Production of Oxygen Enriched Air by Rapid Pressure Swing Adsorption

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Abstract. A novel rapid pressure swing adsorption (RPSA) process is described for production of 25–50% oxygen enriched air. The embodiment consists of one or more pairs of adsorbent layers contained in a single adsorption vessel. The layers undergo simultaneous pressurization-adsorption and simultaneous depressurization-purge steps. A total cycle time of 6–20 seconds is used. The process yields a very large specific oxygen production rate and a reasonable oxygen recovery for production of 20–50 mole% oxygen enriched gas.

It is demonstrated by a simple mathematical model of isothermal single adsorbate pressure swing ad(de)sorption concept on a single adsorbent particle that the specific production rate of a PSA process cannot be indefinitely increased by reducing the cycle time of operation when adsorbate mass transfer resistances are finite.

Introduction

Numerous pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) process cycles have been designed during the last thirty years for production of oxygen-enriched air stream from ambient air (Sircar, 1989; Ruthven et al., 1994; Keller et al., 1987). These processes mostly use a nitrogen-selective (thermodynamic) zeolite adsorbent for producing an oxygen-enriched air stream containing 25–95 mole% O_2. They differ by the modes and conditions of operation of the adsorption, the desorption, and the other complementary steps used in the process cycle as well as by the type of adsorbent and the number of parallel adsorbers employed in the design. The net production capacity of the oxygen-enriched stream by these processes generally vary only between 0.02–0.08 millipound moles per pound of total adsorbent in the system per cycle of operation. This low production capacity is caused by (a) inherently low quantity of oxygen produced per unit amount of nitrogen adsorbed from the ambient air, (b) loss of a part of the co-adsorbed and void gas oxygen from the adsorber during the depressurization step of the process, and (c) loss of a part of product oxygen which is used as purge gas to desorb the nitrogen. The fractions of these oxygen losses are different for different process designs and the adsorbent used, but the typical oxygen recovery in product from the feed air varies between 20–60%. The net production rate

(lb moles/hour/lb of adsorbent) of the oxygen-enriched gas depends on the total cycle time for the process. Typically, a total cycle time of 60–240 seconds is employed in order to accommodate various steps of the process which are introduced to enhance the overall efficiency (decrease adsorbent inventory and energy) of the PSA or VSA air separation process.

It may be apparent that the net production rate of the oxygen-enriched product gas can be increased if the total process cycle time is reduced. This concept of rapid pressure swing adsorption (RPSA), however, may have limitations because (a) a short total cycle time may not permit the conventional practice of using several sequential cycle steps in the process design, thereby reducing the separation efficiency, and (b) the existence of a finite adsorbate mass transfer resistance for adsorption may introduce only a marginal increase in the production rate when the cycle time is indefinitely reduced.

A RPSA process for air separation using a zeolite and a single packed bed adsorber was introduced by Jones, Keller and Wells (1980), and Keller et al. (1987). The cyclic process steps consisted of (a) introducing compressed air to the adsorber for a short period of time, and then (b) stopping introduction of air for a short period, followed by (c) countercurrent depressurization of the adsorber to near ambient pressure through the feed end. An oxygen-enriched product gas was continuously withdrawn through the product end of the

adsorber during the entire period of time (steps a–c). Several modifications of this process were also proposed (Earls and Long, 1980; Dangieri and Cassidy, 1983) by employing two or more parallel adsorbers and by introduction of a product oxygen repressurization step between steps (c) and (a) above. This process in its original form has been extensively evaluated by Pritchard and Simpson (1986), and Chou and Wu (1994) using 5 A zeolite as the adsorbent. Typical cycle times of 0.5–3, 0.5–1.0 and 2–10 seconds for steps (a), (b) and (c) respectively, were used by these authors.

More recently, Sakoda and Suzuki (1992) reported a RPSA process for air separation where a fixed layer of a zeolite adsorbent was mounted at the mouth of a cylinder fitted with a piston. Air was sucked into the cylinder through a valve during the downward stroke of the piston which also created a lower pressure in the adsorbent causing desorption of nitrogen which was discharged through another valve. Air was compressed and passed through the adsorbent layer during the upward stroke of the piston causing adsorption of nitrogen and production of an oxygen-enriched gas stream at the outward end of the adsorbent layer. A very short piston stroke time of 0.25–1.0 seconds was used in this concept.

The purpose of this work is to report on a novel RPSA cycle designed and patented by Air Products and Chemicals, Inc. (Sircar, 1991). It can be very efficiently used for production of oxygen-enriched gas (25–60 mole% O_2) from ambient air.

Kinetic Limitation of RPSA Concept

It was mentioned earlier that a finite adsorbate mass transfer resistance for adsorption can limit the increase in the production rate of a RPSA process by decreasing the total cycle time. This point is demonstrated below by considering the isothermal adsorption and desorption of a single adsorbate from an inert gas on a single spherical adsorbent particle of radius Z.

It is assumed that the adsorbent particle is subjected to a periodic gas phase partial pressure change of the adsorbate at a constant temperature. The gas phase partial pressure is held constant at p_A during the adsorption step (time t_A), and then it is held constant at p_D ($<p_A$) during the desorption step (time t_D). n_A^* and n_D^* are, respectively, the equilibrium specific amounts (moles/lb) adsorbed at pressures p_A and p_D. f_A and f_D are, respectively, the fractional adsorbate uptake and loss during the cyclic steady state process. f_A and f_D are functions of t_A and t_D for a given set of p_A and p_D. One may then write

$$f_A(t_A) = \left[\frac{\bar{n}_A - \bar{n}_D}{n_A^* - \bar{n}_D}\right] \qquad (1)$$

$$f_D(t_D) = \left[\frac{\bar{n}_D - \bar{n}_A}{n_D^* - \bar{n}_A}\right] \qquad (2)$$

where $\bar{n}_A$ and $\bar{n}_D$ are, respectively, the average specific amounts adsorbed (moles/lb) at the end of the adsorption and desorption steps under cyclic steady state condition. The specific steady state working capacity of the adsorbent particle for adsorbate removal (N) is given by

$$N = (\bar{n}_A - \bar{n}_D) \qquad (3)$$

N is a function of t_A and t_D.

The specific steady state working capacity of the adsorbent particle for adsorbate removal (N^*) when there is no adsorbate mass transfer resistance ($f_A = f_D = 1$) is given by

$$N^* = (n_A^* - n_D^*) \qquad (4)$$

Consequently, the inefficiency (ε) introduced by the existence of a finite adsorbate mass transfer resistance for adsorbate removal by the adsorbent particle is

$$\varepsilon = \frac{N}{N^*} = \frac{f_A \cdot f_D}{(f_A + f_D - f_A \cdot f_D)} \qquad (5)$$

For the special case, when the adsorption and desorption times are same ($t_A = t_D = \bar{t}$) it follows that

$$\varepsilon = \left[\frac{f}{2 - f}\right]; \quad f = f(\bar{t}) \qquad (6)$$

where $f(=f_A = f_D)$ is the fraction of uptake or loss of the adsorbate during the adsorption and desorption steps of the cycle.

Assuming that the rate of ad(de)sorption on the adsorbent particle can be described by the Linear Driving Force (LDF) model, one can write (Ruthven et al., 1994):

$$\frac{d\bar{n}(t)}{dt} = k[n^* - \bar{n}(t)] \qquad (7)$$

where $\bar{n}(t)$ is the average specific amount adsorbed (moles/lb) by the adsorbent particle at time t after the adsorption or desorption step of the cycle has started. n^* is the corresponding specific amount adsorbed (moles/lb) at equilibrium with the gas phase partial pressure of the adsorbate during the step. k(time^{-1})

is the overall adsorbate mass transfer coefficient for the ad(de)sorption process. Equation (7) can be integrated to get

$$f_A(t_A) = 1 - e^{-kt_A}; \ f_D(t_D) = 1 - e^{-kt_D} \quad (8)$$

It follows that when $(t_A = t_D = \bar{t})$, ε is given by

$$\varepsilon = \frac{N(\bar{t})}{N^*} = \frac{1 - e^{-k\bar{t}}}{1 + e^{-k\bar{t}}} \quad (9)$$

The net rate $(R = \text{moles/lb/time})$ of adsorbate removal by the cyclic process is given by

$$\frac{R}{N^*} = \frac{1}{2\bar{t}} \left[\frac{1 - e^{-k\bar{t}}}{1 + e^{-k\bar{t}}} \right] \quad (10)$$

Equation (10) shows that for a finite value of k, R increases as $\bar{t}$ is decreased, but the following limiting value of R is obtained by applying L' Hospital rule when $\bar{t} \to 0$,

$$R(\bar{t} \to 0) = \frac{k}{4} N^* \quad k = \text{finite} \quad (11)$$

On the other hand, when $k \to \infty$ Eq. (10) reduces to

$$R(k \to \infty) = \frac{N^*}{2\bar{t}} \quad (12)$$

Equation (12) shows that in the absence of an adsorbate mass transfer resistance (local equilibrium case), the net rate of adsorbate removal increases indefinitely as $\bar{t}$ is reduced, while Eq. (11) shows that R has a finite limiting value at $\bar{t} \to 0$ when k is finite. Figure 1 shows a plot of (R/N^*) as a function of $\bar{t}$ for different values of k (seconds^{-1}) according to Eq. (10). It shows that (R/N^*) for a given $\bar{t}$ decreases as k decreases. In particular, the limiting value of R at $\bar{t} \to 0$ decreases drastically as k decreases. In other words, no substantial gain in the net rate of adsorbate removal by the adsorbent particle can be achieved by reducing $\bar{t}$ beyond a certain value when k is finite. Operation of the ad(de)sorption process under local equilibrium conditions $(k \to \infty)$ or near it provides the best increase in net rate of adsorbate removal by reducing the cycle time.

The specific instantaneous amount adsorbed $[n(r, t)]$ at a radius r within the spherical adsorbent particle at time t can be described as a quadratic function of the radius for the LDF model of adsorbate mass transfer (Ruthven et al., 1994). Thus, one may write
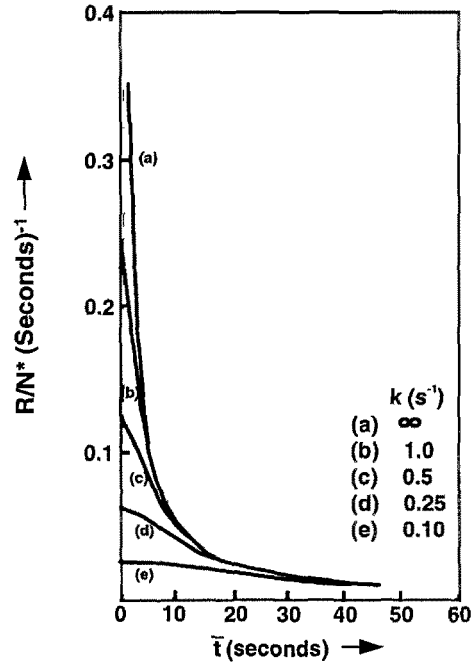
$$n^* - n(x, t) = [C(t)R^2][1 - x^2] \quad (13)$$

Fig. 1. Limiting net rate of adsorbate removal by a single particle by PSA concept.

where $x(= r/Z)$ is dimensionless radius. Equation (13) is derived by assuming that the specific amount adsorbed at the surface of the spherical particle $(r = Z x = 1)$ is at instantaneous equilibrium $[n(Z, t) = n^*]$ with the superincumbent gas phase adsorbate concentration and that the adsorbate loading profile is symmetrical $[(\frac{\partial n}{\partial r})_t = 0$ at $r = 0$ for all $t]$ within the particle. C is a function of time only.

The average specific adsorbate loading $[\bar{n}(t)]$ for the whole particle at time t is given by

$$\bar{n}(t) = 3 \int_0^1 n(x, t) x^2 dx = n^* - \frac{2}{5} C(t) R^2 \quad (14)$$

Equation (14) is equivalent to the basic LDF mass transfer mechanism [Eq. (7)] provided that

$$-\frac{d \ln[C(t)]}{dt} = k; \quad C(t) = C(0)e^{-kt} \quad (15)$$

Equation (15) defines the function $C(t)$. $C(0)$ is the value of function C at the start of the ad(de)sorption process. The function C is different for the adsorption and the desorption steps.

The specific amounts adsorbed at any value of x within the particle at the end of adsorption $[n_A(x, \bar{t})]$ and desorption $[n_D(x, \bar{t})]$ steps under cyclic steady state conditions can be calculated using Eqs. (13) and
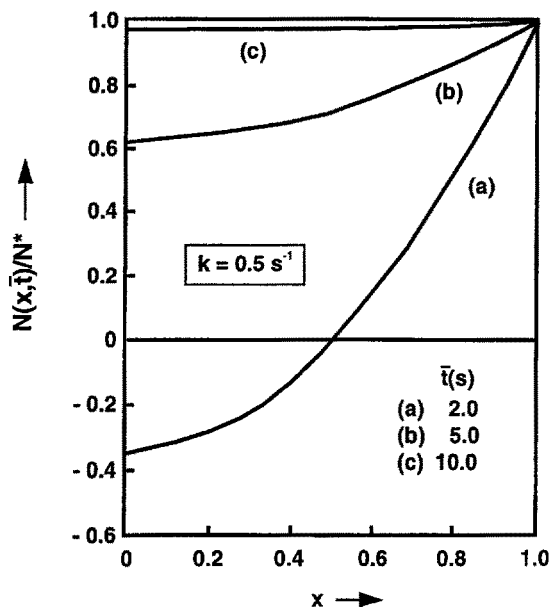
Fig. 2. Radial working capacity for adsorbate removal in a single particle by PSA concept.

(15) and a steady state local working capacity [$N(x, \bar{t})$] can be obtained as

$$\frac{N(x, \bar{t})}{N^*} = 1 - \frac{5e^{-k\bar{t}}}{[1 + e^{-k\bar{t}}]}(1 - x^2) \qquad (16)$$

Equations (14) and (16) can be combined to obtain Eq. (9) as required.

Figure 2 is a plot of Eq. (16) for different values of $\bar{t}$ at a given value of k. It shows that when the cycle time is large (curve c), the steady state local working capacity in the entire particle approaches the equilibrium working capacity (N^*). On the other hand, when the cycle time is small, (curves a and b), a large variation in the steady state local working capacity can exist within the particle including a negative working capacity (curve a) in certain portions of the particle. The reason for negative working capacity is that the adsorbent is undergoing desorption in that part of the adsorbent particle during the time period when the gas phase pressure is held at p_A and it is undergoing adsorption when the gas phase pressure is held at p_D. This causes the slowdown of the improvement in the net rate of adsorbate removal by the particle by reducing the cycle time indefinitely when the adsorbate mass transfer resistance is finite.

The above described simple model analysis illustrates the possibility of diminishing return in the rate of production of a RPSA process when the adsorbate

mass transfer resistances are finite. The adsorbate mass transfer coefficient (k) can be increased by decreasing the adsorbent particle size (reducing diffusional path length) when meso- or macro pore resistance dominates the rate of adsorption. This is the case for adsorption in most pelletized adsorbents containing micro crystals of zeolites. Smaller particle size, however, increases pressure drop for gas flow through a packed bed of the adsorbent particles. This can reduce the effective equilibrium capacity for the adsorbate across the length of the packed bed during the adsorption step of a PSA process and inhibit the desorption process by pressure reduction and purge. A large pressure drop across the adsorbent bed during the low pressure purge step can significantly inhibit the desorption efficiency. Consequently, there may be a limit of how small a particle size can be used in a PSA process which, in turn, can introduce a finite mass transfer resistance for a practical PSA system.

Novel RPSA Process for Air Separation

The novel RPSA process uses a single adsorption column which contains one pair (Fig. 3a) or more than one pair (Fig. 3b) of zeolitic adsorbent layers. Each pair of adsorbent layers is separated by a perforated screen which introduces a predesigned resistance to gas flow between them. Each layer of adsorbent in each pair undergoes the following two sequential cyclic process steps:

(a) Simultaneous pressurization with air and selective adsorption of nitrogen in order to produce an oxygen enriched gas stream. A part of this gas is withdrawn as the product gas and the balance is used as purge gas to the companion layer after its pressure is reduced across the screen. The gas pressure in the layer rises from near ambient to the highest pressure level of the cycle in a short time during this step.

(b) Simultaneous countercurrent depressurization and countercurrent purge with a part of the oxygen enriched gas produced by the companion layer in order to desorb the nitrogen adsorbed in step (a). The gas pressure in the layer decreases from the highest pressure level of the cycle to near ambient in a short time during this step.

Each adsorbent layer can contain a sublayer of a desiccant material at the air feed contact end in order to remove the water and carbon dioxide from ambient
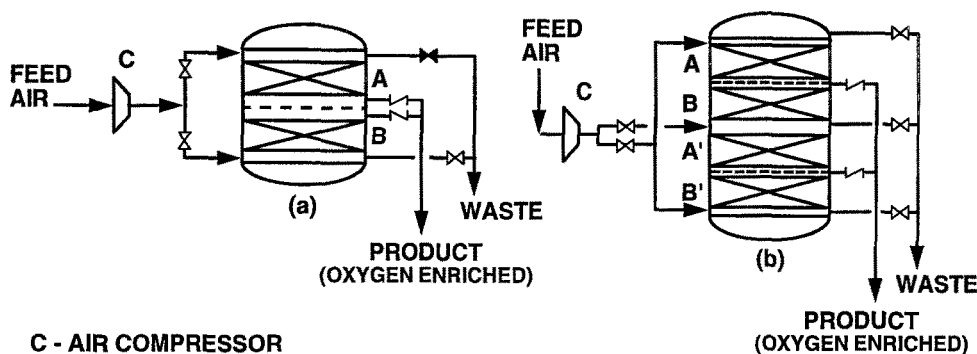
Fig. 3. Schematic embodiments of novel rapid pressure swing adsorption concept.

air prior to air separation by the zeolitic sublayer. The RPSA system is also equipped with appropriate valving for directing air flow to a particular layer of adsorbent and for removing the product and desorbed gases as shown by the schematics in Fig. 3. The cycle times for steps (a) and (b) are equal and the total cycle time for the process ranges between 6–20 seconds.

Thus, according to Fig. 3a, layer A undergoes step (a) of the process for 3–10 seconds while layer B undergoes step (b) of the process for the same duration of time. Then they switch roles and layer A undergoes step (b) while layer B undergoes step (a). This allows a continuous introduction of air feed and a continuous withdrawal of oxygen enriched product gas from the adsorber.

For the configuration of Fig. 3b, feed air is simultaneously introduced to layers A and B^1 for a period of 3–10 seconds (step a) while the respective companion layers B and A^1 simultaneously undergo step (b). Then the feed air is simultaneously introduced through layers B and A^1 for a period of 3–10 seconds (step a) while the respective companion layers A and B^1 simultaneously undergo step (b). This concept of stacking layers by pairs in a single adsorber vessel significantly increases the production capacity of the adsorber and reduces the capital cost. Again, the system contains appropriate hardware (valves, gas headers, etc.) for continuous introduction of air feed and product withdrawal.

The concept of stacking layers in a single adsorber can be easily extended to include more than two pairs in order to increase the productivity of the adsorber. Thus, the configuration of the proposed RPSA system provides ample opportunity to scale-up to very large sizes without requiring additional columns. It also makes the system portable. Furthermore, this allows the use of a moderate gas flow rate (lb moles/hour/cross sectional

area of layer) through each layer during steps (a) and (b) of the process without significantly increasing the cross-sectional area of the layers for large production rate.

The height of each layer can be between 6 to 36 inches. The adsorbent particle size can be between 0.2–1.0 mm in diameter (60–20 mesh) in order to increase the adsorbate mass transfer coefficients without paying severe pressure drop penalties. The process steps are operated close to local equilibrium conditions.

Performance of RPSA Process

The performance of the above described RPSA process was evaluated in a process development unit illustrated by Fig. 4. It consisted of two layers of NaX zeolite (5.8 inches in diameter and 7.0 inches long each) containing 4.5 lbs of zeolite in each layer. The helium void of each layer was 0.076 ft^3. The adsorbent particles had a mesh size of 30–50 ($\sim$0.5 mm diameter). Dry air at a pressure of $\sim$32 psig and at ambient temperature was used as feed gas and the final desorption pressure was $\sim$2 psig. The total cycle time was 12 seconds (6 seconds for each step (a) and (b)). Figure 5 shows the steady state pressure-time profiles for both layers. Steady state was typically reached after 10–20 cycles of operation.

The adsorbent was regenerated by heating at 350°C under a flow of dry nitrogen for 8 hours before the process performance data were measured. A data acquisition software called Labtech Notebook/XE manufactured by Laboratory Technologies, Inc. was used in conjunction wtih an IBM model PS2/30 PC equipped with two RTI-815 (Analog Devices, Inc.) data acquisition boards. The flow rates, quantities, compositions
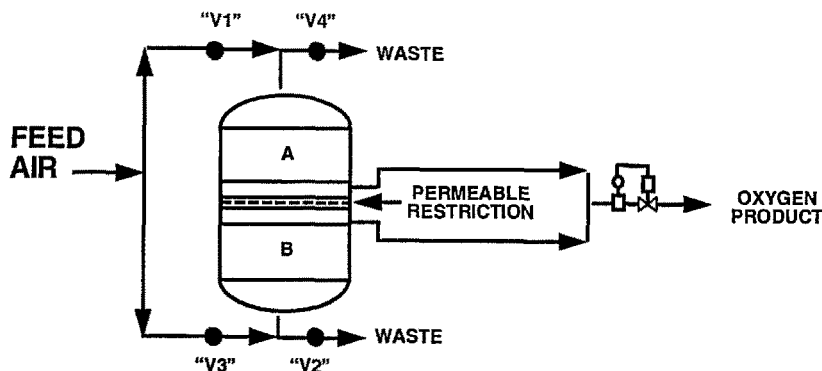
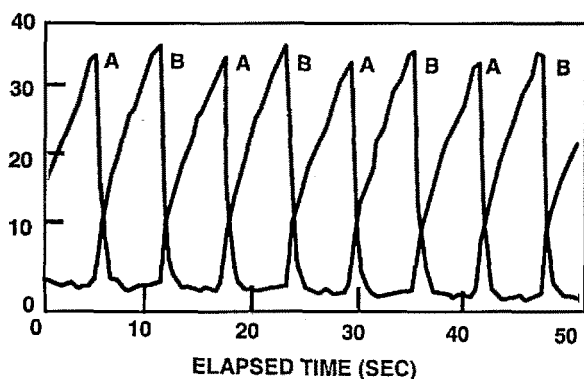*Fig. 4.* Schematic of rapid pressure swing adsorption test apparatus.

Fig. 5. Cyclic pressure-time profiles for the adsorbent layers *A* and *B*: total cycle time of 12 seconds.

and pressures of all inlet and outlet streams to and from the RPSA system were measured every two seconds. A Thermox oxygen analyzer (Amtek, Inc.) was employed to measure gas compositions. Dry test meters (American Meter Co.) were used to monitor the product and depressurization gas quantities. A mass flow controller (MKS, Inc.) was used to control the air feed rate. Pressure transducers (Data Instruments Co.) and thermocouples (type *T*) were employed to follow pressure and temperature changes within the adsorbent layers during the cycle. The individual component mass balances were closed within ±4%.

According to the schematic of Fig. 4, the process was run by simultaneously opening valves V_1 and V_2 for 4–6 seconds (valves V_3 and V_4 closed) and then opening valves V_3 and V_4 for 4–6 seconds (valves V_1 and V_2 closed). A check valve in the oxygen product line controlled the pressure (5–15 psig) of the oxygen enriched product gas. The quantity of oxygen enriched gas withdrawn per cycle was controlled by a manual regulating

valve. Another regulating valve was installed between the two adsorbent layers of the test unit in order to control the purge gas flow rate between the layers and to provide the flow restriction between the layers.

The feed air can be compressed to the highest pressure level of the cycle and then introduced into the adsorber. Alternatively, the feed air pressure can be ramped from near ambient pressure to the highest pressure level of the cycle during step (a) of the process. The second choice significantly reduces the energy of compression. The oxygen enriched gas can be withdrawn at a positive pressure.

Figure 6 shows the overall performance of the process. It plots specific production rate (standard liters of product/liter of total adsorbent volume/hour) for the oxygen enriched gas and oxygen recovery (amount of oxygen in product gas/amount of oxygen in feed air, %) as functions of oxygen product purity (mole%). Both specific oxygen production rate and recovery decrease as the oxygen product purity is increased. However, a very large (>200 SL/L/HR) specific oxygen production rate and a decent (>30%) oxygen recovery can be achieved by the process when the oxygen product purity is less than 50%. The specific oxygen production rates shown by Fig. 6 are 10–20 times larger than those exhibited by conventional PSA processes.

Figure 7 shows the comparative oxygen recoveries by the present RPSA process and the conventional Skarstrom PSA process using NaX zeolite as the adsorbent. Published experimental performance data (circles) for the Skarstrom cycle (Skarstrom, 1972) are compared with the performance of the present RPSA cycle (triangles) reported in Fig. 6. Both processes were run using an adsorption pressure of ~30 psig and a desorption pressure of ~0 psig. The oxygen recovery is defined by the ratio of the amount of oxygen produced
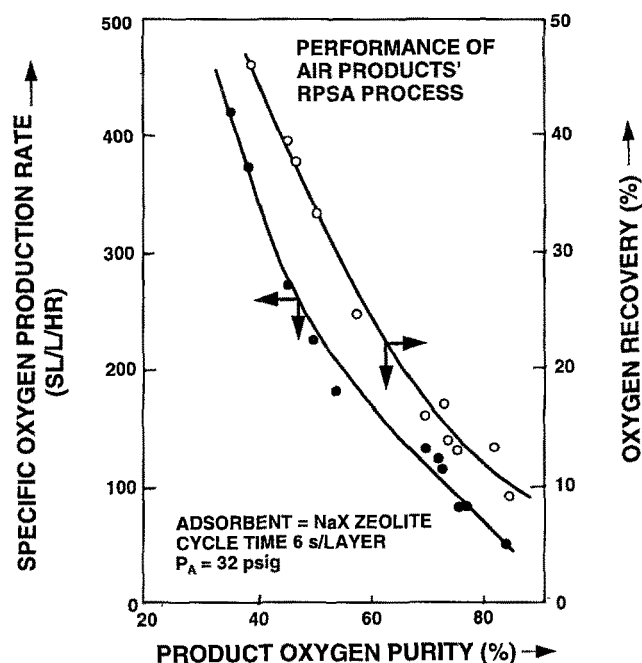
Fig. 6. Specific oxygen production rate and oxygen recovery as functions of product oxygen purity by novel RPSA process.
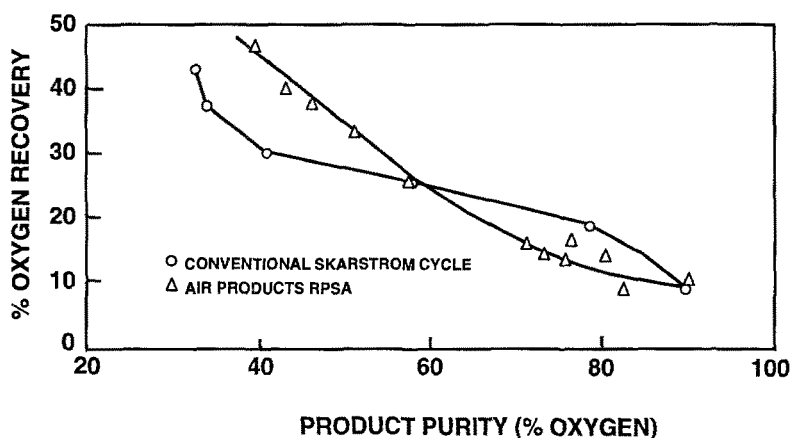

Fig. 7. Comparison between oxygen recovery by novel RPSA process and conventional Skarstrom process using NaX zeolite.

(as oxygen enriched air) by the process to the amount of oxygen fed into the system (as ambient air) per cycle of operation. The Skarstrom cycle consisted of four separate steps including (a) adsorption of air at 30 psig to produce an oxygen enriched air stream, (b) counter-current depressurization to 0 psig, (c) countercurrent purge with a part of the oxygen enriched product gas at 0 psig and, (d) cocurrent pressurization to 30 psig with feed air. Dry air was used in these tests. The total cycle time was several minutes.

It may be seen from Fig. 7 that the oxygen recoveries by the present RPSA process are larger than those of the conventional Skarstrom cycle when the oxygen purity in the product gas is less than 60%. Thus, the present process can produce an oxygen enriched gas (25–50% O_2) with somewhat higher oxygen recovery but an order of magnitude larger specific production rate compared to a conventional PSA oxygen process. This translates to an order of magnitude reduction in the adsorbent inventory for a given oxygen production

rate. The use of a single adsorber and smaller number of valves in the process also reduces the capital cost for the system.

The RPSA process was also run using a total cycle time of 8 seconds (4 seconds for steps (a) and (b) each). The performance was found to be very similar to those shown by Fig. 6. This indicated that no further improvement in the specific production rate could be achieved by the process by lowering the cycle time due to kinetic limitations discussed earlier.

Conclusions

A rapid pressure swing adsorption (RPSA) process was designed using NaX zeolite for production of 25–50% oxygen enriched air with very large specific production rate (>240 SL/L/HR at 50% O_2) and decent oxygen recovery ($>30\%$ at 50% O_2) and by using an ad(de)sorption pressure envelope of 3–1 atmospheres. The total cycle time for the process is 12 seconds. It cannot be reduced indefinitely in order to increase the specific production rate due to finite adsorbate mass transfer resistances. The novel concept of stacked adsorbent layers in a single adsorber vessel introduces design flexibility for large production rates and minimizes hardware requirements.

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