Review

Benchmarking Thermodynamic Models for Optimization of PSA Oxygen Generators

Michael L. Carty and Stephane Bilodeau

Appendices

A) The Principle of Pressure Swing Adsorption

Pressure swing adsorption (PSA) is the process by which ambient air passes through an internal filtration system (e.g. a molecular sieve [zeolite granules or membranes]), which has a large enough total surface area to separate nitrogen (N_2) from the air, concentrating the remaining oxygen (O_2) to a known purity. It typically consists of an air compressor, dryer, filters, dual separation chambers, a reservoir, and controls.

PSA is an economic and reliable method used to separate mixed gas into individual gases while achieving a high purity level. PSA is a non-cryogenic air separation process which essentially means it is a process that uses near ambient temperatures for the production of nitrogen or oxygen in contrast to the cryogenic distillation techniques of gas separation which take place are very low temperatures and is a process commonly employed in chemical and petrochemical processes in commercial practices.

During the Skarstrom-type cycle (see Figure A1), gases are separated under pressure based on the species molecular characteristics and affinity for an adsorbent material. PSA is used to recover hydrogen from coking or conversion gases or to split oxygen and nitrogen from the air.

In pressure swing adsorption, specialized adsorbent materials adsorb the gas molecules such as oxygen, carbon dioxide, water vapor, and other gases under high pressure except for nitrogen. PSA systems for oxygen production were first used during the 1970s and since then the technology has overall shown rapid improvement.

The concentration of oxygen can be reduced to meet the required purity levels. During adsorption in one tower, the second tower is regenerated just by depressurization to ambient pressure. Regeneration can also be referred to as "purging" and is the process in which the gases except for nitrogen accumulated during the cycle are stripped away. The Oxygen enriched off-gas is then vented to the outside atmosphere and after so many minutes adsorption in one tower switches over to the second tower and the first one is regenerated.

Each PSA system uses specialized adsorbent materials such as zeolites, molecular sieves, activated carbon, etc. These substances are used as a trap, ideally adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material hence the name pressure swing adsorption. This adsorption process is based upon the gas molecules binding to these absorbent materials, preferably only the gas, which is to be absorbed, while all other gases in the mixture pass through the adsorbent bed.

Here it is essential to understand the difference between adsorption and absorption. The Pressure Swing Adsorption separation system is based on the principle of adsorption. Adsorption is a surface-based procedure while absorption involves the whole volume of the material. The adsorption method is when the gas or liquid molecules adhere to the surface of the adsorbent. This process creates a film of the adsorbate on the surface of the adsorbent.

The individual modes of operation that constitute a single-bed PSA cycle are shown in Figure S1. During the first stage, the (less strongly adsorbed) O_2 is collected from the effluent stream, and the strongly adsorbed N_2 is captured by the adsorbent. Next, the adsorbent inside the bed is regenerated with a combination of depressurization and purge steps.
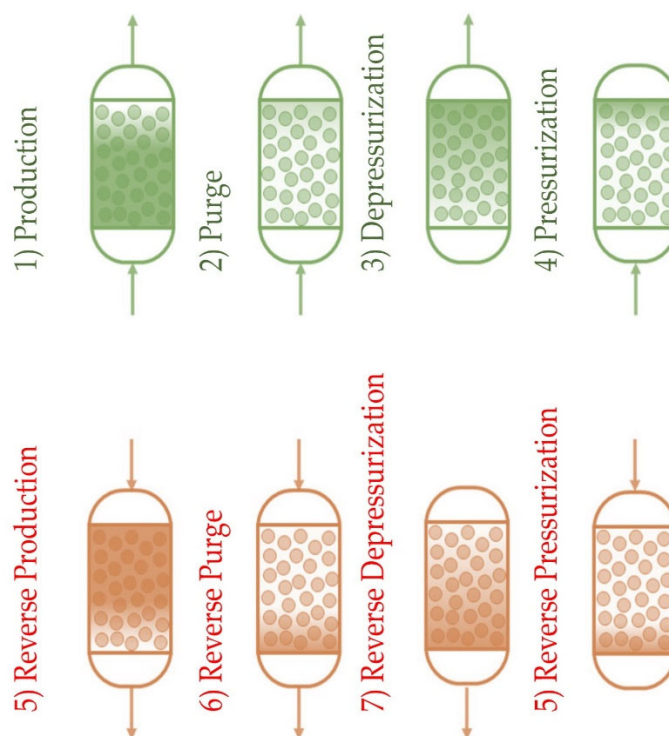

Figure S1. The PSA-based MOC cycle divided into eight processes, with the shade representing the adsorbent column saturated with oxygen adsorbate.

This cycle comes with several advantages. One of them is reusing the oxygen product later during steps 2 and 4. This boost regeneration of the adsorbent column improves the oxygen product purity generated during

step 1. Also, as Oxygen is produced only during a fraction of overall cycle operation, multiple beds could be designed and operated in an integrated way to result in continuous oxygen product generation.

A PSA System essentially consists of two or more adsorption towers filled with absorbent materials, filters, and a storage tank. One of the benefits of a PSA system is that stabilizes the purity of the gas. This is generally done by the manufacturer of the generator based on 2 main points: The amount of absorbent materials in the tower and the amount of time the air is in the towers. Of course, the quality of the materials used will also affect the purity of the gas produced.

To simulate the adsorption processes for air separation operating under a pressure swing, we consider it to be based on a Skarstrom-type cycle consisting of a repetition of four different steps (see Figure S2):
(1) The generation of high-pressure products,
(2) Depressurization,
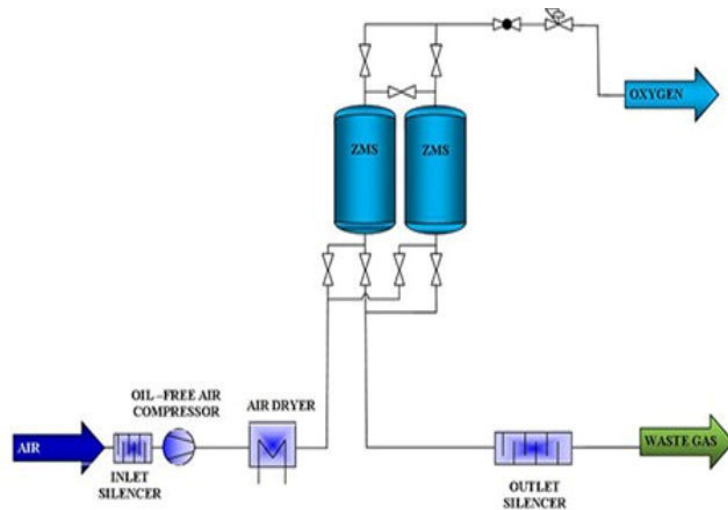(3) The low-pressure purge and,
(4) The Pressurization.

Figure S2. PSA (Skarstrom-type cycle) generic process including [1] Pressurization of the Inlet Gas [2] Adsorption of the inlet gas at high pressure [3] depressurization to the atmospheric pressure, where it releases C02, at the bottom of the desorption column and [4] desorption of C02 gas from the adsorbent with a purging gas.

After having passed the [1] Pressurization, [2] Adsorption at high pressure, and then [3] depressurization to the atmospheric pressure, with [4] desorption of C02 gas from the adsorbent with purging gas, the gases are then introduced into the first tower and pressurized, resulting in C02 adsorption. The applied pressure is then transferred to the second tower. While the second tower is pressurized the first tower is depressurized, and the carbon dioxide is separated. During the desorption steps, the inlet C02 gas stream is stopped and N2 is only introduced to desorb C02 after the depressurization.

This cycle then continues switching from an adsorption tower to a desorption tower.

B) Assumptions and conservation equations

Typically, a NAPDE-based simulation model is used and coupled with a limited gray box optimization solver for the design, synthesis, and optimization of PSA systems. Such optimization-based analysis could then result in the generation of feasible process performance curves. Additionally, we can simulate the use of different zeolites. These material-specific characteristics, when combined with an in-depth analysis of PSA flexibility, we take advantage of the simulation-based optimization framework to assess the impact of varying material properties, bed design, and operating conditions of operation on the performance of the process.

The mathematical models of mass, energy, momentum, adsorption equilibrium, and LDF Equations are bound to a set of assumptions that are listed below.

Assumptions:
(1) The gas phase is considered an ideal gas.
(2) No radial variation in gas concentration, temperature, and pressure.
(3) Pressure drop along the bed is calculated by the Ergun equation.
(4) The gas and solid phase are always in thermal equilibrium.
(5) The porosity of the bed and adsorbent particle is uniform along the bed.
(6) The mass transfer coefficient (interphase) is expressed by the linear driving force (LDF) model.
(7) Extended-Langmuir model is used to describe the adsorption behaviors.

Although PDE models have higher predictive ability, rigorous optimization using PDE models remains a challenge. One of the approaches studied in the literature is to discretize PDEs and convert them into algebraic equations. The resulting optimization model then becomes a large-scale non-linear programming problem. Although promising results were obtained, the level of discretization used in this work was moderate to keep the non-linear model tractable and in doing so some degree of accuracy was lost.

In the second approach, the cycle is simulated by assimilating the process to the 'Single Bed Approach' and applying it until the achievement of cyclic steady-state conditions (CSS). Followed step by step throughout the entire separation cycle, the evolution of properties (including concentration, pressure, and velocity profiles) in the simulated column is monitored throughout the calculation process. The interplay with the second bed (third and more if need be) is accounted for through the introduction of a set of 'interaction modules' (I). All adsorbent beds undergo the same steps in a given cycle and are assumed to be identical (i.e., with the same length, feed positive cross-sectional area (Abed), interstitial porosity (ε_i), particle porosity (ε_P), amount of adsorbent (and kind), particle size, solid (ϱ_S) and bulk densities (ϱ_B). In a sequential buffer profile, all the properties of the selected

leaving stream are taken and transferred as input data once necessary in the boundaries of the process cycle.

If the system is modeled using a set of algebraic equations, optimization can be performed using existing local and global solvers. However, in many cases, an algebraic model may not be available or may not be adequate to allow detailed optimization. A more realistic model that considers the spatial and temporal variation of the properties of the system could be given by a set of partial differential equations (PDEs). An alternative and promising optimization strategy is to use simulation data to optimize while maintaining a high level of model accuracy. Of course, using a high discretization number will increase the computation time of the simulation. Therefore, the challenge is to get the optima using a few evaluations.

The 3 main Conservation equations are generally aa follow, but they are detailed (or simplified) further depending on the exact thermodynamic model that is used and also complemented with Momentum Balance and Adsorption Balance:

Mass Balance

$$-\varepsilon_b D_{ax,i} \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial^2 (v_g c_i)}{\partial z^2} + \left(\varepsilon_b + (1-\varepsilon_b)\varepsilon_p\right)\frac{\partial c_i}{\partial t} + \rho_s(1-\varepsilon_b)\frac{\partial c_i}{\partial t} = 0$$

S1)

Energy Balance in the Gas Phase

$$-k_g \frac{\partial^2 T_g}{\partial z^2} + C_{pg}v_g\rho_g\frac{\partial T_g}{\partial z} + \varepsilon_b C_{vg}\rho_g\frac{\partial T_g}{\partial t} + P\frac{\partial v_g}{\partial z} + h_f\left(T_g - T_s\right) + \frac{4h_{wg}}{D_b}\left(T_g - T_w\right) = 0$$

S2)

Energy Balance in the Solid Phase

$$-k_g \frac{\partial^2 T_s}{\partial z^2} + C_{ps}\rho_s\frac{\partial T_s}{\partial z} + \rho_s \sum_{i=1}^{n}(C_{pg,i}q_i)\frac{\partial T_s}{\partial t} + \rho_s \sum_{i=1}^{n}\Delta H_i\frac{\partial q_i}{\partial t} - h_f\left(T_g - T_s\right) = 0$$

S3)

For these conservation equations, the following parameters are considered: C molar concentration of mixture, C_i molar concentrations of component i, c_{pg} specific heat capacity of gas phase, c_{pg} specific heat capacity of gas phase, c_{ps} specific heat capacity of adsorbent, c_{pw} specific heat capacity of column wall, h_{in} heat transfer coefficient with inner wall of column, h_{out} heat transfer coefficient with outer wall of column, Δh_i heat of adsorption of component i, ΔH_i heat of adsorption of component i, k_i mass transfer coefficient of component i, P pressure, R universal gas constant, R_{in} inner radius of column, R_{out} outer radius of column, t time, T temperature of adsorption bed, T_f ambient temperature, T_w wall temperature, x_i mass fraction of component i $y_{i,}$, ε_b bed porosity, ρ_g mass concentration (density) of mixture gas, ρ_l mass concentrations of component i, ρ_b bed density of adsorbent, ρ_p particle density of adsorbent, ρ_s skeletal density of adsorbent.

C) Other design considerations

While PSA oxygen generator plants are designed to concentrate Oxygen from ambient air scale, output capacity, and performance vary substantially according to calculated oxygen demand, and environmental and operating conditions. Especially in smaller settings (from the primary to the tertiary), optimization of the units should also integrate the distribution of Oxygen produced from PSA plants. The ease of implementation of a small, packaged, PSA unit is coming with a limited production capacity. But the medium-sized PSA unit might be more attractive for actual demand, when, for example, the number and scale of beds must be quickly increased in a secondary or tertiary level hospital.

Although complex, with many parameters and unknowns, modeling is important because specific adsorption technologies being considered for MOC include pressure swing adsorption (PSA) units, which operate dynamically with multiple operating modes and periodic cycles. The operating context is essential to correctly simulate the process and can vary considerably, not only from one installation to another but also from time to time, according to the procedures in progress, while being in the same operating environment. For example, in real operation, at any given time, Oxygen can be piped directly from the oxygen tank attached to the unit to quarters or further compressed to fill cylinders via an additional booster and refill ramp/manifold.

Since the requirements in terms of the quantity of final use of oxygen products differ, many optimization case studies can be carried out with different operating conditions. In this model, ten decision variables are used to generate the optimal cycle design and the functioning of the PSA for air separation. These include the air supply flow, 3 operating pressure variables, 4 cycle stops, the purge flow speed factor, and the apparent density of the adsorbent.

The effect of pressure, temperature, bed size, and other parameters on oxygen concentrator efficiency was also considered to determine the appropriate device design. As an example, to give perspective, Table S1 shows a comparison of tank size, materials used, flow rate, and the use of an air compressor oxygen analyzer to ensure proper monitoring of units.

Table S1. Example of Operating Conditions (Tank Size, Material Used, Flow, and Air Compressor) and Performance.

Flowrate	Operating Conditions	Sodium Zeolite	Lithium Zeolite
5 L/min	Tank size (2x)	$35*7.5*0.3$ cm$_3$	$33*5*0.2$ cm$_3$
	Oxygen purity	93-96 %	98-99 %
	Air compressor	135 L/min	100 L/min
10 L/min	Tank size (2x)	$43*7.5*0.25$ cm$_3$	$33*5*0.2$ cm$_3$
	Oxygen purity	94-96 %	97-99 %
	Air compressor	280 L/min	140 L/min

An early evaluation using, for validation purposes, the methods discussed in the previous section, made it possible to obtain interesting results. In particular, in combination, a device producing 22 L/m with a purity corresponding to 93% oxygen, in addition to a production of 10 L/m with a purity of 98% oxygen. By extending the approach and comparing different configurations of zeolite, the following observations can be made by simply adjusting the parameters concerned:

• The air compressor used in the lithium zeolite oxygen concentrator is smaller than that used in the sodium zeolite. Indeed, the volume of the sodium reservoir is twice as large as that using lithium, which requires additional pressure to increase the flow.
• While moisture filters or air dryers are very important to ensure that the device works longer, the air cooling unit is a very important part, the more efficient the cooling, the higher the purity of Oxygen is high.
• For small oxygen concentrators, lightweight lithium zeolite would be a better "thermodynamic" option, but generally, for lower material costs and larger volumes such as small plants, sodium zeolite would be the best choice.
• Two tanks of sodium zeolite (45 cm x 7.5 cm x 3 mm) need 3 to 4 kg of sodium zeolite to produce 10 liters per minute with an oxygen purity of 94 at 97%. In turn, this requires a 2 HP compressor to produce around 290 l/min. While two lithium zeolite tanks (25cm x 7cm x 3mm) need 1.8-2.2 kg of lithium zeolite to produce 10 liters per minute with 95-98% oxygen purity. A 1 hp compressor is then required to produce approximately 155 L/m.

PSA units are important medical devices, and systematic approaches to ensuring their quality and maintenance are essential to reducing hypoxemia-associated mortality. Management, clinicians, and technicians are needed to ensure effective implementation and timely maintenance of oxygen concentrators.

D) Examples of variables Bounds for Process Optimization

The following tables outline the variables Bounds for Process Optimization using that could be used in 3 NAPDE-based models (Table S2), and the Process Simulation Parameters utilized for solving the NAPDE-based process simulation (Table S3)

Table S2. Example of Decision variable bounds on design and operation of adsorption based MOC.

Input variable(s)	Unit	Lower bound	Upper bound
Feed flow rate	mol/s	0.01	0.25
Step pressure	bar	-3.5*	3.5
Step duration	s	1	10
Purge flow velocity factor	-	0.1	3
Adsorbent bulk density	kg ads./m³ bed	0.35 $\rho_{p,ads}$	0.65 $\rho_{p,ads}$

Table S3. Example of Parameters utilized for solving the NAPDE-based process simulation.

Input variable(s)	Unit	Value
Axial gas heat conductivity	J/(m·s·K)	0.29
Bed length	m	0.127
Bed radius	m	0.05
Bed-wall heat transfer coefficient	W/(m²·K)	70
Feed temperature	K	298
Number of cycles	-	50
Number of spatial nodes	-	10
N_2 viscosity	Pa · s	1.78×10^{-5}
O_2 viscosity	Pa · s	2.02×10^{-5}
Particle diameter	m	0.035
Wall heat capacity	J/(kg·K)	502
Wall density	kg/m³	7800