesis, Imperial College, London.
- Park, J., Kim, J., Cho, S., Kim, J. and Yang, R. T., 1998, Adsorber dynamics and optimal design of layered beds for multicomponent gas adsorption, *Chem. Eng. Sci.*, vol. 53, pp. 3951-3963.