Simulation and Optimization of Small Oxygen Pressure Swing Adsorption Units

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A dynamic model of small valveless pressure swing adsorption (PSA) and vacuum and pressure swing adsorption (VPSA) units for the production of oxygen was developed for the purpose of simulation and optimization. This valveless operation, very often used in commercial units, results in a more complex cycle than the classic Skarstrom cycle, differing in the optimization conclusions and presenting specificities that cannot be ignored in the modeling and simulation. Three different commercially available adsorbents were evaluated for use in these units: Oxysiv 5 and Oxysiv 7 from UOP and SYLOBEAD MS S 624 from Grace Davison. The units’ performances (product recovery and power consumption) using each adsorbent were compared for cycles with the same pressure ratio. The simulation results were found to be in agreement with experimental results obtained on a commercial unit.

Introduction

The first pressure swing adsorption (PSA) unit was probably invented by Finlayson and Sharp in 1932 (GB Patent 365092). Their patent describes a single-bed process involving a pressurization step and a sequence of depressurizations. In the early 1940s (DE Patent 871886), Kahle developed a two-bed adsorption system for air-drying and carbon dioxide removal. In 1958, two different pressure swing adsorption units to separate air were patented: one by Skarstrom and the other by Guérin de Montgareuil and Dominé. In the Skarstrom cycle, the saturated bed is purged at a low pressure by a fraction of the light product. The Guérin de Montgareuil and Dominé unit was a very versatile PSA plant that could operate with many adsorbents and used vacuum desorption. However, because of the low separation factor between oxygen and nitrogen on the available zeolites, these pressure swing cycles allowed only modest separations.

Since the first zeolite mineral (stilbite) was described in Sweden in 1756 by Baron Cronstedt, these materials have undergone major developments. From 1949 through the early 1950s, zeolites A, X, and Y were discovered by Milton and Breck at the laboratories of the Linde Air Products Division of Union Carbide Corporation. In 1964 (U.S. Patent 3,140,931), McRobbie from Union Carbide Corporation, specified a zeolite for oxygen PSA units. The initial PSA process using 13X zeolite in a two-bed process was patented in 1966 by Skarstrom (U.S. Patent 3,237,377, filed by Exxon). Since then, many improvements in the PSA and vacuum swing adsorption (VSA) oxygen processes have been driven by the development of zeolite adsorbents with higher nitrogen capacities and selectivities.

In the early- to mid-1970s zeolites such as NaX and CaA made possible the development of the first economical PSA units for oxygen separation from air at a relatively small scale. These units started being commercialized in 1970. In 1988, second-generation zeolite adsorbents were developed for air separation by vacuum swing adsorption, making VSA competitive with cryogenic distillation. These second-generation adsorbents, such as CaX, and third-generation adsorbents, such as LiX, together with improved processes (vacuum and pressure swing adsorption, VPSA, or VSA) have dramatically reduced both capital and operating costs.

The developments on zeolites made the PSA and VPSA units smaller, making them viable for other applications such as oxygen generation systems on board military aircrafts or for medical purposes. In 1975, small oxygen PSA units producing 2–4 L/min of 85–95% oxygen became widely used in hospitals for treating patients with respiratory illness. Armond, in 1976, described an electric-powered compact apparatus using zeolite molecular sieve to generate breathing air for medical use. In 1984 (U.S. Patent 4,477,264), Kratz and Sircar patented a medical oxygen generator for domiciliary purposes generating a 90% O2 product. Currently, about 500 000 of these units are sold per year worldwide, and different cycles are still being developed: Recently, Sequa Technologies, Inc., developed a portable multicolour pressure swing adsorption unit for medical oxygen production that makes use of a rotary valve. These medical oxygen concentrators have a configuration that differs from the original Skarstrom cycle in the simplicity of the assembly and in the resulting complexity of the adsorption cycle. For economic reasons, the solenoid on-off valves that are used in the Skarstrom cycle to control the pressurization step are replaced by check valves, and the needle valves often used in experimental PSA units for controlling the purge flow rate are replaced by calibrated orifices. As a result, the pressurization step cannot be controlled, and it depends on the volume of the storage tank and the production flow rate. The cycle also has only two stages, both with the same duration: a stage that begins with the column pressurization and ends after the production and a stage that begins with the column depressurization and ends after the purge.

In terms of optimization, the conclusions obtained for a standard PSA or VPSA unit operating a Skarstrom
cycle are not applicable to these oxygen concentrators, which follow an adsorption cycle that is more complex to simulate and optimize. For example, the pressure history during a cycle in an oxygen concentrator changes completely when different product flow rates are selected, whereas in the Skarstrom cycle, the pressure history stays approximately constant.

In this paper, we present the simulation and optimization of these small PSA and VPSA oxygen concentrator units with three different commercially available adsorbents: OxySiv 5 and OxySiv 7 from UOP and SYLOBEAD MS S 624 from Grace Davison. The product recovery and power consumption with each adsorbent are compared for both operation modes and the same pressure ratio. The simulation and optimization results are validated by comparison to experimental data obtained from a commercial unit.

Mathematical Model

The theoretical model considers a pressure swing adsorption (PSA) unit or a vacuum and pressure swing adsorption (VPSA) unit with two stages (four steps). Stage 1 consists of two steps: pressurization and production. Stage 2 occurs in the other column simultaneously with stage 1 and also consists of two steps: depressurization (or vacuum) and purge. These units are composed of two fixed adsorbent beds, calibrated orifices located in the feed, purge and vent streams, and a storage tank.

Figure 1 illustrates these small pressure swing adsorption units.

Considering that, for a given cycle, column 1 (C1 in Figure 1) is at the first stage, column 2 (C2 in Figure 1) would, therefore, be at stage 2. The adsorption-columns and storage-tank (ST in Figure 1) pressure histories for this situation are presented in Figure 2.

Because there are two check valves before the storage tank, there is never a flow of gas from the tank to the adsorption columns. On the other hand, every time the pressure inside the tank (line ST in Figure 2) is lower than the pressure of at least one of the columns, gas coming from the higher-pressure column will be entering the tank.

When column 1 is at stage 1, it is being fed, and column 2 is depressurizing or under vacuum. As a result, column 1 is pressurizing (line C1 in Figure 2) until it reaches the storage-tank pressure (point B in Figure 2). At this point, column 1 starts producing.

Simultaneously, column 2 is depressurizing (line C2 in Figure 2) until its pressure reaches the column 1 pressure (point A in Figure 2). Meanwhile, because the adsorption columns are connected at the top, there is a flux of gas from column 2 to column 1 in an equalization-like step. After the pressure in column 1 becomes higher than that in column 2 (point A in Figure 2), the latter will start to be purged with the gas coming from column 1. When the production ends, the adsorption columns switch stages.

The following assumptions were made in the formulation of the mathematical model: perfect gas behavior; axially dispersed plug flow; uniform cross-sectional void fraction; uniform adsorbent properties along the adsorption column; negligible radial gradients; instantaneous temperature equilibrium between gas, adsorbent, and column wall; ideal distribution of the gas when it enters the adsorption column; negligible pressure drop (this assumption is usually valid for small units); and isothermal operation, which was shown in our previous work to be a reasonable approximation for oxygen separation.11

The dimensionless model equations can be written as follows:

Interparticle Total Mass Balance

\[
\frac{\partial \Pi^*}{\partial \theta} = -\Pi^* \frac{\partial u^*}{\partial x} - T^* \sum_{i=1}^{n_c} N_i^* \tag{1}
\]

Interparticle Partial Mass Balance

\[
\frac{\partial y_i}{\partial \theta} = -u^* \frac{\partial y_i}{\partial x} + \frac{1}{Pe} \frac{\partial^2 y_i}{\partial x^2} + \frac{T^*}{Pe} \sum_{j=1}^{n_c} y_j \left( N_j^* - N_i^* \right), \quad i = 1, n_c \tag{2}
\]

where \( \Pi^* \) is the dimensionless total pressure, \( \Pi^* = P/P_{ref} \), and \( P \) is the column pressure; the subscript ref denotes the reference state. \( \theta \) is the dimensionless time variable, \( \theta = t/\theta_{ref} \), \( t \) is the time variable; and \( \theta_{ref} \) is the bed time constant defined as \( \theta_{ref} = L/u_{ref} \), where \( u_{ref} \) is the reference interstitial velocity. \( u^* \) is the dimensionless interstitial velocity, \( u^* = u/L_{ref} \); \( x \) is the dimensionless spatial coordinate, \( x = z/L \), where \( z \) is the spatial coordinate and \( L \) is the adsorption-column length; and \( T^* \) is the dimensionless temperature, \( T^* = T/T_{ref} \), where \( T \) is the operating temperature. \( N_i^* \) is the dimensionless molar flow rate of the \( i \)th component, \( N_i^* = N_i/\theta_{ref} \).
where $N_i$ is the molar flow rate, $c_{ref}$ is the reference fluid-phase molar concentration, $c_{ref} = \frac{P_{ref}}{RT_{ref}}$, where $R$ is the universal gas constant, $\epsilon_s$ is the bed void fraction, $P_c$ is the Peclet number for mass transfer, $P_c = u_{ref}L/D_{ax}$, where $D_{ax}$ is the effective axial dispersion coefficient. Finally, $n_c$ is the number of components in the mixture.

The molar flow rate is given by the equation 12

$$N_i = (1 - \epsilon_p)\rho_s \left( \frac{\partial q_i}{\partial t} + \epsilon_p \frac{\partial c_i}{\partial t} \right)$$

where $\rho_s$ is the adsorbent apparent density, $q_i$ is the average molar concentration in the adsorbed phase, and $c_i$ is the average molar concentration in the fluid phase.

**Intraparticle Mass Transfer.** The linear driving force (LDF) model was used for describing the intraparticle mass transfer, considering instantaneous equilibrium between the inter- and intraparticle gas phases, $\frac{\partial c}{\partial t} = \epsilon_s \frac{\partial c_i}{\partial t}$. This model can be used only for long cycles; the use of more complex models can be expected to lead to only minor differences in the results obtained and would result in an increase of the computational time. Because the analyzed separation is equilibrium-dominated, the assumption of such a simple model is valid.

The linear driving force model in dimensionless form is given by

$$\frac{\partial q_i^*}{\partial \theta} = R_p^i \alpha_i^0 (q_i^* - \bar{q}_i^*)$$

where $q_i^*$ is the i-th-component dimensionless molar fraction in the adsorbed phase, $q_i^* = q_i/q_{ref}$; $\bar{q}_i^*$ is the i-th-component dimensionless molar concentration in the adsorbed phase, $q_i^* = q_i/q_{ref}$; and $q_{ref}$ is the reference-component molar concentration in the adsorbed phase at reference conditions, $q_{ref} = q(P_{ref}T_{ref})$. $\alpha_i^0$ is the ratio between the LDF kinetic coefficients, $k_{i}$ of the i-th and reference components, $\alpha_i^0 = k_i/k_{ref}$ and the coefficient $k$ is directly proportional to the effective macropore diffusivity coefficient. $R_p^i$ is the ratio between the bed time constant and the particle diffusion time constant, $R_p^i = k_{ref} \epsilon_s \xi_p$; $\epsilon_s^i$ is the i-th-component dimensionless molar concentration in the fluid phase, $\epsilon_s^i = c_i/c_{ref}$; $\epsilon_s^f$ is the i-th-component dimensionless molar concentration in the fluid phase, $\epsilon_s^f = c_i/c_{ref}$ and $c_{ref}$ is the reference-component molar concentration in the fluid phase at reference conditions, $c_{ref} = P_{ref}^{1/RT_{ref}}$.

The dimensionless adsorbent molar flow rate is given by

$$\frac{\partial q_i^*}{\partial \theta} = \xi_a \frac{\partial \bar{q}_i^*}{\partial \theta} + \xi_p \frac{\partial \epsilon_s^i}{\partial \theta}$$

where $\xi_a$ is the adsorbed-phase capacity factor, $\xi_a = \rho_a[(1 - \epsilon_b)/\epsilon_b]q_{ref} c_{ref}$, with $\rho_a$ as the adsorbent apparent density, and $\xi_p$ is the fluid-phase capacity factor, $\xi_p = \epsilon_p[(1 - \epsilon_b)/\epsilon_b]$, with $\epsilon_p$ as the particle void fraction.

**Adsorption-Column Mass Balance.** The adsorption-column pressure results from the following mass balance equation:

$$u_{in}^*P_{in}^* = u_{out}^*P_{out}^* + \frac{\partial P_{in}^*}{\partial \theta} + T^*\int_0^{n_c} N_i^* \, dx$$

where $u_{in}^*$ and $u_{out}^*$ are, respectively, the dimensionless interstitial velocities of the gas entering and exiting the column.

**Storage-Tank Total Mass Balance.** Assuming that the adsorption column and tank have the same diameter, the storage-tank total mass balance equation can be written in dimensionless form as

$$u_{in}^*P_{in}^{T*} = u_{out}^*P_{out}^{T*} + \frac{L^*}{P_{in}^{T*}} \frac{\partial P_{in}^{T*}}{\partial \theta}$$

where the superscript $T$ stands for storage tank, $u_{in}^*$ and $u_{out}^*$ are the dimensionless velocities of the gas entering and leaving the tank, respectively, and $L^*$ is the storage-tank length.

**Storage-Tank Partial Mass Balance**

$$\frac{\partial \bar{q}_i^{T*}}{\partial \theta} = \frac{P_{in}^{T*}}{L^*} (\bar{q}_i^* - \bar{q}_i^{ref^*}) - \frac{\partial P_{in}^{T*}}{\partial \theta} \frac{\partial P_{in}^{T*}}{\partial \theta}, \quad i = 1, n_c$$

where $\bar{q}_i^{T*}$ is the i-th-component molar fraction of the gas entering or leaving the tank.

**Pressure Drop Model in Orifices.** For modeling the molar velocity across a valve orifice, the following equations were used:

$$u_i^* P_i^* = C_v (P_i^* P_d^* T^*/M),$$

where $C_v$ is the dimensionless valve parameter

$$C_v = 2.035 \times 10^{-2} \frac{T_{ref}}{\epsilon_p^{u*} \sqrt{\frac{P_{ref}}{P_{in}^{T*}}} \frac{T_{ref}}{0.53}}$$

and $K_d$ is the valve parameter; $P_i^*$ and $P_d^*$ are the dimensionless upstream and downstream pressures, respectively; $T^*$ is the dimensionless temperature; $M$ is the molecular weight of the gas passing through the orifice, which was considered to be given by $M = \sum_{i=1}^{n_c} \gamma_i M_i$; the superscript 0 stands for standard temperature and pressure conditions (STP); and

$$P_{in}^{T*} = \sqrt{\frac{0.53 P_{in}^*}{P_d^*}}$$

Therefore, the dimensionless molar velocities, $u_i^*$, across the orifice in the feed, in the vent, before the storage tank, and across the purge orifice were considered to be given by

$$(P_i^* P_d^* T^*/M) = \begin{cases} 1.179 \sqrt{\frac{P_{in}^2 - P_{d}^2}{P_{in}^* M}} & P_i^* > 0.53P_u^* \\ \frac{1}{P_{in}^* M} & P_i^* \leq 0.53P_u^* \end{cases}$$

(11)
where \( P^{\text{Hi}} \) and \( P^{\text{Lo}} \) are the dimensionless high and low pressures, respectively.

The dimensionless molar flow rate of the gas leaving the adsorption column with the highest pressure is given by

\[
u^{*} = \frac{\nu_{\text{purge}}}{P^{*}_{\text{other column}}} + \frac{\nu_{\text{in,ref}}}{\epsilon_{b}} \tag{16}\]

If the pressure inside the storage tank is higher than the pressures inside the columns, then \( \nu_{T}^{*} = 0 \).

**Boundary Conditions.** When column 1 is pressurizing/producing and column 2 is depressurizing/purging, the boundary conditions are as follows

**Column 1**

\[
x = 0: \quad \frac{1}{Pe} \frac{\partial y_{i}}{\partial x} = u_{\text{in},i}(y_{i} - y_{i,\text{in}})
\]

\[
u^{*} = \frac{C_{v}}{P^{*}_{1}} f(P^{\text{Hi}}, P^{*}_{1}, T^{*}_{\epsilon}, M)
\]

\[
\frac{\partial y_{i}}{\partial x} = 0, \quad P^{*}_{1} \geq P^{*}_{2}
\]

\[
x = 1: \quad \frac{1}{Pe} \frac{\partial y_{i}}{\partial x} = u^{*}(y_{i} - y_{i,\epsilon_{b}}) + \frac{\nu_{\text{in,ref}}}{\epsilon_{b} P^{*}_{1}}, \quad P^{*}_{1} < P^{*}_{2}
\]

\[
u^{*} = \frac{C_{v}}{P^{*}_{1}} f(P^{*}_{1}, P^{*}_{2}, T^{*}_{\epsilon}, M)
\]

**Column 2**

\[
x = 0: \quad \frac{\partial y_{i}}{\partial x} = 0
\]

\[
u^{*} = -\frac{C_{v}}{P^{*}_{2}} f(P^{*}_{2}, P^{*}_{1}, T^{*}_{\epsilon}, M)
\]

\[
\frac{\partial y_{i}}{\partial x} = 0, \quad P^{*}_{2} \geq P^{*}_{1}
\]

\[
x = 1: \quad \frac{1}{Pe} \frac{\partial y_{i}}{\partial x} = u^{*}(y_{i} - y_{i,\epsilon_{b}}), \quad P^{*}_{2} < P^{*}_{1}
\]

\[
u^{*} = -\frac{C_{v}}{P^{*}_{2}} f(P^{*}_{2}, P^{*}_{1}, T^{*}_{\epsilon}, M)
\]

\[
u^{*} = \frac{C_{v}}{P^{*}_{2}} f(P^{*}_{2}, P^{*}_{1}, T^{*}_{\epsilon}, M) + \frac{\nu_{\text{in,ref}}}{\epsilon_{b} P^{*}_{2}}, \quad P^{*}_{1} < P^{*}_{2}
\]

For medical oxygen pressure swing adsorption units, it is important to keep the storage-tank output molar velocity, \( u_{\text{out,ref}}^{*} P^{*}_{\text{ref}} \), constant so that the unit is continuously producing

\[
u_{\text{out,ref}}^{*} P^{*}_{\text{ref}} = \frac{Q^{0}_{\text{prod}}}{A u_{\text{ref}}} T \frac{P^{0}}{T^{0}} \tag{17}\]

where \( Q^{0}_{\text{prod}} \) is the product flow rate, \( A \) is the adsorption-column cross-sectional area, and the superscript 0 stands for standard temperature and pressure conditions (STP).

As a consequence, in the simulation, the amount of gas entering the storage tank has to be high enough to ensure that the pressure inside the tank is always higher than atmospheric pressure.

**Initial Conditions.** At \( \theta = 0 \), the adsorption columns and storage tank are at atmospheric pressure and filled with air for both PSA and VPSA units: \( P^{*} = P_{\text{atm}}, y_{i} = y_{i,\epsilon_{b}} V \), where \( y_{i,\epsilon_{b}} \) is the molar fraction of the gas entering the column.

**Numerical Solution**

The model includes one interparticle total mass balance equation, eq 1; a set of \( n_{c} - 1 \) interparticle partial mass balance equations, eqs 2; the linear driving force equation, eq 4; one adsorption-column mass balance equation, eq 6; one storage-tank total mass balance equation, eq 7; and a set of \( n_{c} - 1 \) storage-tank partial mass balance equations, eqs 8. For the two adsorption columns, we have a coupled system of \( 2(n_{c} - 1) \) partial differential equations and \( 2(n_{c} + 1) + n_{c} \) ordinary differential equations. The resulting system of partial differential equations and ordinary differential equations was solved using a method that combines the use of high-resolution schemes (such as SMART\textsuperscript{17}) with an adaptive multiresolution approach inspired by wavelet theory.\textsuperscript{18} This method offers very good numerical stability, accuracy, and computational time.

**Cyclic-Steady-State Convergence.** In this kind of process, as each adsorption column passes through different stages, a cyclic steady state (CSS) must be considered, i.e., the product purity must be the same for consecutive cycles. In this work, the CSS was considered to be reached when the purity and recovery did not change, in two consecutive cycles, by more than 0.01% (absolute).

**Simulation and Optimization Data**

To accomplish the simulation work, adsorption data had to be experimentally measured for the adsorbents studied: UOP’s Oxysiv 5 and Oxysiv 7 and Grace Davison’s SYLOBEAD MS S 624. These adsorbents are generally used for air separation. Oxysiv 5 is a 13X-(NaX)-type zeolite,\textsuperscript{6} Oxysiv 7 is a LiX-type zeolite;\textsuperscript{19} and according to Grace Davison, MS S 624 is a binderless 5A-type zeolite.

Table 1 presents the particle diameter and void fraction, \( \epsilon_{p} \), of each adsorbent. The particle void fraction and the average pore diameter were determined using a mercury porosimeter (Poromaster 60 from Quantachrome).
Table 2. Adsorption Isotherm Parameters for the Three Adsorbents at 20 °C

<table>
<thead>
<tr>
<th></th>
<th>$Q_{\text{max}}$ (mol/kg)</th>
<th>$b \times 10^5$ (Pa$^{-1}$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxysiv 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.0704</td>
<td>0.1015</td>
<td>1</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.0704</td>
<td>0.0369</td>
<td>1</td>
</tr>
<tr>
<td>Ar</td>
<td>3.0704</td>
<td>0.0340</td>
<td>1</td>
</tr>
<tr>
<td>Oxysiv 7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>5.6780</td>
<td>0.0333</td>
<td>1.5001</td>
</tr>
<tr>
<td>O$_2$</td>
<td>4.3445</td>
<td>0.0332</td>
<td>0.9920</td>
</tr>
<tr>
<td>Ar</td>
<td>5.1977</td>
<td>0.0238</td>
<td>0.9926</td>
</tr>
<tr>
<td>MS S 624</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.6453</td>
<td>0.2262</td>
<td>0.9454</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2.6453</td>
<td>0.0753</td>
<td>0.9454</td>
</tr>
<tr>
<td>Ar</td>
<td>2.6453</td>
<td>0.0717</td>
<td>0.9454</td>
</tr>
</tbody>
</table>

Table 2 presents pure-component adsorption parameters for the three adsorbents studied, at 20 °C. These single-component adsorption data were obtained by the gravimetric method using a Rubotherm magnetic suspension balance and confirmed by the volumetric method using an in-house-developed setup. For the adsorption data measurements, the adsorbents were regenerated at 375 °C with a current of helium passing through the adsorbent in order to allow the complete regeneration of the adsorbent.

Because the maximum capacities, $Q_{\text{max}}$, and the Langmuir–Freundlich equation parameters, $n$, are the same for the three components for Oxysiv 5 and MS S 624, the multicomponent adsorption was predicted by the multicomponent Langmuir–Freundlich equation:

$$q_i = Q_{\text{max}} \frac{b_i y_i P_i \sum_j^{n_c} y_j P_j^{1/(n-1)}}{1 + \left( \sum_j^{n_c} y_j P_j \right)^{1/n}}$$  \(18\)

For Oxysiv 7, the maximum capacities and the Langmuir–Freundlich equation parameters $n$ are not the same for the three components, which reveals a thermodynamic inconsistency. For this reason, the multicomponent adsorption was predicted by the ideal adsorption solution theory (IAST).

The feed to the units was air (78% nitrogen, 21% oxygen, and 1% argon) at 20 °C. However, because the adsorption isotherms for oxygen and argon, for each adsorbent, are practically identical, the feed was considered to be a pseudo-binary mixture of 78% nitrogen and 22% oxygen.

Concerning mass transport, the effective diffusivity, $D_e$, for a system controlled by macro- and mesopore molecular diffusion is given by:

$$D_e = \frac{\epsilon_D D_{AB} C_{ini}}{r_p q_{ini}}$$  \(19\)

where $D_{AB}$ is the molecular diffusivity evaluated from the Chapman–Enskog equation; $r_p$ is the particle tortuosity, considered to be 3; and $C_{ini}$ and $q_{ini}$ are the initial molar concentrations in the fluid and adsorbed phases, respectively.

The LDF kinetic coefficient is given by:

$$k = 15 \frac{n^2}{r_p^2}$$  \(20\)

where $r_p$ is the particle radius.

Table 3. Ratio between LDF Kinetic Coefficients at 0.1 MPa and 20 °C

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\alpha_O^{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxysiv 5</td>
<td>2.71</td>
</tr>
<tr>
<td>Oxysiv 7</td>
<td>6.71</td>
</tr>
<tr>
<td>MS S 624</td>
<td>2.96</td>
</tr>
</tbody>
</table>

In Table 3 are presented the ratios between the LDF kinetic coefficients, $\alpha_i^D = k_i/k_{ref}$, for each adsorbent. Nitrogen is the reference component, and so, $\alpha_{N_2}^D = 1$.

Finally, Table 4 lists the reference variables adopted in the simulations.

Model Parameters

The model parameters are introduced below and their physical meanings are briefly discussed:

(i) $\epsilon_{N_2}$ is the adsorbed-phase capacity factor. It depends on the adsorption data and the bed packing. It is the ratio between the amounts of gas in the adsorbed phase and in the interparticle gas phase at the reference pressure and temperature. Assuming negligible wall effects, given that the bed length is 100 times greater than the adsorbent diameter and the bed diameter is 90 times larger than the adsorbent diameter, and a packing of small identical spherical particles, the value of $\epsilon_{N_2} = 0.36$ can be used for the bed void fraction.

(ii) $P_H$ and $P_L$ are the high and low pressures, respectively. In small medical oxygen pressure swing adsorption units, the high pressure is limited to 0.3 MPa; this was the value used in the simulations of the PSA unit. The low pressure was atmospheric pressure: 0.1 MPa. For the VPSA unit simulation, the values chosen for the high and low pressures were 0.04 and 0.12 MPa, respectively. Hence, the pressure ratio $P_H/P_L$ is kept constant for both operating modes.

(iii) $P_e$ is the Peclet number for mass transfer. A few correlations are available for predicting the Peclet number, but the velocity must be known. One of the advantages of the methodology used here is the possibility of optimizing the unit to work with several ratios of column volumes and product flow rates, so that the velocity does not need to be known a priori. For small-scale units, the values for the Peclet number are between 500 and 1000. We used a Peclet number of 600 in all simulations because there are no noticeable changes in the process performance for higher values.

(iv) Two mass-transfer parameters are used:

(a) $R_e^D$ is the ratio between the bed time constant and the particle time constant. The bed time constant, $\theta_{ref}$, is related to the production flow rate and column volume. The particle diffusion time constant is the inverse of the reference-component LDF coefficient, $k_{N_2}$.

(b) $\alpha_o^D$ is the ratio between the diffusivity coefficients. As nitrogen was chosen to be the reference component, $\alpha_{N_2}^D = 1$. The values of $\alpha_o^D$ were calculated for each adsorbent and are presented in Table 3.

Optimization Variables

In the analysis of the model to improve the unit’s performance, the following optimization variables were
chosen: (i) \( \theta_{\text{press/prod}} \), the dimensionless pressurization/production time; (ii) \( \frac{L}{LT} \), the ratio between the adsorption-column length and the storage-tank length (it is assumed that both columns and storage tank have the same internal diameter); (iii) \( C_{v}^{p} \), the feed valve parameter; (iv) \( C_{v}^{T} \), the storage-tank valve parameter; (v) \( C_{v}^{P} \), the purge valve parameter; and (vi) \( C_{v}^{T} \), the vent valve parameter.

The significance of each variable and its influence on the process performance are described below.

**Dimensionless Pressurization/Production Time.** The dimensionless pressurization/production time, \( \theta_{\text{press/prod}} \), represents the duration of one stage, that is, the time during which one adsorption column goes through pressurization and production while the other column is being depressurized and purged. If the pressurization/production time is too short, not all of the column adsorption capacity is used, which will be translated into a lower recovery. On the other hand, if \( \theta_{\text{press/prod}} \) is higher than the optimum value, it will result in a reduction of the purity of the product leaving the column, as the breakthrough time might be exceeded.

**Ratio between the Column Length and Storage-Tank Length.** Assuming that the adsorption column and storage tank have equal cross sections, the relation between their volumes is translated into the ratio between the column length and the storage-tank length, \( \frac{L}{LT} \), which will influence the pressurization time. The slope of line ST in Figure 2 increases with increasing \( \frac{L}{LT} \). This means that, if the storage tank is too small, the column might start producing before the intended high pressure is reached. Then again, if the tank is too large, the unit takes too much time to reach the steady state. Mendes et al.\(^{24}\) concluded that the rate of pressure increase influences the product purity and recovery.

**Feed Valve Parameter.** The feed valve parameter, \( C_{v}^{p} \), is related to the velocity inside the column that is at stage 1. An increase in this variable value will be translated into a steeper line C1 in Figure 2. As a result, both points A and B in Figure 2 are reached earlier, which means that the pressurization time of the column that is at stage 1 and the depressurization time of the other column will be shorter. As a consequence, the production and purge will start sooner and therefore will last longer.

If the \( C_{v}^{p} \) value is too high, the purge might start too soon, while the adsorption column at stage 2 is still at a high pressure. On the other hand, if \( C_{v}^{p} \) is too low, it might not be possible to reach the necessary high pressure within a suitable time, consequently reducing the separation achieved.

**Storage-Tank Valve Parameter.** The storage-tank valve is used to control the columns’ production flow rate. The storage-tank valve parameter, \( C_{v}^{T} \), influences the pressure inside the storage tank. For high \( C_{v}^{T} \) values, the pressure inside the storage tank will be closer to the pressure of the column that is producing, as a higher flow rate will be entering the storage tank. By decreasing this parameter, i.e., decreasing the flow rate entering the storage tank, the ratio between the purge flow rate and the flow rate of the stream exiting the column that is at stage 1 will increase. Therefore, the storage-tank valve parameter influences the product recovery and purity.

**Purge Valve Parameter.** The purge valve parameter, \( C_{v}^{P} \), directly influences the purge flow rate. Therefore, this variable has a significant influence on the product recovery and purity.

**Vent Valve Parameter.** The vent valve parameter, \( C_{v}^{T} \), affects the column depressurization similarly to how \( C_{v}^{p} \) influences the column pressurization. An increase of this variable value will imply a steeper line \( C2 \) in Figure 2, as the higher the \( C_{v}^{T} \) value, the faster the depressurization, and the sooner the beginning of the purge. If the \( C_{v}^{T} \) value is too low, the pressure inside the adsorption column that is depressurizing might remain higher than the pressure inside the storage tank, in which case, this column would produce. The production in the column that is at stage 1 would then start simultaneously with the purging of the other column. In Figure 2, this would be represented by the overlapping of points A and B.

**Optimization Procedure.**

In the optimization of a pressure swing adsorption unit, the goal is to maximize the cumulative cash flow within the equipment lifetime, LT. The cumulative cash flow is a function of the operating costs, OC; the investment, I; and the product value, \( P_{\text{val}} \). Assuming a 0% interest rate, the following objective function, \( F_{\text{obj}} \), can be defined

\[
F_{\text{obj}} = P_{\text{val}} LT - OCLT - I
\]  

where \( Q_{\text{in}} \) and \( Q_{c} \) are the average inlet and vent flow rates \([\text{m}^{3} \text{ (STP)/year}]\), respectively; EC is the energy cost \([$/\text{J}]\); and \( W_{c} \) and \( W_{e} \) are the theoretical amounts of work \([\text{J} / \text{m}^{3} \text{ (STP)}]\) done by the compressor and vacuum pump (naturally, for PSA units, \( W_{c} = 0 \), respectively. For a single-stage compressor, these values are given by\(^{25}\)

\[
W_{c} = \left( \frac{\gamma}{\gamma - 1} \right) \frac{P_{\text{atm}}}{T_{0}} \left[ \left( \frac{P_{H}}{P_{\text{atm}}} \right)^{(\gamma - 1)/\gamma} - 1 \right]
\]

\[
W_{e} = \left( \frac{\gamma}{\gamma - 1} \right) \frac{P_{\text{atm}}}{T_{0}} \left[ 1 - \left( \frac{P_{L}}{P_{\text{atm}}} \right)^{(\gamma - 1)/\gamma} \right]
\]

where \( \gamma \) is the ratio between the specific heat capacity at constant pressure and the specific heat capacity at constant volume (for air, \( \gamma = 1.4 \)) and the superscript 0 stands for standard temperature and pressure conditions (STP).

The investment depends on the costs of the adsorbent, \( C_{\text{ads}} \), the column, \( C_{\text{col}} \), the storage tank, \( C_{\text{ST}} \); the compressor, \( C_{\text{comp}} \); and other equipment such as valves, orifices, tubes, and fittings, \( C_{\text{other}} \). For a VPSA unit, the investment also depends on the cost of the vacuum pump, \( C_{\text{vpump}} \), and can be given by the following expression

\[
I = C_{\text{ads}} + C_{\text{col}} + C_{\text{ST}} + C_{\text{comp}} + C_{\text{vpump}} + C_{\text{other}}
\]
where \( c_{\text{ads}} \) is the adsorbent price ($/m^3); \( c_{\text{col}} \) is the column price, which is a function of the column volume, \( V \); \( c_{\text{ST}} \) is the storage-tank price (when made of the same material, \( c_{\text{ST}} \) is the same as \( c_{\text{col}} \), which is a function of the storage-tank volume, \( V^T \); and \( \beta_i \), \( \kappa_i \), and \( \gamma_i \) are correlation parameters.26

The product value can be defined as

\[
P_{\text{val}} = Q_{\text{prod}} \times p
\]

where \( Q_{\text{prod}} \) is the production flow rate [m\(^3\) (STP)/year] and \( p \) is the product price.

The objective function can be written as follows

\[
F_{\text{obj}} = \frac{F_{\text{obj}}}{Q_{\text{prod}}} = \left[ p - \left( \frac{Q_{\text{in}}}{Q_{\text{prod}}} \right)^{\gamma_1} \right] \frac{V}{Q_{\text{prod}}} c_{\text{ads}} - (P^H)^{\beta_1} c_{\text{col}}. \]

\[
- \frac{V}{Q_{\text{prod}}} (P^H)^{\beta_2} c_{\text{ST}} - \frac{\kappa_1}{Q_{\text{prod}}} \frac{Q_{\text{in}}}{Q_{\text{prod}}} \gamma_1 \left( \frac{Q_{\text{v}}}{Q_{\text{prod}}} \right)^{\gamma_3} - \frac{\kappa_2}{Q_{\text{prod}}} \frac{Q_{\text{in}}}{Q_{\text{prod}}} \gamma_2 \left( \frac{Q_{\text{v}}}{Q_{\text{prod}}} \right)^{\gamma_4} = \frac{\kappa_3}{Q_{\text{prod}}^{1-\gamma_4}} \left( \frac{Q_{\text{v}}}{Q_{\text{prod}}} \right)^{\gamma_5} \frac{\kappa_4}{Q_{\text{prod}}^{1-\gamma_4}} \left( \frac{Q_{\text{in}}}{Q_{\text{prod}}} \right)^{\gamma_5} \frac{\kappa_5}{\gamma_5} \left( \frac{Q_{\text{in}}}{Q_{\text{prod}}} \right)^{\gamma_5}
\]

For PSA units, the parameters \( \kappa_3 \) and \( \kappa_4 \) are nil. Assuming that the columns and storage tank have the same cross-sectional area, we can write the objective function in terms of the product purity, \( P_r \), product recovery, \( R_p \); and the model parameter \( R_p^b \).

\[
F_{\text{obj}} = \left\{ \frac{\gamma_1}{Q_{\text{prod}}^{1-\gamma_4}} \right\} \frac{\gamma_5}{Q_{\text{prod}}^{1-\gamma_4}} \left( \frac{Q_{\text{v}}}{Q_{\text{prod}}} \right)^{\gamma_5}
\]

For small pressure swing adsorption units, the operating costs are negligible when compared to the invest-

ment costs.11 Therefore, the optimization can be performed to maximize the recovery, \( R_p \). This approach has the advantage of being independent of the adsorbent, column, storage-tank, and energy prices.

The power consumption per unit flow rate, \( \Psi \), expressed in megajoules per cubic meter, of a VPSA unit can be calculated by dividing the operating costs (see eq 22) by the product flow rate, resulting in the following expression

\[
\Psi = \int_0^{\theta_{\text{prod}}} \left[ 10^{-1} \gamma_1 \gamma_2 (P^H)_{\text{col}} \left( \frac{P_{\text{atm}}}{P^H} \right)^{\gamma_1} \right] d\theta
\]

For a PSA unit, it is given by

\[
\Psi = \int_0^{\theta_{\text{prod}}} \left[ 10^{-1} \gamma_1 \gamma_2 (P^H)_{\text{col}} \left( \frac{P_{\text{atm}}}{P^H} \right)^{\gamma_1} \right] d\theta
\]

The optimization was carried out using a successive quadratic-programming algorithm (SQP)27 developed in our previous work.11

The following restriction was imposed on the product purity (purity of oxygen plus argon): \( P_r = 0.99 \), about 94.5% in oxygen.

**Optimization Results**

The optimization results for the three adsorbents considered as a function of \( R_p^b \) (\( R_p^b = \kappa_2 R_p^b / \gamma_5 \)) are presented in the next figures.

Figure 3 shows the maximum product recoveries for (a) the PSA unit and (b) the VPSA unit.

Figure 4 shows the power consumption per unit product flow rate expressed in megajoules per cubic meter for (a) the PSA unit and (b) the VPSA unit.

As can be seen, both the PSA and VPSA units have a high performance when using Oxysiv 7. This adsorbent allows the use of lower \( R_p^b \) values in the VPSA, which means that, because the adsorption kinetic coefficients do not differ significantly among the adsorbents, the adsorption column can be smaller or the product flow rate can be higher for Oxysiv 7 compared to the other adsorbents. The smallest VPSA unit with Oxysiv 7 has about one-half the volume of the smallest unit with MS 624 for the same production flow rate and purity. However, Oxysiv 7 is more expensive than the other adsorbents studied. Judging from the results obtained, for the same recovery, the use of Oxysiv 7 is advantageous if it costs less than about twice the price of the other adsorbents.

The VPSA unit was found to have the lowest power consumption per unit product flow rate, but except with Oxysiv 7, it should have about twice the volume or produce one-half the product flow rate of a PSA unit. In PSA, a unit with Oxysiv 7 or MS 624 should produce twice the product flow rate or should have one-half the volume compared to one with Oxysiv 5.

Relating the power consumption achieved with the three adsorbents, we verified that PSA units with MS 624 and Oxysiv 5 consume, respectively, about 1.2 and 1.3 times more than the unit with Oxysiv 7. The power
The optimum ratios between the column and storage-tank lengths for the PSA and VPSA units are presented in Figure 5a and b, respectively. It can be observed that PSA allows, in comparison to VPSA, a higher ratio between the column and storage-tank lengths, which means that smaller tanks can be used. For small $R_p^b$ values, i.e., smaller units or higher product flow rates, the storage tank has to be larger.

The optimum purge valve parameters for the PSA and VPSA units are presented in Figure 7a and b, respectively.
As a consequence, the unit will take more time to reach the cyclic steady state. Medical oxygen pressure swing adsorption units must start producing oxygen with a purity above 82% in a very short time interval. Another disadvantage is that the optimum found for small $R_p^b$ values is not robust, which means that slight variations in the operating conditions result in significant variations in the unit performance. This “instability” can be observed in the abrupt variation of the optimization variables for small $R_p^b$ values. Therefore, this region should be avoided.

The PSA operating mode requires lower values of the purge valve parameters and longer cycles than VPSA. Oxysiv 7 and MS S 624 allow higher pressurization/production times than Oxysiv 5 in both operating modes. This is expected because these two adsorbents exhibit higher capacities for nitrogen than Oxysiv 5.

The optimal storage-tank valve parameter, feed valve parameter, and vent valve parameter were found to be independent of the unit size and product flow rate. Table 5 presents the optimum values found for these variables for the different adsorbents.

This essentially means that an optimal unit should have pressure drops in the feed, vent, and storage-tank tubes that are as small as possible.

### Comparison between Simulation and Experimental Results

A comparison between the simulation and the real results was conducted using a commercially available small medical oxygen pressure swing adsorption unit filled with Oxysiv 5 and working in the same pressure range as the simulations presented (0.1–0.3 MPa). The unit was tested for a set pressurization/production time and for different production flow rates. The unit characteristics are presented in Table 6.

The purge valve parameter, $K_v^P$, was measured experimentally. The storage-tank and vent valve parameters, $K_v^T$ and $K_v^V$, respectively, were determined by fitting the simulated pressure histories to the measured pressure histories of one of the experiments. It was then verified that the simulated results obtained with these parameters also yielded very good agreement with the other experimental data for different flow rates.

The feed flow rate given by the unit’s compressor was experimentally found to be described by the following correlation

$$
\text{In contrast to eq 12, the use of eq 37 implies the knowledge of the production flow rate and is not limited by the high pressure. However, for the purpose of optimizing an already-existing unit, because the product flow rates are set, this equation can be used, so that actual information about the compressor’s performance is incorporated into the optimization procedure.}
$$

The pressure drop along the bed was measured and verified to be negligible, validating the assumption made in the formulation of the model.

Experimental and simulation curves of purity and recovery as a function of the production flow rate are presented in Figure 8 and are in good agreement.

The simulated pressure histories, inside the columns, for each operating condition tested were also in agreement with the experimental results, as can be seen in Figure 9.
Simulation of this specific kind of cycle has never been previously published in the open literature. This work contributes to a better understanding of the operation of these units and establishes an efficient strategy for expeditiously obtaining the optimal values for a set of relevant variables, leading to improved design and performance.

Oxysiv 7 was found to provide the best performance for both VPSA and PSA units, followed by MS S 624 and Oxysiv 5. The use of Oxysiv 7 and MS S 624 in PSA and Oxysiv 7 in VPSA will result in smaller units or higher production flow rates. However, Oxysiv 7 has a higher cost compared to the other adsorbents studied. The decision on which adsorbent to use must be based on an economic judgment.

As expected, vacuum and pressure swing adsorption units were found to be less power-consuming per unit product flow rate than a pressure swing adsorption unit operating with the same pressure ratio, despite the fact that the former require larger units. The balance between power consumption and portability must be considered in light of the unit’s application. Currently, power consumption is often considered as a less relevant issue for these units. However, together with other factors such as noise level and portability, it might acquire significance in highly competitive markets.

The work presented in this paper can help in determining which adsorbent and operation mode are most suitable to face the market’s demands.

**Acknowledgment**

The work of J.C.S. was supported by FCT Grant SFRH/BD/6817/2001. The work of A.F.P. was supported by Project Growth GRD1-2001-40257. This research was also supported by funds from this project and from FCT Project POCTI/EQU/38067/2001.

**Nomenclature**

\( c_{\text{ref}} \) = reference fluid-phase molar concentration, \( c_{\text{ref}} = P_{\text{ref}}/T_{\text{ref}} \)

\( C_v \) = valve parameter

\( D_{ax} \) = effective axial dispersion coefficient, \( \text{m}^2/\text{s} \)

\( k = \text{LDF kinetic coefficient}, \text{L/s} \)

\( K_c = 1 \) parameter

\( L = \text{adsorption-column length}, \text{m} \)

\( L_T = \text{storage-tank length}, \text{m} \)

\( N = \text{molar flow rate}, \text{mol/(m}^3\text{-s)} \)

\( N^* = \text{dimensionless molar flow rate}, N^* = N/\theta_{\text{ref}}(c_{\text{ref}}/c_{\text{std}}) \)

\( n_c = \text{number of components in the mixture} \)

\( P = \text{total pressure}, \text{Pa} \)

\( Pe = \text{Pe} \) number for mass transfer, \( Pe = u_{\text{ref}}D_{ax} \)

\( q = \text{average molar concentration in the adsorbed phase}, \text{mol/kg} \)

\( q = \text{molar concentration in the adsorbed phase, mol/kg} \)

\( Q_{\text{prod}} = \text{product flow rate, m}^3/\text{(STP/s)} \)

\( R = \text{universal gas constant, (Pa}\cdot\text{m}^3)/(\text{mol} \cdot \text{K}) \)

\( R_p = \text{ratio between the bed time constant and the particle diffusion time constant}, R_p = k_{\text{ref}}\theta_{\text{ref}} \)

\( t = \text{time variable}, \text{s} \)

\( T = \text{temperature}, \text{K} \)

\( u = \text{interstitial molar velocity}, \text{m/s} \)

\( u^* = \text{dimensionless interstitial velocity}, u^* = u/\theta_{\text{ref}} \)

\( u^t = \text{dimensionless velocity of the gas entering or leaving the storage tank} \)

\( x = \text{dimensionless spatial coordinate}, x = z/L \)

\( y = \text{molar fraction in the gas phase} \)
$z = \text{spatial coordinate, m}$

**Greek Symbols**

$\alpha_i^D = \text{ratio between the diffusivity coefficients, } \alpha_i^D = k_i/k_{\text{ref}}$

$\epsilon_b = \text{bed void fraction}$

$\epsilon_p = \text{particle void fraction}$

$\gamma = \text{ratio between the specific heat capacity at constant pressure and the specific heat capacity at constant volume}$

$\rho_a = \text{adsorbent apparent density, kg/m}^3$

$\theta = \text{dimensionless time variable, } \theta = t/\theta_{\text{ref}}$

$\theta_{\text{ref}} = \text{bed time constant, } \theta_{\text{ref}} = L/\theta_{\text{ref}}$

$\zeta_a = \text{adsorbed-phase capacity factor, } \zeta_a = \rho_a[(1 - \epsilon_b)\epsilon_b]^{1/\theta_{\text{ref}}}$

$\zeta_p = \text{fluid-phase capacity factor, } \zeta_p = \epsilon_p(1 - \epsilon_b)/\epsilon_b$

$\Psi = \text{power consumption per product unit flow rate, MJ/m}^3$

**Subscripts**

$i = \text{i}th \text{ component}$

$\text{ref} = \text{reference}$

**Superscripts**

$^* = \text{dimensionless}$

$F = \text{feed}$

$H = \text{high}$

$L = \text{low}$

$P = \text{purge}$

$T = \text{storage tank}$

$V = \text{vent}$

**Literature Cited**


**Received for review April 13, 2004**

**Revised manuscript received September 2, 2004**

**Accepted October 11, 2004**