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Oxygen Production by Pressure Swing Adsorption

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Abstract

The specific oxygen production capacity and the oxygen recovery of a pressure swing adsorption (PSA) process for the production of oxygen from ambient air by selective adsorption of nitrogen can be increased by operating the process at a superambient temperature. The higher temperature operation provides more efficient desorption of nitrogen from the adsorbent which more than off-sets the detrimental effects of the lower selectivity and capacity of adsorption of nitrogen from air at the elevated temperature. The concept is demonstrated by evaluating the performance of an eight-step PSA-oxygen process to produce a 90% oxygen product stream at different temperatures. It is shown that 10% higher oxygen production capacity and 14.5% larger oxygen recovery can be obtained by operating the PSA process at 60°C compared to its performance at 30°C. The PSA process and its performance data from a pilot plant are discussed.

Many pressure swing adsorption (PSA) processes for the production of oxygen enriched gases containing 80-95% oxygen from ambient air have been developed in the last 20 years (*1-4*). These processes use a nitrogen selective adsorbent such as a zeolite for the fractionation of air. The processes consist of cyclic sequences of adsorption, desorption, and other complementary steps, and they differ by the modes in which these steps are carried out (*1*).

One group of these processes carries out the adsorption step at a near-atmospheric pressure level to produce the oxygen-enriched product gas. The desorption of adsorbed nitrogen is then achieved by evacuating the

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adsorber to a subatmospheric pressure level. The vacuum is applied in a direction opposite to that of the feed air flow (countercurrent). A vacuum pump is used for the evacuation step, and an air blower is used to supply the feed air to the adsorber.

The second group of processes carries out the adsorption step at a superatmospheric adsorption pressure level to produce the oxygen-enriched product gas. The nitrogen desorption is achieved by reducing the adsorber pressure to a near-ambient pressure level followed by flowing a part of the oxygen-enriched product gas through the adsorber at the near-ambient pressure level. This last step is called "purging the adsorber." Both the pressure reduction and the purge steps are carried out countercurrent to the direction of feed air flow. An air compressor is used to supply the feed air at the adsorption pressure level.

Nitrogen-enriched desorbed gases are wasted in both types of processes. A typical composition of this waste gas is 84–92% nitrogen, 7.5–15.5% oxygen, and the balance argon on a dry and carbon-dioxide-free basis. All of these processes are designed to operate at near-ambient temperature. An aftercooler is used to cool the air feed leaving the air compressor or the air blower.

The key variables for optimization of these PSA processes for a given oxygen product purity (Y_Q) are the oxygen product recovery (R) and the specific oxygen production capacity (Q). Q is defined as the amount of oxygen product produced per cycle of operation per unit amount of total adsorbent used in the PSA system. R is given by

$$R = QY_Q/0.21F$$

where F is the total amount of air feed to the adsorber per cycle of operation per total amount of adsorbent in the PSA system. The optimization goals are to maximize Q, which minimizes the total adsorbent inventory (W) in the PSA system, and to maximize R, which minimizes the amount of feed air to be processed. An increase in the value of R reduces the size of the feed air blower or the compressor and their power consumption. This last advantage is critical for the second group of PSA-oxygen processes where the entire energy of air separation is supplied through feed air compression. The power consumed by the feed air compressor per unit amount of oxygen produced is inversely proportional to R.

The purpose of this study is to demonstrate that the variables Q and R for the second group of PSA-oxygen processes can be optimized by carrying out the steps of the process, not at near-ambient temperature as normally practiced, but at a superambient temperature.

CONCEPT FOR OPTIMIZATION

The oxygen losses in a PSA-oxygen process of the second group occur during the countercurrent pressure reduction and oxygen purge steps.

The inter- and intra-adsorbent particle void space in the adsorber essentially contains air at the end of the adsorption step. The adsorbed phase also contains a significant amount of co-adsorbed oxygen if the selectivity of adsorption for nitrogen is not very high. The amount of the void and the co-adsorbed oxygen can be large, particularly if the adsorption pressure is moderate to high. A large fraction of these oxygen molecules is lost during the pressure reduction step even though practical PSA processes incorporate many different complementary steps to preserve or recover a part of these oxygen molecules. These steps include (a) one or more pressure equalization steps where a part of the void gas is transferred to another adsorber prior to the pressure reduction step for nitrogen desorption (*5*, *6*), or (b) the cocurrent depressurization step where a part of the void oxygen is recovered as an oxygen-enriched gas of product or near-product quality before the countercurrent nitrogen desorption by pressure reduction begins (*7*, *8*). This second type of complementary step is carried out by stopping the adsorption step when there is still some nitrogen adsorption capacity left in the adsorber and then reducing the adsorber pressure to an intermediate pressure level by expanding the gas in the direction of feed air flow (cocurrent). A portion of the void nitrogen is adsorbed during this step in the previously unused portion of the adsorber and an oxygen-enriched gas of product like quality is produced.

The countercurrent oxygen purge step introduces a portion of the oxygen-enriched product gas produced during the adsorption step into the adsorber for further desorption of the adsorbed nitrogen. A major part of these oxygen molecules is also lost in the purge effluent. The minimum amount of purge gas required per unit amount of feed air processed (P/F) for effective cleaning of the oxygen product end of the adsorber is given by the ratio (P_D/P_A) of the purge gas (P_D) to feed air (P_A) pressure (*4*, *9*). P is the specific amount of purge gas used per cycle of operation per unit amount of the total adsorbent in the PSA system.

The purge step achieves the major portion of nitrogen desorption from the adsorber in the PSA cycle. The extent of nitrogen desorption in this step determines the available nitrogen adsorption capacity of the adsorber in the subsequent adsorption step which, in turn, controls the quantities F and Q. Obviously, as the quantity of the purge gas is increased, more nitrogen is desorbed from the adsorber. However, the

oxygen recovery (R) decreases as P increases. Thus, there is a trade-off between increasing Q and decreasing R.

The desorption process by purge is essentially controlled by the thermodynamics of adsorption, and the assumption of local equilibrium between the gas and the adsorbed phases is approximately valid (*10*). This condition dictates that the desorption of nitrogen by oxygen purge will be easier if the nitrogen is not adsorbed too strongly. In other words, the extent of nitrogen desorption from the adsorber for a given amount of oxygen purge will be larger if the selectivity of adsorption of nitrogen over oxygen is smaller (*10*).

The selectivity of adsorption of nitrogen over oxygen on a zeolitic adsorbent for any given gas pressure and composition can be reduced by increasing the adsorbent temperature. However, it is not practical to raise the adsorbent temperature in a PSA process only during the desorption by purge step due to the short cycle times used. Consequently, one has to run the entire PSA cycle at an elevated temperature in order to get the advantage of easier desorption of nitrogen by oxygen purge. The operation at a higher temperature, on the other hand, reduces the nitrogen adsorption capacity of the adsorber during the adsorption step. It also increases the relative amount of co-adsorbed oxygen in this step due to lower nitrogen selectively of adsorption at the higher temperature. Thus, the overall performance of the PSA process operated at an elevated temperature will be determined by the relative temperature coefficients of the nitrogen adsorption capacity and selectivity from air and of the extent of nitrogen desorption by oxygen purge.

PRELIMINARY EVALUATION OF THE CONCEPT

We experimentally measured the temperature coefficient of the nitrogen adsorption capacity from a synthetic air mixture (79.0% N_2 + 21.0% O_2) at pressures of 4.7 and 1.0 atm on a zeolite (sodium mordenite) by flowing the gas mixture at various temperatures through a thermostated packed adsorbent column (1 in. diameter and 36 in. long), and monitoring the effluent gas flow quantity and composition as functions of time. The column was saturated with pure oxygen at the feed gas pressure and temperature prior to each breakthrough experiment. The nitrogen adsorption capacities from air at different pressures and temperatures were then calculated from the first moments of the nitrogen breakthrough curves and the feed air flow rates. Figure 1 shows the results. The specific nitrogen adsorption capacity of the adsorber at an air

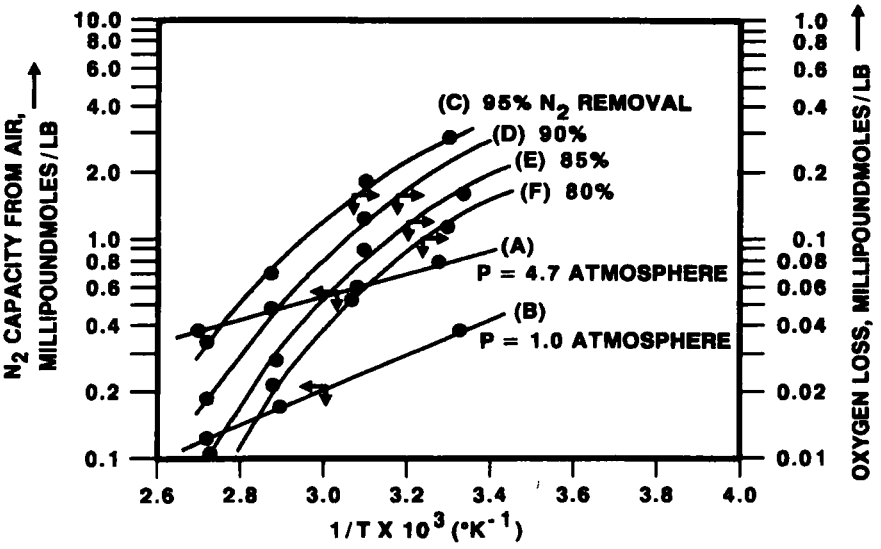

FIG. 1. Effects of adsorbent temperature on the nitrogen adsorption capacity of mordenite from air and on the amount of oxygen lost during desorption of nitrogen from mordenite by purge with oxygen. Curves A and B: Specific nitrogen adsorption capacities from air at different pressures. Curves C-F: Specific amount of oxygen lost to remove different quantities of adsorbed nitrogen.

pressure of 4.7 atm decreased by a factor of 1.4 and 2.0 when the adsorbent temperature was raised from 30 to 60 and 94°C, respectively. The corresponding decreases in the nitrogen capacities at the adsorption pressure of 1 atm were by factors of 1.7 and 2.8.

We also measured the temperature coefficient of the extent of nitrogen desorption from the mordenite by oxygen purge by saturating the above described column with pure nitrogen at 1 atm and at different temperatures followed by flowing a stream of pure oxygen through the column at 1 atm and the initial column temperature. The effluent gas flow quantities and compositions were measured as functions of time. The specific quantity of nitrogen desorbed from the column and the specific quantity of oxygen lost with it were then estimated by integrating the measured composition-quantity characteristics of the desorbed gas. These results are plotted in Fig. 1 (Curves C-F) as the specific quantities of oxygen lost as functions of the adsorbent temperatures for different extents of nitrogen desorption from the column. The extents of desorption are represented in these figures by the percentages of the initial

quantities of nitrogen removed from the adsorber. The figures show that the temperature coefficient of the specific amount of oxygen loss during nitrogen desorption from the mordenite by oxygen purge is much larger than that for the nitrogen adsorption capacity from air. For example, the specific amounts of oxygen lost during purge to remove 80% of the adsorbed nitrogen from the column decreased by factors of 3.0 and 36.0 when the adsorbent temperature was raised from 30 to 60 to 94°C, respectively. The corresponding decreases in the nitrogen adsorption capacities from air were much smaller.

The pure gas and binary nitrogen (Component 1) and oxygen (Component 2) adsorption characteristics on the mordenite were reported elsewhere (*11*). Table 1 shows the selectivity (S) of adsorption of nitrogen over oxygen on the mordenite as well as the specific amounts of adsorption (N_i^a) of the component i (= 1, 2) from a 79.0% N_2 + 21.0% O_2 gas mixture at a total pressure of 3.0 atm as functions of temperatures. These properties were calculated using the mixed gas Langmuir isotherm model which described the adsorption of nitrogen and oxygen on the mordenite very well (*11*). The specific amounts of these components in the void gas (N_i^v) and the total specific amounts ($N_i = N_i^a + N_i^v$) of these components present in the adsorber at the system pressure and temperature are also shown in Table 1. It may be seen that the ratio N_2/N_1 increases as the adsorbent temperature is increased. Thus, the loss of oxygen during the pressure reduction step of the PSA process using this adsorbent will increase with increasing system temperature. A part of the void gas should be preserved by techniques described earlier in order to reduce this oxygen loss in a practical PSA process.

These preliminary studies indicated that the decrease in the oxygen loss during the purge step in a PSA-oxygen process of the second group due to operation of the PSA cycle at an elevated temperature can more than off-set the negative effects that it will have in the performance of the adsorption and the pressure reduction steps. Consequently, an improved overall performance of the PSA-oxygen process can be achieved by operation at an elevated temperature.

PERFORMANCE OF A PSA-OXYGEN PROCESS AT AN ELEVATED TEMPERATURE

In order to demonstrate the actual performance of a PSA-oxygen process at different temperatures, we conducted a pilot-plant test. The test unit contained four adsorbers in parallel. Each adsorber was 4 in. di-

TABLE 1
Equilibrium Air Adsorption Characteristics on Mordenite at a Total Pressure of 3.0 atm

Temperature (°C)	Nitrogen selectivity (S)	Nitrogen adsorption[a]			Oxygen adsorption[a]			
		Adsorption (N_1^a)	Void (N_1^v)	Total (N_1)	Adsorption (N_2^a)	Void (N_2^v)	Total (N_2)	(N_2/N_1)
30	3.88	0.863	0.095	0.958	0.059	0.025	0.084	0.088
40	3.55	0.734	0.092	0.826	0.054	0.024	0.079	0.096
50	3.25	0.614	0.089	0.703	0.050	0.024	0.074	0.105
60	3.00	0.511	0.087	0.598	0.045	0.023	0.068	0.113
70	2.78	0.420	0.084	0.504	0.040	0.022	0.063	0.124
90	2.42	0.285	0.080	0.365	0.031	0.021	0.052	0.144

[a]All quantities in millipound moles/lb of adsorbent.

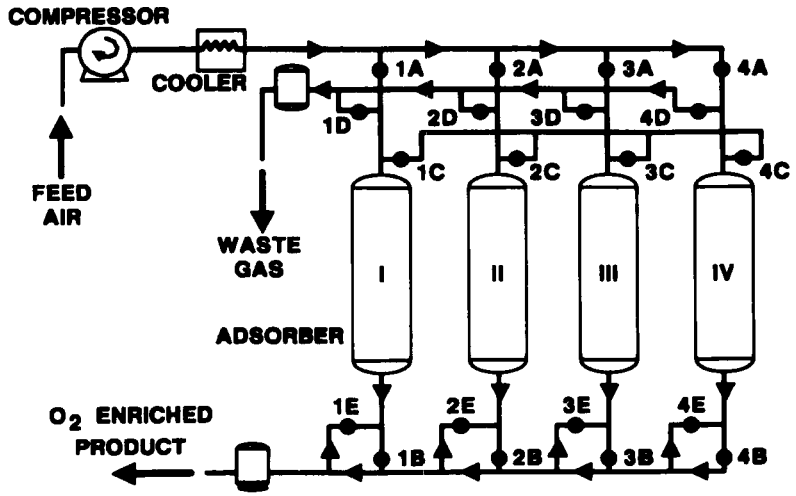

FIG. 2. Schematic of the pilot plant for the PSA-oxygen process.

ameter and 144 in. long. They were packed with the mordenite adsorbent. The total amount of adsorbent in the system (W) was 168 lb. Figure 2 is a schematic flow diagram of the test unit which shows the locations of the gas manifolds and the switch valves. A dry and CO_2-free air was used as the feed gas. The feed air pressure was 3.04 atm and the feed gas temperature was controlled by heating or cooling the air. The four column pilot unit, the gas manifolds, and the switch valves were enclosed in an air bath which controlled the temperature of the entire system. The following PSA-oxygen process, which was developed and patented by Air Products and Chemicals (*12*), was tested.

DESCRIPTION OF THE PSA-OXYGEN PROCESS

The PSA-oxygen process consisted of the following cyclic steps. Each adsorber went through each step of the cycle in a sequence.

(a) *Adsorption.* The feed air was passed through an adsorption column at the highest pressure level (P_A) of the PSA cycle and an oxygen-enriched product effluent was withdrawn at about the feed air pressure. The step was continued until the oxygen

concentration of the effluent stream started to deviate from the preset product gas composition.

(b) *Pressure Equalization I.* At the end of Step (a), the adsorber was connected with another adsorber which had just finished Step (f) below. A part of the void and desorbed gases was transferred from the first column to the second. The flow of gas from the first column was countercurrent to the direction of feed gas flow and that into the second column was cocurrent to the direction of feed flow. The two columns had the same pressure of P_I ($<P_A$) at the end of this step.

(c) *Pressure Equalization II.* The adsorber was then connected to another companion adsorber which had just finished Step (e) below, and these two adsorbers were pressure equalized to an intermediate pressure level of P_{II} ($<P_I$). The gas flow directions in this step were similar to that of Step (b).

(d) *Pressure Reduction.* The adsorber pressure was then reduced from P_{II} to the atmospheric pressure level (P_D) in a countercurrent flow direction. The desorbed gases formed a part of the total waste gas from the system.

(e) *Purge.* At the end of Step (d), the adsorber was countercurrently purged at 1 atm pressure with a part of the oxygen-enriched product gas then being produced by another adsorber undergoing Step (a). The effluent desorbed gases formed the remaining part of the waste gas from the system.

(f) *Repressurization I.* After purging, the adsorber was connected with another adsorber undergoing Step (c), and the two adsorbers were pressure equalized to a pressure level of P_{II}.

(g) *Repressurization II.* The adsorber was then connected with another adsorber undergoing Step (b), and its pressure was raised to the level of P_I.

(h) *Repressurization III.* Finally, the adsorber was brought back to the adsorption pressure level (P_A) by countercurrently introducing another part of the oxygen-enriched product gas then being produced by another adsorber undergoing Step (a) of the process. The adsorber was now ready to commence a new PSA cycle starting from Step (a).

The above described eight-step process was run in a continuous manner using the four column pilot plant. Table 2 shows the schematic of operation of the columns in a complete cycle. A total cycle time of 10 min was used in the runs. The flow rates and compositions of each gas stream

TABLE 2
Schematics of the Operation of the Adsorbers during a PSA Cycle[a]

Time	Adsorber I	Adsorber II	Adsorber III	Adsorber IV
$0-t_1$	AD	RII	P	PEI
t_1-t_2	AD	RIII	P	—
t_2-t_3	AD	RIII	P	—
t_3-t_4	AD	RIII	RI	PEII
t_4-t_5	AD	RIII	—	PR
t_5-t_6	AD	RIII	—	PR
t_6-t_7	PEI	AD	RII	P
t_7-t_8	—	AD	RIII	P
t_8-t_9	—	AD	RIII	P
t_9-t_{10}	PEII	AD	RIII	RI
$t_{10}-t_{11}$	PR	AD	RIII	—
$t_{11}-t_{12}$	PR	AD	RIII	—
$t_{12}-t_{13}$	P	PEI	AD	RII
$t_{13}-t_{14}$	P	—	AD	RIII
$t_{14}-t_{15}$	P	—	AD	RIII
$t_{15}-t_{16}$	RI	PEII	AD	RIII
$t_{16}-t_{17}$	—	PR	AD	RIII
$t_{17}-t_{18}$	—	PR	AD	RIII
$t_{18}-t_{19}$	RII	P	PEI	AD
$t_{19}-t_{20}$	RIII	P	—	AD
$t_{20}-t_{21}$	RIII	P	—	AD
$t_{21}-t_{22}$	RIII	RI	PEII	AD
$t_{22}-t_{23}$	RIII	—	PR	AD
$t_{23}-t_{24}$	RIII	—	PR	AD

[a]AD = adsorption, PE = pressure equalization, PR = pressure reduction, P = purge, and R = repressurization.

going into and out of the PSA system were monitored as functions of time, and the process performance data were recorded after cyclic steady-state operation was achieved. This usually took 6–10 cycles of operation. However, the data reported in this paper were gathered after at least 30 cycles of operation.

A series of runs were made to produce an oxygen-enriched product gas containing about 90–92.0% O_2. The system temperature was varied between 30 and 65°C. A (P/F) ratio of about 0.33, which was the minimum theoretical (P/F) ratio for the adsorption (P_A = 3.04 atm) and the desorption (P_D = 1.0 atm) pressures of the test runs was used. The overall and the oxygen material balances for these runs checked within ±2%.

RESULTS AND DISCUSSIONS

Table 3 summarizes the pilot plant test results. The quantities F, P, and Q reported in this table are given as millipound moles of gas/pound of total adsorbent in the PSA system/cycle of operation. The oxygen recoveries (R) are given in percentages.

It may be seen that both the specific oxygen production capacity (Q) and the oxygen recovery (R) increase for the PSA process described in this work as the adsorbent temperature is increased. The best performance is obtained at a temperature of 60°C when Q and R reach their maximum values. Both Q and R substantially decrease when the adsorbent temperature is raised above 60°C.

The initial improvement in the performance of the PSA process with increasing adsorbent temperature is due to the fact that efficient desorption of nitrogen from the adsorber at a higher system temperature during the oxygen purge step of the process (Step e) more than off-sets the negative effects of the lower nitrogen adsorption capacity of the adsorber realized in Step (a) and the higher oxygen loss during Step (d). On the other hand, when the PSA process is operated at a much higher temperature (>60°C), the detrimental effects of higher temperatures on process Steps (a) and (d) dominate the overall performance.

The data in Table 3 show that the operation of the PSA process at 60°C provides about 14.5% higher oxygen recovery and about 10.0% higher specific oxygen production capacity than those at the near-ambient temperature (30°C) operation. These figures translate to 10.0 and 14.5% reductions, respectively, in the adsorbent inventory and the air compressor size and power.

TABLE 3
Pilot-Plant Test Data[a]

System temperature (°C)	Air feed (F)	Oxygen purge (P)	P/F	Oxygen product		
				% O_2	Quantity (Q)	Recovery (R)
30.0	0.378	0.127	0.338	90.3	0.0330	37.5%
45.0	0.378	0.138	0.364	91.0	0.0343	39.2%
50.0	0.381	0.119	0.314	91.0	0.0368	41.8%
60.0	0.363	0.129	0.356	90.4	0.0362	42.9%
65.0	0.325	0.106	0.327	92.0	0.0265	35.8%

[a] F, P, and Q are in millipound moles/lb of adsorbent/cycle.

The adiabatic gas temperature rise during compression of ambient air to the adsorption pressure of 3.0 atm is about 180°C. The compressed air can be cooled down to 60°C to supply the feed gas to the PSA system operating at a superambient temperature. Thus, there is no extra energy needed to provide the hot feed air to the PSA system.

CONCLUSIONS

The overall performance of a PSA-oxygen process is determined by the interacting performances of each step of the process. Consequently, the conditions for optimum operation of the PSA process may not be the conditions for the best performance of each of the individual steps of the process. The relative importance of the individual steps of the process and the interactions between them must be analyzed in order to establish the optimum conditions of operation of the process. For the eight-step PSA-oxygen process described in this work, the more efficient operation of the nitrogen desorption step by oxygen purge at higher than ambient temperature overcomes the less efficient operations of the adsorption and the pressure reduction steps at the elevated temperature. This results in a better overall performance of the process at 60°C than that at 30°C. However, this relative advantage disappears when the system temperature is raised further and the overall performance starts to decline.

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