Kinetic Separation of Oxygen and Argon Using Molecular Sieve Carbon

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Abstract.   A pressure-swing adsorption (PSA) simulation study was performed for the separation of a mixture of 95% O_2 and 5% Ar using a molecular sieve carbon (MSC) as the adsorbent. Two PSA cycles have been outlined to maximize the recovery of either argon or oxygen as a high purity product. The effect of cycle parameters such as cocurrent depressurization pressure, purge/feed ratio, pressure ratio and adsorption pressure on the separation of O_2/Ar has been studied. It was found that it is feasible to obtain an argon product of purity in excess of 80% with reasonably high recovery using one of the cycles. The other cycle is capable of producing high purity oxygen (>99%) at high recovery (>50%) with reasonably high product throughputs. The PSA process can be conducted at room temperature and hence has an advantage over conventional processes like cryogenic distillation and cryogenic adsorption.

Keywords: oxygen, argon, kinetic separation, molecular sieve carbon, pressure swing adsorption

Introduction

Air separation represents an important class of gas separation processes in the chemical industry today. Separation of oxygen and nitrogen from air is usually carried out by either of two methods: (1) cryogenic distillation (i.e., rectification), by exploiting the differences in relative volatilities of the two components; or (2) adsorptive processes like pressure swing adsorption (PSA), which take advantage of preferential adsorption of one component with respect to the other on a suitable adsorbent (Yang, 1987). However, air also contains a small amount of inert gases such as argon, which have physical properties similar to those of oxygen. As a result, the oxygen product streams from either cryogenic or adsorptive air separation units contain a substantial amount of argon as an impurity. A typical O_2 product stream from an air separation unit has a composition of 95% O_2, 4% Ar and 1% N_2. Often high purity O_2 is needed for specific uses and hence impurity removal becomes important. Furthermore, the recovery of argon with preferably a high purity is desirable since

argon has significant uses in applications like welding, electrical appliances, and degassing in steel production.

Although the removal of the N_2 impurity is relatively easy (e.g., a zeolite bed can be used since it preferentially adsorbs N_2 compared to O_2 and Ar), separation of O_2 and Ar poses a difficult problem due to their similar physical properties. Currently three methods are commercially used for O_2 and Ar separation: (1) cryogenic distillation in a sidearm argon column with multiple stages of rectification stages (Howard et al., 1995; Xu et al., 1997), (2) catalytic hydrogenation of the O_2 from a crude Ar stream to form water, which is subsequently removed by condensation, and, (3) cryogenic adsorption with molecular sieves like 4A or 5A zeolite at low temperatures in the range of $-157°C$ to $-179°C$ (Kovak et al., 1992). However, the cryogenic methods are highly energy intensive since the system needs to be maintained at very low temperatures whereas O_2 recovery is not possible in the catalytic hydrogenation method. Besides, in case of cryogenic distillation, a large number of equilibrium stages are required for separation thus increasing capital costs.

The purpose of this study is to theoretically explore the feasibility of using a PSA process to perform a separation of a 95% O_2 and 5% Ar mixture at room temperature. A number of sorbents have been studied in the literature for this purpose. Since Ar is in a smaller amount compared to O_2, a sorbent with a preferential adsorption capacity for Ar would be ideal. However a study of the existing literature revealed that although some sorbents such as mordenite, calcium chabazite (Furuyama et al., 1984; Knaebel et al., 1987; Maroulis and Coe, 1989; Jasra et al., 1996), and Ag-mordenite (Knaebel and Kandybin, 1993) showed a small adsorptive preference for Ar compared to O_2, the equilibrium selectivity was not high enough to enable the separation. Kinetic separation of O_2 and Ar using molecular sieve carbon (MSC) is another possibility. It was shown by Ma et al. (1991) that MSC such as the Bergbau-Forschung MSC (BF-MSC) adsorbed O_2 almost 30 times faster than Ar and hence this sorbent is a potential candidate for the desired separation.

An example of O_2/Ar separation using MSC is available in patent literature. Hayashi et al. (1985) disclosed a process for separating a mixture consisting of approximately 94% O_2, 4% Ar and 1% N_2 using 5 stages of PSA beds comprising of 5A zeolite molecular sieves in one stage to eliminate the N_2 impurity, and 3A molecular sieve carbon (MSC) in the other stages to separate O_2 and Ar. Using an apparatus for removal of O_2 by catalytic hydrogenation to H_2O in an intermediate stage, it was claimed that it was possible to enrich the Ar stream to 99% purity.

It has been shown in a study by Ma et al. (1991), that the ratio of the diffusivity of O_2 to that of Ar in the Takeda 3A MSC is actually lower than that in the BF-MSC. Hence, the kinetic separation of O_2 and Ar using BF-MSC should be superior to that of Takeda 3A MSC, which was similar to the sorbent in the example given above. The present work discusses a simulation study of two PSA cycles employing the BF-MSC as a sorbent, to provide either high purity Ar or high purity O_2 as per the requirement. The performance of the PSA cycle with respect to changes in adsorption pressure, pressure ratio, and purge/feed ratio is explained.

Description of PSA Model

The PSA process described in this work was simulated using a model similar to that described by Sun et al. (1996). In order to avoid repetition, only the basic assumptions are listed here. The model used assumes the flow of a gaseous mixture of only two adsorbable components (O_2 and Ar) in a fixed bed packed with spherical adsorbent particles of the same size and shape. The heats of adsorption of O_2 and Ar on MSC are low (about 3.5 kcal/mol), and preliminary test runs showed that the temperature changes during the adsorption/desorption steps were within 1°C. Hence the bed was considered to be essentially isothermal in the actual runs. Axial dispersion for mass transfer was assumed but dispersion in the radial direction was taken to be negligible. Axial pressure drop was neglected and the ideal gas law was assumed to hold since pressures involved were reasonably low. Also the gas was assumed to have constant viscosity. The adsorption kinetics was described by a Fickian diffusion model with concentration independent diffusivities. Any kinetic interference between the two components was neglected, that is, the cross-term diffusivities were omitted from the model.

The pure component equilibrium amounts adsorbed on the respective adsorbents were fit using the Langmuir isotherm. The equilibrium loading under mixture conditions were then predicted by the extended Langmuir equation in the simulation model:

$$q_k^* = \frac{q_{m_k} b_k p_k}{1 + \sum_{j=1}^m b_j p_j} \quad k = 1, 2. \qquad (1)$$

The model comprising essentially of a set of mass balance equations was solved by using a numerical finite difference scheme discussed by Sun et al. (1996) by a computer code written in FORTRAN programming language.

Adsorption Isotherms and Diffusivities

The adsorbent used in the present study is the Bergbau-Forschung molecular sieve carbon (BF-MSC). The adsorption of O_2 and Ar on this sorbent (as well as on Takeda 3A MSC) has been studied by Ma and co-workers (1991) for the pressure range of 0–1.3 MPa (0–13 atm) at 303 K. The pressure range selected for the simulations in this work were well within these experimental limits. Table 1 shows the Langmuir isotherm parameters given by Ma et al. (1991) as well as the values for the diffusivity constants (D/r^2) for O_2 and Ar on the MSC. The bed dimensions (diameter and height) used in the simulation are shown in Table 2. As mentioned above, the pressure drop is neglected. Figure 1 shows the isotherms plotted for a range of 0–2 atm, which is also the range for the PSA simulation runs in

Table 1. Langmuir isotherm parameters and diffusivity constants for adsorption of O_2 and Ar in Bergbau-Forschung MSC at 30°C (Ma et al., 1991).

Component	q_m (mmol/g)	Langmuir parameters b (atm^{-1})	Diffusivity constant D/r^2 (s^{-1})
O_2	1.62	0.2655	5.2×10^{-3}
Ar	1.66	0.1935	1.7×10^{-4}

Table 2. Adsorption bed characteristics and operating conditions used in the PSA simulations.

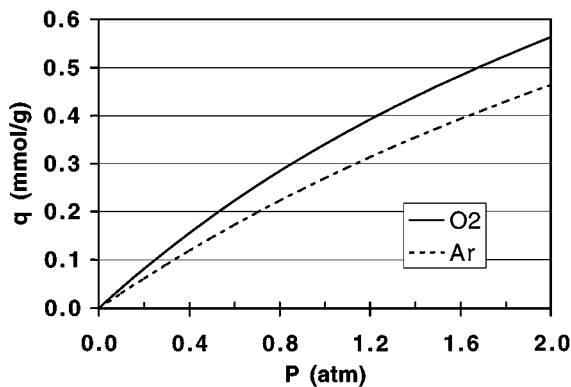|	
Bed lengths:	
Ar-cycle	0.76 m
O_2-cycle	4.54 m
Diameter of adsorber bed	0.25 m
Bed external porosity	0.40
Bed density	700 kg/m^3
Bed temperature	303 K (ambient)
Feed gas composition	95% O_2, 5% Ar
Axial dispersion coefficient (D_{ax})	2.0×10^{-5} m^2/s

Figure 1. Adsorption isotherms of oxygen (solid line) and argon (dotted line) on Bergbau-Forschung MSC at 30°C. Data from Ma et al. (1991).
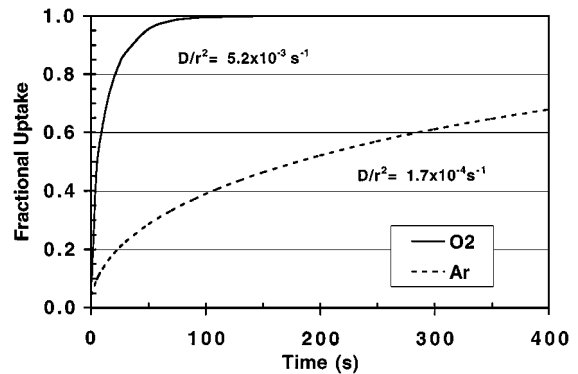

Figure 2. Adsorption uptake curves of oxygen (solid line) and argon (dotted line) on Bergbau-Forschung MSC at 30°C. Data from Ma et al. (1991).
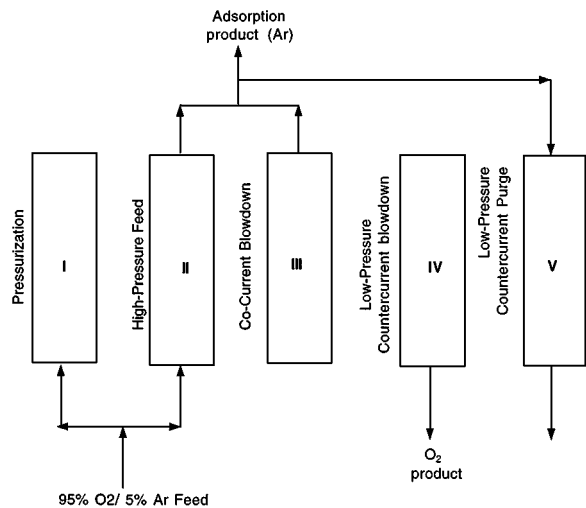

Figure 3. Schematic diagram of the five-step PSA cycle used for obtaining high purity argon from an O_2/Ar mixture.

this work. It can be seen that the equilibrium loadings of the two components are fairly close and hence equilibrium separation would not be possible. However, from the plot of the rate of adsorption data shown in Fig. 2, it appears that kinetic separation is a possibility. The feasibility is further strengthened from the fact that the ratio of the diffusivities of O_2 and Ar for the BF-MSC is about 30. In comparison, the ratio of O_2 and N_2 diffusivities in MSC is about 36 (Chen et al., 1994), and kinetic air separation using this sorbent is known to be a commercial success.

Description of the PSA Cycles

In the present work, two different modes of PSA operation are discussed. The type of PSA cycle to be used would depend on whether high purity O_2 or high purity Ar is the desired product. If high purity Ar is desired, a Skarstrom-type cycle with countercurrent low-pressure purge with Ar should be used, as shown in Fig. 3. For the Ar enrichment purpose, a 5-step cycle was used which consisted of the following steps: (I) pressurization with the feed gas (mixture of 95% O_2 and 5% Ar on molar basis) to a high pressure (P_H); (II) high pressure adsorption with feed gas, i.e., feed step;

(III) low pressure co-current blowdown to an intermediate pressure (P_{CD}); (IV) countercurrent blowdown to a low pressure (P_L) (V) low pressure countercurrent purge with part of the product obtained in steps (II) and (III). The product, which refers to the Ar-enriched stream here, is obtained by a volumetric combination of the product streams obtained from the feed step (II) and the cocurrent blowdown (III) steps. For this cycle (henceforth referred to as the "Ar-cycle"), the product recovery is defined as:

Ar product recovery

$$= \frac{(\text{Ar from steps II and III}) - (\text{Ar used in step V})}{(\text{Ar fed in step I and step II})} \tag{2}$$

However, if high purity O_2 is the desired product, the cycle needs to be altered for this purpose. A four-step PSA cycle similar to that used by Kikkinides et al. (1993) was used for the O_2-enrichment PSA process and is depicted in Fig. 4. The steps involved in each cycle were as follows: (I) pressurization with the feed gas (mixture of 95% O_2 and 5% Ar on molar basis); (II) high pressure adsorption with feed gas, i.e., feed step; (III) high pressure cocurrent purge with part of the O_2-rich product obtained in step (IV); (IV) countercurrent blowdown to a low pressure. For this cycle (henceforth referred to as the "O_2-cycle"), the product refers to the O_2-rich stream obtained in the desorption step (IV). In 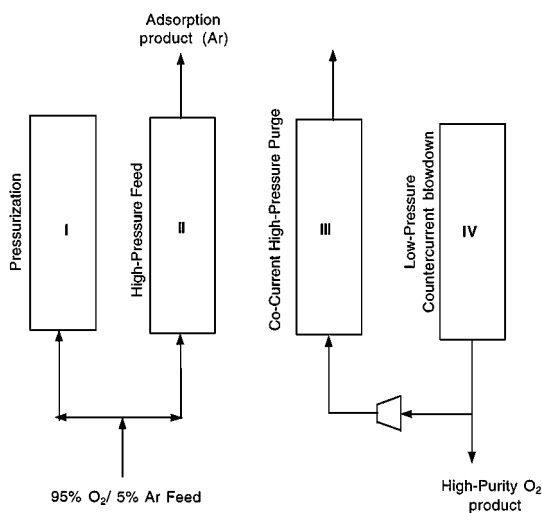addition, an Ar-enriched stream is also obtained as product of the feed step (II). The various process variables used in this work were defined as follows:

O_2 product recovery

$$= \frac{(O_2 \text{ from step IV}) - (O_2 \text{ used for purging in step III})}{(O_2 \text{ fed in step I and step II})} \tag{3}$$

Purge-to-feed ratio (P/F)

$$= \frac{(O_2 \text{ used to purge in step III})}{(O_2 \text{ fed in step I and step II})} \tag{4}$$

Pressure ratio

$$= \frac{\text{High pressure during adsorption } (P_H)}{\text{Low pressure during purge } (P_L)} \tag{5}$$

Another important parameter used to gauge the adsorbent's productivity is the product throughput (also referred to as productivity in this work). For both the cycles discussed above, it is defined as follows:

Product throughput

$$= \frac{\text{Amount (kg) of product produced per hour}}{\text{Amount (kg) of adsorbent}} \tag{6}$$

It is well known that for a PSA process, there exists a distinct interrelation between the product purity, recovery and throughput. In order to optimize these three performance parameters, the cocurrent depressurization pressure (P_{CD}) was adjusted in the Ar-cycle, whereas the purge-to-feed ratio was adjusted in the case of the O_2 cycle.

The time for each step for the above cycles has to be judiciously selected, since adsorption and desorption time has a significant impact on the performance for a PSA cycle designed for kinetic separation. It was found from preliminary runs, the separation was optimal for cycles with short time duration. The operating parameters used in the PSA simulations for both the O_2-cycle and the Ar-cycle are summarized in Table 2 and the time for the steps in the two cycles are given in the subsequent sections.

Results and Discussion

Argon Enrichment

For the Ar-cycle simulations, adsorption was carried out at 1.0 atm while desorption was done at 0.2 atm. The time for each step was as follows: (I) Pressurization (5 s), (II) Feed (30 s), (III) Cocurrent blowdown

Figure 4. Schematic diagram of the four-step PSA cycle used for obtaining high purity oxygen from an O_2/Ar mixture.

Table 3. PSA operating parameters for the 5-step cycle for producing high purity argon using BF-MSC at 30°C. Time for each step: (1) Pressurization (5 s), (2) Feed (30 s), (3) Cocurrent blowdown (10 s), (4) Countercurrent blowdown (5 s), (5) Countercurrent purge (30 s). Adsorption at $P_H = 1.0$ atm, desorption at $P_L = 0.2$ atm.

Run No.	P_{CD} (atm)	Interstitial feed velocity U_F (m/s)	Interstitial purge velocity U_P (m/s)	Adsorption product (Ar) % purity	Adsorption product (Ar) % recovery	Adsorption product (Ar) throughput (kg of product/h/kg of adsorbent) $\times 10^3$
1	0.80	0.05	0.008	69.20	67.92	0.243
2	0.85	0.05	0.008	80.38	42.61	0.152
3	0.90	0.05	0.008	87.00	14.85	0.053

(10 s), (IV) Countercurrent blowdown (5 s), (V) Countercurrent purge (30 s). The co-current depressurization pressure was adjusted between 0.8–0.9 atm to obtain a range of feasible purities and recoveries. The operating conditions of the PSA cycle and the purities and recoveries of the adsorption (Ar) product obtained in the simulation runs are given in Table 3. The PSA performance is also depicted in Fig. 5. From the figure, it can be seen that although Ar purities as high as 88% can be obtained using the MSC as a sorbent, the corresponding Ar recovery is low (about 15%). The product recovery can be improved, however, by decreasing the co-current depressurization pressure (P_{CD}) with a consequent decrease in product purity. Recoveries of the order of 70% are possible when lower Ar purities of the order of 70% can be tolerated. Further enrichment

of Ar is possible by adding more PSA stages or using a catalytic deoxygenation process such as hydrogenation to remove the residual oxygen. However, the oxygen product obtained in the countercurrent blowdown was found to have low purity (88–92%) and hence another cycle needs to be used if high purity oxygen is the desired product.

A comparison can be made with experimental results disclosed by Hayashi et al. (1985). Using a feed of 4.5% Ar, 93.6% O_2, and 1.9% N_2, the authors performed PSA in a 3A MSC bed between 2.0 atm and 0.2 atm, and obtained a product of 33% Ar, 52.3% O_2 and 14.7% N_2. The accompanying Ar yield was 69%. The performance of the simulations presented in this work is slightly better. This is so because the D_{O_2}/D_{Ar} ratio for the Bergbau-Forschung (BF) MSC (33.3) used in this work is more than twice that for 3A MSC (12.5) (Ma et al., 1991). Hence the BF-MSC is expected to give a better performance than 3A MSC.
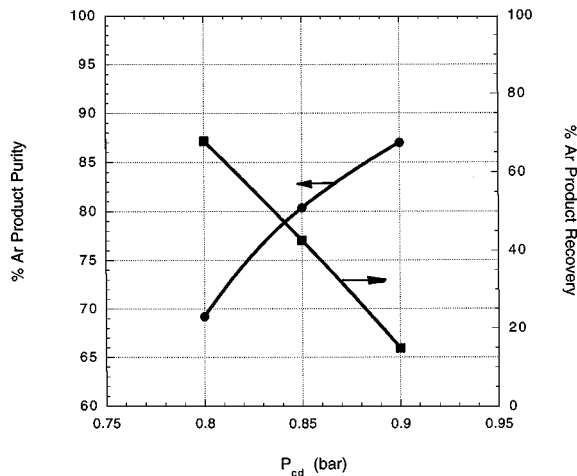
Oxygen Enrichment

For the O_2-cycle, two modes of PSA operation were considered: (1) Subatmospheric pressure-swing, with adsorption at 1.0 atm and desorption either at 0.1 or 0.2 atm; (2) Transatmospheric pressure-swing, with adsorption at 2 atm and desorption at 0.2 atm. The operating parameters used in the various simulations as well as the O_2 product purities, recoveries and throughputs are summarized in Table 4.

The O_2 product purities and recoveries obtained for different purge/feed ratios are shown in Figs. 6–8. For the vacuum-swing runs, pressure ratios (P_H/P_L) of 5 and 10 were employed. Adsorption was carried out at 1.0 atm, while desorption was carried out at 0.1 atm (Fig. 3) and 0.2 atm (Fig. 4). An examination of Figs. 6 and 7 reveal O_2 purities as high as 99.3% can be

Figure 5. % Purity and % recovery of the argon product obtained as the adsorption product in the five-step Ar-cycle versus the cocurrent depressurization pressure (P_{CD}). Adsorption pressure $P_H = 1.0$ atm, desorption pressure $P_L = 0.2$ atm.

Table 4. PSA operating parameters for the 4-step cycle for producing high purity oxygen using BF-MSC at 30°C. Time for each step: (1) Pressurization (5 s), (2) Feed (15 s), (3) Cocurrent purge (15 s), (4) Countercurrent blowdown (5 s).

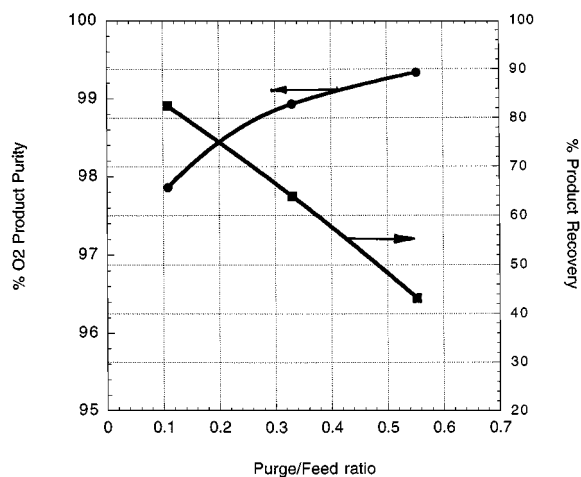| Run No.	P_H (atm)	P_L (atm)	Interstitial feed velocity U_F (m/s)	Interstitial purge velocity U_P, (m/s)	Adsorption product (O_2) % purity	Adsorption product (O_2) % recovery	Adsorption product (O_2) throughput (kg of product/h/kg of adsorbent) $\times 10^3$
1	1.0	0.1	0.8	0.20	97.86	82.52	10.08
2	1.0	0.1	0.8	0.60	98.93	63.99	7.78
3	1.0	0.1	0.8	1.00	99.33	43.17	5.23
4	1.0	0.2	0.8	0.20	97.81	76.36	8.62
5	1.0	0.2	0.8	0.60	98.87	55.71	6.27
6	1.0	0.2	0.8	1.00	99.30	32.98	3.69
7	2.0	0.2	1.0	0.10	97.75	70.29	17.58
8	2.0	0.2	0.8	0.60	99.07	52.22	11.57
9	2.0	0.2	1.0	0.80	99.30	36.64	8.98

Figure 6. % Purity and % recovery of the oxygen product obtained as the desorption product in the four-step O_2-cycle versus the purge/feed ratio. Adsorption pressure $P_H = 1.0$ atm, desorption pressure $P_L = 0.1$ atm.

Figure 7. % Purity and % recovery of the oxygen product obtained as the desorption product in the four-step O_2-cycle versus the purge/feed ratio. Adsorption pressure $P_H = 1.0$ atm, desorption pressure $P_L = 0.2$ atm.

obtained with O_2 recoveries in the region of 40–50%. Recoveries could be improved upto 70% by lowering the purge/feed ratio with a consequent loss of purity to 98%. In general, by changing the pressure ratio from 5 to 10, the product purity was not affected significantly, however, there was an improvement in product recovery by about 10%. The optimal pressure ratio for the process would be evident only after a detailed economical analysis, which is beyond the scope of the present work.

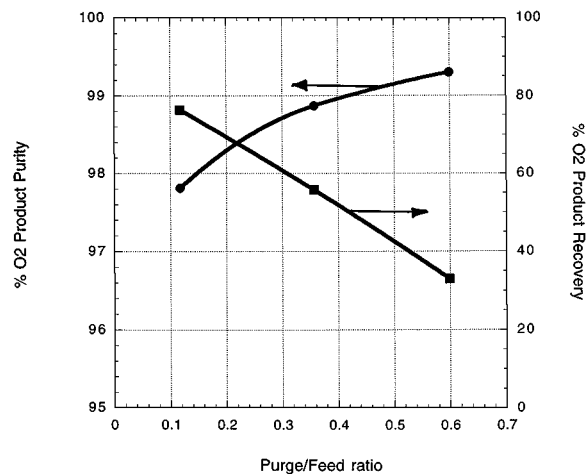Figure 8 shows the PSA performance obtained using a higher adsorption pressure of 2 atm. Similar to the subatmospheric runs, a pressure ratio of 10 was employed to study the effect of operating at higher pressure, that is, a desorption pressure of 0.2 atm was employed. A comparison of Figs. 6 and 8 shows that for the same purge/feed ratios, the product purity shows a small increase by operation at higher adsorption pressure. However the product recovery seems to drop more steeply. Since the pressure swing range for the transatmospheric runs was large, the consequent bed capacity for O_2 adsorption also increased and hence larger throughputs could to be tolerated. The low recovery was probably caused due to a breakthrough of the O_2
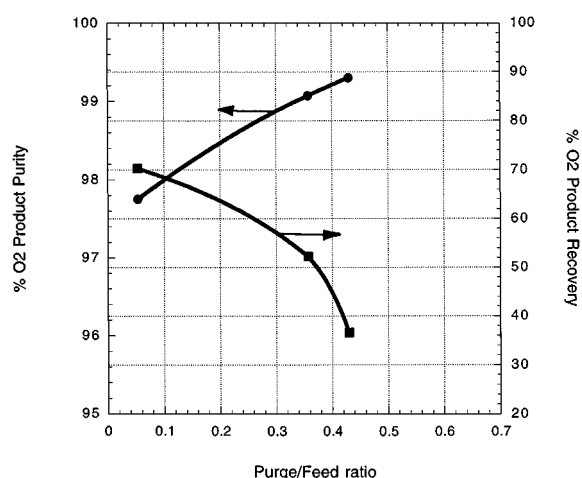
Figure 8. % Purity and % recovery of the oxygen product obtained as the desorption product in the four-step O_2-cycle versus the purge/feed ratio. Adsorption pressure $P_H = 2.0$ atm, desorption pressure $P_L = 0.2$ atm.

concentration wavefront during the purge step. A study of Table 4 shows that the product throughputs for the high feed pressure runs (runs 7–9) were on an average higher than those for the low feed pressure runs (runs 1–6), which compensates for the decrease in recovery. The product throughputs obtained for runs 7–9 are of the same order as those reported by Leavitt (1991) for O_2/N_2 separation using LiX zeolite. However, unlike the previously described Ar-cycle, the product of the adsorption step (argon) was found to be in low in purity (10–15%) and hence this cycle cannot provide high grade argon product.

Conclusions

In this study, the feasibility of obtaining high purity O_2 and Ar from a mixture of 95% O_2 and 5% Ar (v/v) using a PSA process with Bergbau Forschung MSC as a sorbent was demonstrated. Two types of cycles, namely the 5-step cycle giving high purity Ar as product, and the 4-step cycle for obtaining high purity O_2 product were outlined. It was seen that it is possible to obtain Ar with a purities in excess of 80% at a reasonable recovery in the region of 50% using the 5-step Ar-cycle. Also, high purity O_2 with purities in excess of 99% were obtained at recoveries in the range of 40–60% using the 4-step O_2-cycle. The product throughputs for the O_2-cycle were within reasonable limits, especially when pressure was cycled between 2.0 atm and 0.2 atm. The

PSA process used is not energy-intensive unlike previous techniques like cryogenic distillation/adsorption since the cycle is performed at room temperature.

Nomenclature

b	Langmuir parameter (atm^{-1})
D	Intracrystalline diffusivity of component (m^2/s)
D_{ax}	Axial dispersion coefficient in PSA bed (m^2/s)
p	Partial pressure of component (atm)
P_{CD}	Pressure during cocurrent depressurization step (atm)
P_H	Pressure during adsorption (feed) step (atm)
P_L	Pressure during desorption (purge) step (atm)
q	Adsorbed amount (mmol/g)
q_m	Langmuir parameter (mmol/g)
r	Sorbent crystal diameter (m)
U_F	Interstitial feed velocity (m/s)
U_P	Interstitial purge velocity (m/s)

Acknowledgment

References

Chen, Y.D., R.T. Yang, and P. Uawithya, "Diffusion of Oxygen, Nitrogen and Their Mixtures in Carbon Molecular Sieve," *A.I.Ch.E. J.*, **40**, 577 (1994).

Furuyama, S. and M. Nagato, "Sorption of Argon, Oxygen, Nitrogen, Nitric Oxide, and Carbon Monoxide by Magnesium, Calcium, and Barium Mordenites," *J. Phy. Chem.*, **88**, 1735 (1984).

Hayashi, S., H. Tsuchiya, and K. Haruna, "Process for Obtaining High Concentration Argon by Pressure Swing Adsorption," US Patent 4,529,412, 1985.

Howard, H.E., D.P. Bonaquist, W.M. Canney, and W.A. Nash, "Process for Maximizing the Recovery of Argon from an Air Separation System at High Argon Recovery Rates," US Patent 5,448,893, 1995.

Jasra, R.V., N.V. Choudhary, and S.G.T. Bhat, "Correlation of Sorption Behavior of Nitrogen, Oxygen, and Argon with Cation Locations in Zeolite X," *Ind. Eng. Chem. Res.*, **35**, 4221 (1996).

Kikkinides, E.S., R.T. Yang, and S.H. Cho, "Concentration and Recovery of CO_2 from Flue Gas by Pressure Swing Adsorption," *Ind. Eng. Chem. Res.*, **32**, 2714 (1993).

Knaebel, K.S., K.G. Ikels, and G.W. Miller, "Equilibria of Nitrogen, Oxygen, Argon, and Air in Molecular Sieve 5A," *A.I.Ch.E. J.*, **33**, 194–201 (1987).

Knaebel, K.S. and A. Kandybin, "Pressure Swing Adsorption System to Purify Oxygen," US Patent 5,226,933, 1993.

Kovak, K.W., R. Agrawal, and J.C. Peterson, "Method for Purifying Argon through Cryogenic Adsorption," US Patent 5,159,816, 1992.

Leavitt, F.W., "Air-separation Pressure Swing Process," US Patent 5,074,892, 1991.

Maroulis, P.J. and C.G. Coe, "Calcium Chabazite Adsorbent for the Gas Chromatographic Separation of Trace Argon-Oxygen Mixtures," *Anal. Chem.*, **61**, 1112 (1989).

Ma, Y.H., W. Sun, M. Bhandarkar, and J. Wang, "Adsorption and Diffusion of Nitrogen, Oxygen, Argon, and Methane in Molecular Sieve Carbon at Elevated Pressures," *Separations Technology*, **1**, 90 (1991).

Sun, L.M., P. Le Quere, and M.D. Le Van, "Numerical Simulation of Diffusion-Limited PSA Process Models by Finite Difference Methods," *Chem. Eng. Sci.*, **51**, 5341 (1996).

Xu, J. and J.A. Hopkins, "Process to Produce Oxygen and Argon Using Divided Argon Column," US Patent 5,768,914, 1998.

Yang, R.T., *Gas Separation by Adsorption Processes*, Butterworths, Boston, 1987; reprinted in paperback by Imperial College Press, River Edge, N.J., 1997.