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Shivaji Sircar[a]
[a] AIR PRODUCTS AND CHEMICALS, INC. ALLENTOWN, PENNSYLVANIA

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Air Fractionation by Adsorption

SHIVAJI SIRCAR

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PENNSYLVANIA 18195

Abstract

Pressure swing adsorption (PSA) processes for air separation differ by the modes and conditions of operation of the adsorption, the desorption, and the complementary steps, as well as by the types of adsorbents used. Three commercial PSA processes for air separation are reviewed and compared. The first process uses a zeolitic adsorbent and produces only an oxygen-enriched product gas. The second process uses a carbon molecular sieve and produces only a nitrogen-enriched product gas. The third process uses a zeolite and simultaneously produces both oxygen- and nitrogen-enriched product gases. The performance and separation efficiency of the last process, called the "vacuum swing adsorption (VSA) process," are reported to be superior to the others.

INTRODUCTION

Fractionation of air into oxygen- or nitrogen-enriched gaseous products by pressure swing adsorption (PSA) has attracted considerable attention in recent years, and several PSA processes have been commercialized. The technology can be used to produce an oxygen-enriched stream containing 80–95% oxygen which finds application in biological wastewater treatment, home medical use, enhanced combustion in furnaces and cupolas, etc. Alternatively, a nitrogen-enriched stream containing 95–99.9% nitrogen can be produced which is primarily used for "inert blanketing" in many chemical and metallurgical industries. Another market for small-scale oxygen or nitrogen PSA generators is for use in research laboratories where a ready supply of LOX or LIN is not available.

The principle of separation used by the PSA technology is selective

adsorption of nitrogen or oxygen from air on a solid adsorbent so that an adsorbed phase having a composition different from that of the ambient air is formed when the air is contacted with the solid. This produces a gas stream enriched in the less selectively adsorbed species of the air. The adsorbed components are then desorbed by reducing their superincumbent partial pressures to produce a gas stream enriched in the more selectively adsorbed component of the air. The desorption process also cleans the adsorbent for reuse. Consequently, a practical PSA air fractionation process consists of a cyclic sequence of various adsorption and desorption steps along with other complementary steps. The adsorption is usually carried out by contacting the air with an adsorbent in a packed fixed bed or by flowing the air over the adsorbent bed at the highest pressure level of the cycle. The desorption is generally achieved by lowering the pressure of the bed or by flowing a gas stream enriched in the less selectively adsorbed species of the air through the bed or by a combination of these methods. Complementary steps like pressure equalization, where a part of the void gas from one adsorbent bed is directly transferred to another bed for preservation of the valuable components in the void gas, and pressurization, whereby the adsorbent bed is brought back from its lowest pressure level in the cycle to the highest pressure level, are also practiced in various combinations.

Usually these steps are carried out using two or more adsorbent beds so that when one or more beds are undergoing the adsorption steps, the other beds are carrying out the desorption and the complementary steps of the process in order to get ready for a new adsorption step. Every bed cyclically goes through each step of the process. Thus, each bed operates in a cyclic steady-state manner even though any particular step in the cycle is an unsteady-state process. A typical total cycle time for the PSA process is between one to several minutes. The durations of the individual steps may be equal or not, but a continuous feed air and product gas flow can be achieved by the integrated performance of the multi-bed system. It is also possible to maintain a continuous product gas flow by using gas storage tanks and a lesser number of adsorption beds. The choice is dictated by the economics of the process.

A large number of PSA process concepts for air sepraation have been patented in the last 20 years. They are all based on the principles outlined above. However, they differ by (a) the modes in which the adsorption, the desorption, and the complementary steps are carried out; (b) the conditions (pressure, temperature, gas flow direction) of operations of these steps; (c) the types (nitrogen, oxygen, or both) of the product gases and their qualities (pressure, purity); (d) the recovery of the product components from the feed; (e) the types of machinery (compressors,

vacuum pumps), the number of beds and storage tanks, and other hardware used; and (f) the properties of the adsorbent used for air separation.

Processes also differ by the method used for the removal of the impurities (water and carbon dioxide) from the ambient air prior to nitrogen–oxygen separation. This constitutes an important integral part of the process because water and carbon dioxide are much more strongly adsorbed than nitrogen and oxygen on most adsorbents, and their presence can be significantly detrimental to the air separation process. In particular, the cyclic desorption of these impurities by PSA can be difficult and it may impose certain restrictions on the operating conditions of the process which can influence the overall separation efficiency of the PSA process.

A detailed description of many patented PSA air separation processes can be found in several review articles (*1–5*). The purpose of this paper is to discuss three distinctly different commercial PSA air separation processes. The first process produces only an oxygen-enriched product gas, the second process produces only a nitrogen-enriched product gas, and the third process simultaneously produces both an oxygen- and a nitrogen-enriched product gas from air.

ADSORBENTS FOR AIR SEPARATION

One key element of a PSA air separation process is the adsorbent used for the nitrogen–oxygen separation. All commercial processes use either an inorganic zeolite (synthetic or natural) or an organic carbon molecular sieve (CMS) adsorbent.

Zeolites are polar adsorbents which selectively adsorb nitrogen from air because it has a larger permanent quadrupole (1.52×10^{-26} esu · cm^2) than that for oxygen (0.30×10^{-26}) or argon (0.0×10^{-26}). The capacity, the selectivity, and the heats of adsorption of nitrogen, oxygen, and argon can vary significantly depending on the structure of the zeolite and the cations present within them. Typically, zeolite types A, X, or mordenite, which are ion exchanged with metals of Groups I and II of the periodic table, are used for air separation. An example of isotherms for adsorption of N_2, O_2, and Ar on a sodium mordenite at 23°C is given in Fig. 1a. N_2 is more selectively adsorbed than O_2 and Ar, whose isotherms nearly coincide, indicating that there is practically no selectivity of adsorption between them. Table 1 shows the thermodynamic selectivity of adsorption of N_2 over O_2 as functions of equilibrium gas-phase composition and temperature for this adsorbent. The selectivity of N_2 (Component 1) over

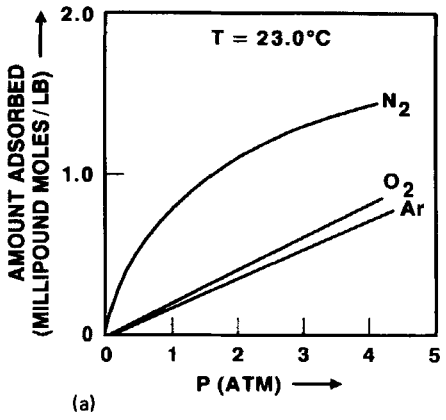

FIG. 1a. Equilibrium adsorption isotherms for N_2, O_2, and Ar on sodium mordenite at 23°C.

O_2 (Component 2) is defined by the ratio (n_1y_2/n_2y_1) where n_i and y_i are, respectively, the specific amounts adsorbed and the equilibrium gas-phase mole fractions of Component i (= 1, 2). The selectivity decreases with increasing N_2 composition and temperature. The kinetics of adsorption of the components of air on most commercial zeolites are usually very fast at near ambient temperatures because the zeolites are used in pelletized forms produced by binding very small (1-5 μm) crystals of the zeolite with a macroporous binder matrix which usually controls the mass transfer resistance of the gases to the zeolitic adsorption sites. For example, a typical diffusional time constant for adsorption of N_2 from air on sodium mordenite is 0.45 s^{-1} (6). Consequently, the separation is based on thermodynamic selectivity of the zeolite for N_2 over O_2 and Ar.

TABLE 1
Selectivity of Adsorption of N_2 Over O_2 on Na-Mordenite at 1 atm

	Nitrogen selectivity		
Mole fraction O_2	0°C	19°C	50°C
0.10	4.81	4.27	3.92
0.30	4.91	4.45	4.12
0.50	5.02	4.66	4.36
0.70	5.12	4.89	4.63
0.90	5.24	5.15	4.95

The carbon molecular sieves for air separation, on the other hand, are made by further narrowing the pore mouths of a small pore activated carbon by depositing nascent carbon produced by thermal cracking of a hydrocarbon (*7*). This is controlled in such a fashion that a CMS with an effective pore mouth diameter between that of nitrogen (3.64 Å) and oxygen (3.46 Å) molecules is produced.

Consequently, when contacted with air, the CMS allows faster diffusion of relatively smaller O_2 molecules into its pore structure than N_2. This produces an oxygen-enriched adsorbed phase based on the kinetic selectivity of the CMS for O_2. The kinetic selectivity and capacity of adsorption for O_2 is time dependent because the CMS does not have a thermodynamic selectivity for O_2 over N_2 and a prolonged contact with air allows the N_2 to eventually diffuse into the CMS pore structure, creating an adsorbed phase of same composition as air (*8*). The kinetic O_2 capacity of the CMS increases with increased contact time, but its kinetic selectivity decreases. Thus, the air contact time on the CMS is a very important variable in establishing the overall separation efficiency by this adsorbent. Both the kinetic selectivity and capacity of CMS for O_2 adsorption decrease with increasing temperature. Figure 1b shows an example of the kinetics of adsorption of N_2 and O_2 on a CMS (*7*). H_2O (2.6 Å) and CO_2 (3.3 Å) diffuse faster than O_2 into a CMS, and they reduce the effective capacity for O_2 and N_2 adsorption, although this effect is less severe for a CMS than that for a zeolite.

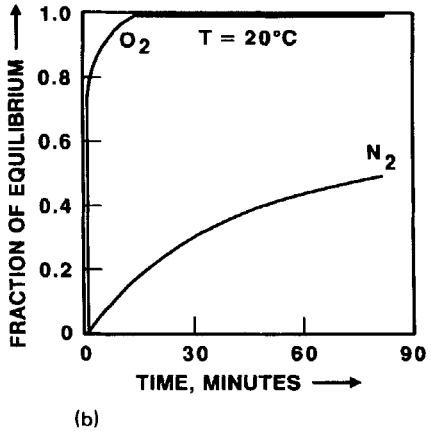

FIG. 1b. Kinetics of uptake of N_2 and O_2 on a molecular sieve carbon. Fraction of equilibrium amount adsorbed-time plots.

PSA PROCESS FOR PRODUCTION OF OXYGEN ENRICHED GAS

This process is patented by the Union Carbide Corporation and it uses a zeolitic adsorbent and the following six steps in the cycle (*9*):

(a) Pressurization of the adsorbent bed from near ambient pressure to an intermediate superambient pressure level by simultaneously introducing compressed air feed through one end of the adsorber and an oxygen-enriched gas through the other end.
(b) Further pressurization of the adsorber to the highest superambient pressure level of the cycle (e.g., 3–4 atm) by introducing the compressed feed air alone through the feed air end.
(c) Depressurization of the adsorber in the direction of air feed flow (cocurrent) to an intermediate pressure level and withdrawing an oxygen-enriched gas through the product end. A part of this gas is used to pressurize another adsorber then undergoing Step (a) and the remaining gas is withdrawn as the oxygen-enriched product.
(d) Further cocurrent depressurization of the adsorber to a still lower but superambient pressure level and withdrawing an oxygen-enriched gas through the product end. A part of this gas is removed as the oxygen-enriched product gas and the remainder is used as the desorption gas (purge) for another adsorber undergoing Step (f) below.
(e) Depressurization of the adsorber to near ambient pressure in the opposite direction of air feed flow (countercurrent). This effluent constitutes a part of the nitrogen-rich desorbed gas which is withdrawn through the feed air end and wasted.
(f) Further desorption of the adsorbed nitrogen by flowing an oxygen-enriched gas through the bed in a countercurrent direction at near ambient pressure. The purge gas is obtained from an adsorber undergoing Step (d) above. The exit gas through the feed end of the adsorber constitutes another part of the nitrogen-rich desorbed gas which is wasted.
(g) Repeat cycle from Step (a).

A continuous air feed and oxygen-enriched product gas withdrawal can be achieved by employing a three-bed embodiment as shown by Fig. 2.

A section of the adsorber at the feed air end is used to remove the H_2O and CO_2 impurities from the ambient air introduced during the cycle Steps (a) and (b). The remaining portion of the adsorber is effective for

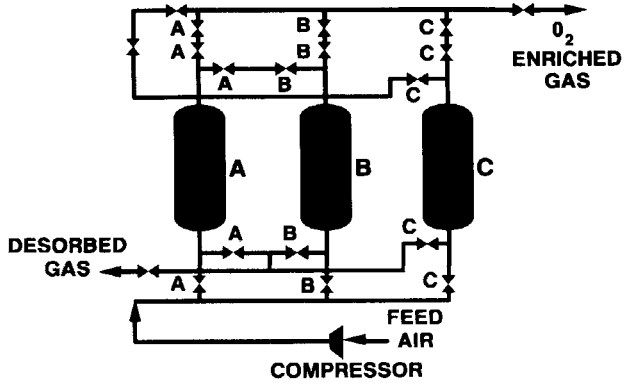

FIG. 2. Schematic flow sheet of Union Carbide PSA Process for production of oxygen-enriched gas.

N_2–O_2 separation. A considerable amount of adsorbed H_2O and CO_2 remains in the bed at the cyclic steady state of the process. A subsequent patent (*10*) discloses that the adsorbent bed of the above process undergoes a severe depression in temperature near the feed end due to self-cooling to supply the heat of desorption of H_2O. This effect deteriorates the performance of the process by lowering the purity and recovery of the oxygen-enriched product gas. In particular, the desorption of water can be difficult when the ambient temperature is cold, and the patent recommends heating the feed end of the adsorber by introducing a certain amount of hot air in Steps (a) and (b) of the cycle. This is achieved by partly retaining the heat of compression of the feed air.

The leading edge of the nitrogen mass transfer zone resides near the middle of the bed at the end of the pressurization steps. Then it moves toward the product end during the cocurrent desorption steps. The adsorbers are designed in such a way that it does not break through the product end. Finally, the zone is pushed back to the feed air end by the countercurrent purge and pressurization by the oxygen-enriched product gas.

Using a 5A zeolite and operating between 3 and 1 atm, the process can produce a 90% O_2 product gas (dry and CO_2 free) with an oxygen recovery of 38.0%. The product gas pressure is typically between 1.0–1.2 atm. The net production capacity is 0.018 mlb mol oxygen enriched gas/lb zeolite/cycle (*10*). The desorbed gas contains 85.7% N_2 (dry basis).

PSA PROCESS FOR PRODUCTION OF NITROGEN-ENRICHED GAS

This process is patented by Bergbau Forschung of Germany. It uses a CMS adsorbent and the following steps in the cycle (*11*, *17*):

(a) Introduction of compressed air into a CMS bed while withdrawing a nitrogen-enriched product gas. The rates of air feed and product withdrawal are different so that a pressure build-up takes place in the bed. The step is continued until the O_2 concentration level in the product gas reaches the maximum permissible value. The bed pressure at that time reaches the highest adsorption pressure level.
(b) Pressure equalization of the bed with another CMS bed by connecting the two beds at both the feed air and the product ends.
(c) Depressurization of the bed to the lowest pressure level of the cycle in the direction opposite to feed air (countercurrent). The desorbed gas constitutes an O_2-rich gas which is wasted.
(d) Partial pressurization of the bed using the gas from another bed undergoing Step (b).
(e) Repeat cycle from Step (a).

The process can be operated between a superambient adsorption pressure level (6–10 atm) and a desorption pressure of 1 atm or between a superambient adsorption pressure (1.8–3 atm) and vacuum (70–100 torr). At least two adsorbers are needed for operation of the process as shown by the flow sheet in Fig. 3.

The nitrogen product is produced at a superambient pressure and its purity continuously decreases during the production Step (a). A product surge tank is required to smooth out the concentration change. H_2O and CO_2 are removed in the feed end of the adsorber and the N_2 product is essentially dry, containing very little CO_2 (<50 ppm). The entire bed acts as a mass transfer zone for this process because of the slow kinetics of adsorption and desorption.

An overall N_2 purity of 96.0–99.9+% can be achieved. The N_2 production capacity and its recovery are strong functions of the product purity, the operating pressure levels, and the ambient temperature. Approximately a twofold decrease in the N_2 production capacity is obtained by increasing the N_2 purity from 98.0 to 99.5% when the process is operated between the pressure levels of 3 atm and 75 torr (*12*). Operating between 6 and 1 atm, the process prodces a 99.5% N_2 product

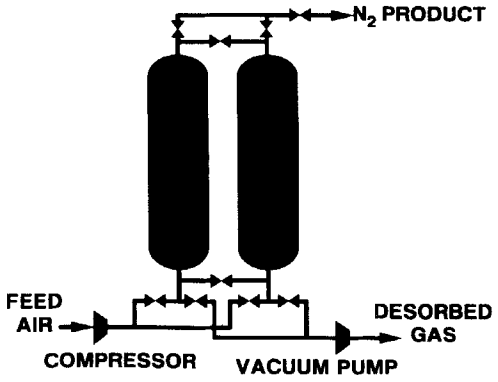

FIG. 3. Schematic flow sheet of Bergbau Forschung PSA Process for production of nitrogen-enriched gas.

with a N_2 recovery of 12.6% and a production capacity of 0.053 mlb mol nitrogen-enriched gas/lb CMS/cycle (*11*). The desorbed gas contains 26.0% O_2 (dry basis).

PSA PROCESS FOR SIMULTANEOUS PRODUCTION OF OXYGEN- AND NITROGEN-ENRICHED GAS

This process is patented by Air Products and Chemicals (*13, 14*). It uses a zeolitic adsorbent. It is the only commercial process for simultaneous production of oxygen- and nitrogen-enriched gases and it operates between a near ambient adsorption pressure and a subatmospheric desorption pressure. The process is thus called a "vacuum swing adsorption (VSA) air separation process."

Figure 4 shows a schematic flow diagram for the process. It consists of two parallel trains (A_1 and A_2) of adsorbers, each with a pretreatment bed containing adsorbents for selective removal of H_2O and CO_2 from air, and a main air separation bed containing the zeolite for air separation. The beds are connected in series. The process steps are as follows.

Adsorption Step

(a) Air at near ambient pressure (1–1.2 atm) is passed through a train of adsorbers which is already pressurized to the feed air pressure

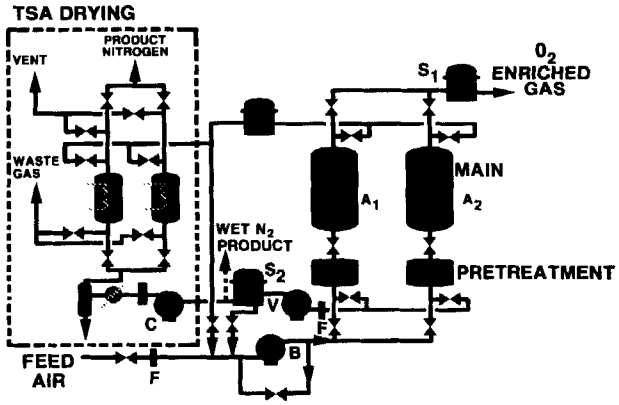

FIG. 4. Schematic flow sheet of Air Products and Chemicals PSA Process for simultaneous production of oxygen- and nitrogen-enriched gas.

level with the oxygen-enriched product gas. The air is introduced using a blower (B) through the feed end of the pretreatment bed which selectively retains the H_2O and CO_2. The purified air then flows into the main bed and the effluent is a dry CO_2-free oxygen-enriched gas. A part of the effluent is withdrawn as the product gas and the remainder is stored in a constnat pressure gas tank (S_1) for use as pressurization gas (Steps e and f). This step is continued until the N_2 concentration in the product gas reaches the maximum tolerance limit.

Nitrogen Rinse Step

(b) A stream of nitrogen-enriched gas is then passed through the train of adsorbers at the feed air pressure in the same direction as feed air flow (cocurrent) using blower B. The effluent from the main bed during this step is a dry, CO_2-free gas which has an airlike composition. A part of this effluent can be recycled as feed air. This reduces the H_2O and CO_2 load on the process. The step is continued until the entire train of adsorbers is essentially saturated with the nitrogen-enriched gas.

Desorption Steps

(c) The train of adsorbers is then evacuated in a direction opposite to that of feed air flow (countercurrent) and a stream of nitrogen-enriched product gas is produced. A vacuum pump (V) is used for this purpose. The gas contains all of the desorbed H_2O and CO_2 from the pretreatment bed. A part of this gas is stored in a constant pressure tank (S_2) for use as the nitrogen rinse gas (Step b) in the companion train of adsorbers and the remainder is withdrawn as the enriched nitrogen product gas.

(d) The evacuation (Step c) is continued until the pressure levels in the train reach a preset value. Then the interconnecting valve between the two adsorbers of the train is closed and the pretreatment bed is evacuated alone to a lower pressure level. The desorbed gas from the pretreatment column forms part of the nitrogen-enriched product gas.

Pressurization Steps

(e) While the pretreatment column is undergoing Step (d), the accompanying main bed is pressurized to feed air pressure level by introducing a part of the previously stored oxygen-enriched gas through the product end (countercurrent).

(f) Finally, the interconnecting valve between the two beds is opened and the pretreatment bed is pressurized countercurrently to the feed air pressure level with the oxygen-enriched gas from the storage tank via the main bed.

(g) The train is now ready to start a new cycle from Step (a).

The process embodiment of Fig. 4 uses two trains of adsorbers and two gas tanks. The gas tanks can be eliminated by adding more trains of adsorbers.

The nitrogen-enriched product gas is produced at near ambient pressure and it contains all of the H_2O and CO_2 introduced by the feed air in Step (a). If a dry N_2 product is desired, the gas can be dried using a conventional thermal swing adsorber (TSA) system as shown in Fig. 4. The TSA adsorbers can be regenerated by heating them with a portion of the dried N_2 product or by using a part of the dry, CO_2-free airlike gas produced as a by-product during the N_2 rinse Step (b) above (*14*). The second choice improves the N_2 recovery of the integrated process.

The operation of the main air separation beds in this process is very efficient. The bed is essentially saturated with the oxygen-enriched product gas at the beginning of the adsorption step. When the air starts flowing through the bed, a Type I adsorption dynamics is created (*15*, *16*). Two pair of mass and heat transfer zones are formed within the bed. The front mass transfer zone (MTZ), which is very sharp, moves much faster than the rear MTZ. The bed ahead of the front MTZ is saturated with oxygen-enriched gas and the bed behind it is essentially equilibrated with air. The heat of adsorption accumulates between the two zones, raising the temperature of the middle equilibrium section, separating the two zones. The adsorption step is terminated when the leading edge of the front MTZ is just short of breakthrough at the product end of the adsorber. The entire bed is essentially saturated with air at this point. During the nitrogen rinse step, another Type I dynamic system is created. The bed ahead of the front MTZ, in this case, is saturated with air and the bed behind it is saturated with the N_2-rich purge gas. This MTZ is longer than the front MTZ for the adsorption step, but it is still small relative to the adsorber length. The front MTZ again moves much faster than the rear MTZ, and the N_2 rinse step is continued until the front MTZ reaches the exit end of the bed or goes out of it. The nitrogen rinse displaces the void air and co-adsorbed O_2 left in the beds from the adsorption step by good purity N_2. Thus, the extent of the N_2 rinse step controls the purity of the N_2 product. For the purest N_2 product, it is desirable that the front MTZ in the N_2 rinse step goes out of the column at the end of that step. The bed is essentially saturated with the N_2-enriched product gas at this point. Thus, the main bed is fully utilized during both the adsorption and the nitrogen rinse steps, realizing the maximum possible capacities for air and N_2 provided by the bed. This is important in achieving high specific production capacity (amount of product gas per unit quantity of adsorbent) which is described later.

The stepwise desorption of the main and the pretreatment beds also adds to separation efficiency. N_2 is more weakly adsorbed on zeolites than H_2O and CO_2. Consequently, the desorption of N_2 from the main bed is relatively easier, and an acceptable N_2 working capacity can be achieved by vacuum swing between ambient pressure and a moderate degree of vacuum. The further evacuation of the pretreatment bed (Step d) alone improves desorption of more strongly adsorbed H_2O and CO_2 without subjecting the entire train of adsorbers to a lower vacuum level which saves power. Figure 5 shows schematics of temperature (left) and pressure (right) variations in the beds during a cycle.

The heat of adsorption of H_2O liberated during its removal in the

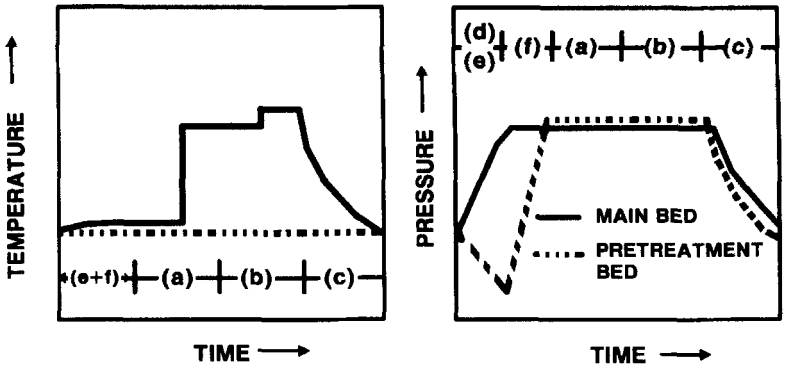

FIG. 5. Schematic of adsorber temperature and pressure changes for the VSA air separation cycle during different steps (a–f) of the process.

pretreatment bed is retained within that bed in near vicinity of the H_2O MTZ. This helps efficient desorption of water during Steps (c) and (d).

The optimum pressure levels of evacuation of the beds is determined by the types of adsorbent used. The pretreatment bed may be packed with zeolites, aluminas, silica gels, and activated carbons or a combination of these adsorbents. These beds are designed to retain H_2O and CO_2 at the warmest condition of operation of the process. Thus, the use of a zeolite in these beds can contribute to air separation when the bed is under-used for impurity removal at colder temperatures.

PERFORMANCE OF THE VSA PROCESS

The VSA air separation process can be used to simultaneously produce a stream of 80–95% O_2 and a stream of 98–99.9+% N_2 from ambient air. The maximum O_2 product purity is 95.0% because the zeolite does not have any selectivity for adsorption of O_2 over Ar, and this limit constitutes the composition of N_2-free air. The process performance data reported here were obtained from a continuous pilot scale unit consisting of a single train of adsorbers using a NaX zeolite in the pretreatment bed and a Na-modenite zeolite in the main bed. The pretreatment bed volume was ~25% of the main bed volume.

The O_2 and N_2 product purities were varied by changing the feed air and the nitrogen rinse quantities in Steps (a) and (b) of the process, respectively. Each data point was measured after a cyclic steady state was

TABLE 2
Cycl Time Format for the Pilot Test Run

	Time (s)				
	0–40	40–60	60–150	150–240	240–280
Pretreatment bed	Step (d)	Step (f)	Step (a)	Step (b)	Step (c)
Main bed	Step (e)	Step (f)	Step (a)	Step (b)	Step (c)

attained. The feed air was at 19°C with a relative humidity of 70–80%. The air pressure was 1.05 atm. The CO_2 concentration of air was 350–400 ppm. The main bed was evacuated to 50–55 torr and the pretreatment bed was evacuated to 25–30 torr. Table 2 shows the cycle time format used in the test.

Figure 6 shows the O_2 production capacity of the process as a function of the O_2 product purity. The nitrogen product purity was maintained at 99.9% N_2 during these runs. The capacity is plotted as millipound moles of O_2-enriched product gas per pound of total zeolite in the train per cycle. It may be seen from Fig. 6 that the O_2 product capacity is a strong function of O_2 purity. About 25% more product can be produced at 80% O_2 purity than at 90% O_2 purity under these conditions of operation.

Figure 7 shows the N_2 production capacity of the process as a function of the N_2 purity (dry basis). The O_2 product purity was maintained

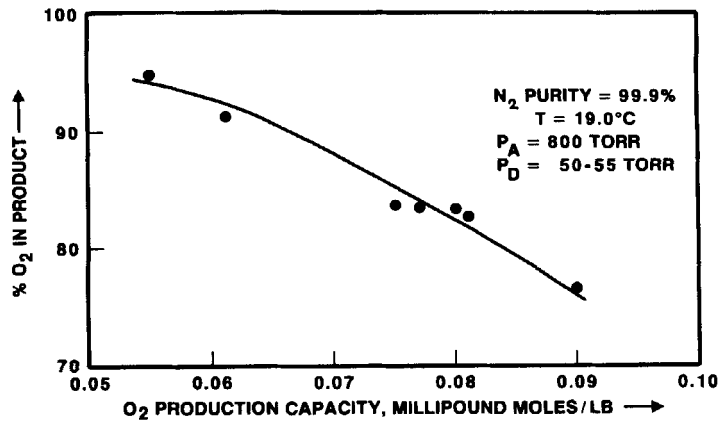

FIG. 6. Oxygen production capacity as a function of purity for the VSA air separation process.

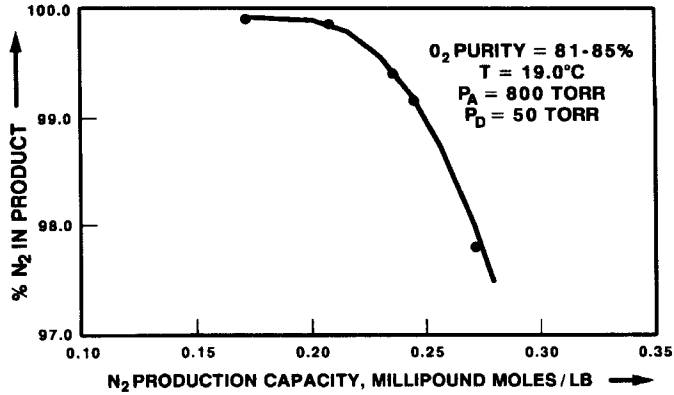

FIG. 7. Nitrogen production capacity as a function of purity for the VSA air separation process.

between 81-85% during these runs. The figure shows that like O_2, the N_2 production capacity is also a strong function of N_2 purity. The N_2 capacity increases as its purity decreases. Approximately 17% more N_2 product can be obtained when the N_2 purity is reduced from 99.5 to 98.0%. However, the rate of increase of N_2 capacity substantially decreases below a N_2 purity of 98.0%. Nevertheless, the decrease in the N_2 production capacity of the VSA process, with increasing N_2 purity, is much less pronounced than that for the Bergbau-Forschung process.

Figure 8 shows the O_2 and N_2 product recoveries from air as functions of the product purities. The process yields very high recovery for both O_2 and N_2. More than 50% O_2 and N_2 recoveries are achieved at the highest purity levels of these products, i.e., 95% O_2 and 99.9% N_2. The recovery of both components decrease with increasing purities as expected. In particular, the N_2 recovery can decrease substantially if the product purity exceeds 99.95+% N_2.

The above-described performance results demonstrate the operational flexibility of the VSA air separation process as well as its high efficiency in simultaneous production of O_2 and N_2 enriched gases. The performance can be further improved by using a better air separation zeolite in the main beds, having a higher selectivity and capacity of adsorption for N_2. A higher N_2 working capacity decreases the size of the main beds for a given production capacity, and a higher N_2 selectivity reduces the coadsorption of O_2 during the adsorption step which, in turn, reduces the N_2 rinse quantity to achieve a certain N_2 purity. This improves the overall

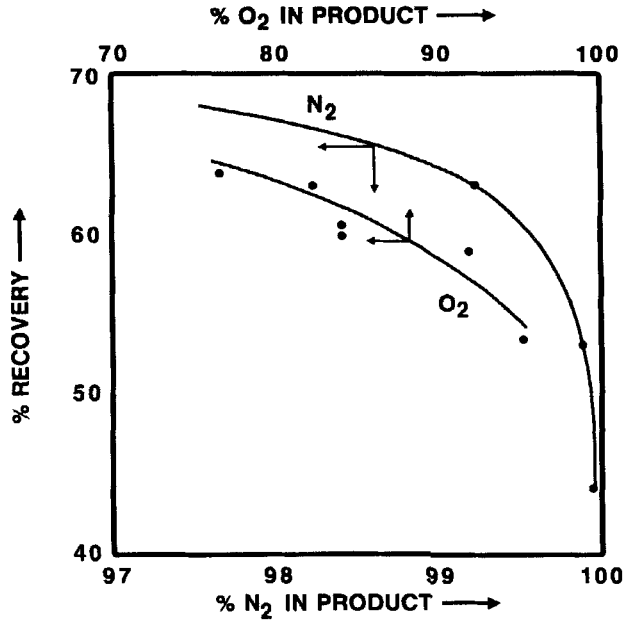

FIG. 8. Nitrogen and oxygen recoveries from air as functions of product purities in the VSA air separation process.

N_2 recovery and the production capacity while reducing the energy of separation.

COMPARISON AMONG THE THREE PROCESSES

The three commercial PSA air separation processes described in this paper significantly differ in the methods by which the adsorption, the desorption, and the complementary steps are carried out even though they produce similar products. This demonstrates that a large variety of process sequences can be synthesized to achieve the same goal. The process performance and the separation efficiency, however, depend strongly on the process design. Table 3 gives a comparison of the performance of the three processes for air separation. The Union Carbide and the Bergbau Forschung process performances were estimated from the examples given in their respective patent disclosures (*9*, *17*).

It may be seen from the table that the VSA air separation process offers

TABLE 3
Comparison of PSA Air Separation Processes

Process	Adsorbent	Operating pressure (atm)		Oxygen product[a]				Nitrogen product			
		Adsorption	Desorption	Purity (%)	Pressure (atm)	Capacity[b]	Recovery (%)	Purity (%)	Pressure (atm)	Capacity[b]	Recovery (%)
Union Carbide PSA (*9, 10*)	5A	3.0	1.0	90.0	1.20	0.0184	38.0	None			
		3.8	1.0	90.9	1.36	0.0177	52.8				
Bergbau Forschung PSA (*11*)	MSC	8.0	1.0	None				99.92[c]	5-8	0.064	15.2
Air Products VSA (*13, 14*)	Mordenite	1.05	0.066	90.0	1.00	0.0670	58.8	99.9[d]	1.0	0.21	53.2

[a]Dry-CO_2 free.
[b]Millipound moles/lb adsorbent/cycle.
[c]Dry, <50 ppm CO_2.
[d]Dry basis.

significantly higher N_2 and O_2 specific production capacities than the other two processes. The recoveries of these components are also much higher for the VSA process. One weakness of the process, however, is that the nitrogen product is wet and needs drying. This can be achieved without the loss of recovery as described earlier. In particular, where both nitrogen- and oxygen-enriched product gases are needed, the VSA process can offer significant advantages. Another important advantage of the VSA process is that the design of the system, scale-up, and process control is relatively simpler because the process operates close to thermodynamic equilibrium conditions as compared with the kinetically controlled Bergbau Forschung process which is more susceptible to fluctuations in operating conditions like temperature, pressure, flow rates, etc.

Another example of the flexibility of operation of the VSA process is that it can be turned into an oxygen generator if no N_2 product is desired by eliminating the N_2 rinse step from the cycle (*18*).

Air Products and Chemicals, Inc. has commercialized the VSA air separation process. Twenty-five small-scale generators for laboratory use and five large-scale generators in the size range of 10–30M SCFH N_2 product have been sold.

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